DEVELOPMENT OF SOL-GEL TECHNOLOGY FOR TEXTILE SURFACE COATING TO ACHIEVE SELF-CLEANING AND ANTIBACTERIAL PROPERTIES

Mutinta Chizyuka

A thesis submitted in partial fulfilment of the requirements of De Montfort University for the degree of Doctor of Philosophy

De Montfort University

Funded by the European Union SAFEPROTEX project

June 2016

ACKNOWLEDGEMENTS

I would firstly like to thank and dedicate this to my father, Dr. George H.B. Chizyuka for being the continued inspiration behind striving for the best. He supported and encouraged my pursuit to be the best that I can be. You are missed dearly.

Secondly, I would like to express my deepest appreciation to my first supervisor Professor Jinsong Shen for his professional guidance, patience and encouragement. Thank you for your consistent support through my research. I would also like to thank my second supervisor Dr. Susannah Walsh for her professional assistance and guidance and my third supervisor Dr. Edward Smith for his precise support and professional advice. It is with their dedicated guidance that I was able to successfully undertaken my research work.

I would also like to thank the European Union for the funding provided for the SAFEPROTEX project.

Many thanks also go to Tarun Chawla, Rachel Armitage, Nasmin Juma and many other colleagues for their contributions and helpful suggestions towards this research project**.**

Finally, to my mother, Mrs Inonge Chizyuka, for her unfailing support and constant love. To Likulunga, Chibuno, Milimo and sister, Chipende, thank you for cheering me through this journey. Your support was unmatched. To my dearest friend Tayo Adeniji for her continued support and encouragement through this research experience.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF EQUATIONS

LIST OF SCHEMES

LIST OF ABBREVIATIONS

ATCC – American Type Culture Collection

ATR / FT-IR – Attenuated Total Reflectance / Fourier Transform – Intra Red

EDX – Energy Dispersive X-Ray

CFU /mL – Colony Forming Unit / Mililitre

GLYMO – 3-glycidopropyltrimethoxysilane

MTES – Methyl-triethoxysilane

OTES – Octyl-triethoxysilane

QUAT – 3-(Trimethoxysilyl) propyl octadecyldimethylammonium chloride

SEM – Scanning Electron Microscopy

WCA – Water Contact Angle

WRN – Water Rating Number

ABSTRACT

With advancements in technology and its influence on most industries, the textile industry continues to pursue innovative techniques to create and meet the growing demand for technical textiles. Self-cleaning textiles have become popular due to promising positive impacts on not just the textile industry, but also on global efforts to improve industrial waste and its impact on the environment. Polyfluorinated chemicals are widely known to provide excellent self-cleaning properties to achieve water and oil repellence, mirroring that of the botanical lotus leaf. Due to their toxic effects on consumers and the environment, research focus, in the pursuit to achieve technical textiles, has been to replace these toxic polyfluorinated chemicals with alternative substances capable of achieve functional properties that these fluorinated substances provide. Various technologies utilised to impart functional properties that include the sol-gel technology, have gained popularity in recent years due to its simpler and cost-effective processes. This sol-gel technology utilises silane precursors, modified easily to incorporate various additives that are applied onto textiles through hydrolysis and condensation reactions, in the presence of a catalyst, to produce an extensive functionalised nanoparticle network on the textile surface.

Alkoxysilanes and quaternary ammonium compounds modified with long carbon chains were used to develop a sol solution that could be applied onto 100% knitted cotton fabric. To involve the fabric in the building of the sol-gel network, 100% treated cotton was agitated in sol solution for 4 hours at 40°C. The soft feel of the cotton fabric was retained when treated cotton fabrics were padded at high pad pressure. This treatment method resulted in treated cotton fabric demonstrating hydrophobicity with water contact angles of 142° and roll-off angles of 16° for self-cleaning properties. The 3-(Trimethoxysilyl) propyloctadecyldimethylammonium chloride silane provided an antibacterial activity of log reduction in CFU/mL of 3 against *S.aureus* and was seen to influence the hydrophobic property. Prolonged contact between fabric and sol demonstrated better durability of properties for sol-gel treated cotton fabric when tested for its durability to washing. Though acidic medium reduced resistance to abrasion, cotton samples treated in acidic conditions with varying silane content regained abrasion resistance and demonstrated an improvement in burst strength. SEM-EDX and ATR / FT-IR analyses were able to illustrate the presence of sol-gel coating and the siloxane bonding on the treated cotton surface, respectively.

CHAPTER 1:

INTRODUCTION

1.1 Background

Textiles are the most commonly used (Mahltig, 2005) and thereby the most popular commodity consumed in society due to their applications in products for everyday use. Their extensive use has led to the continued focus on improvements of textile performance. In recent years, research has focussed on the development of processes and procedures that provide more efficient and reliable textile commodities. The efficiency of textile products leads to the manufacture of high quality standard products aiming to meet consumer needs. Functionalisation of textiles has gained popularity over recent years due to the enormous benefits that have been observed through its use in enhancing textile performance. The concept of fabric enhancement, and therefore functionalisation, can be dated back to ancient Egypt where the refining of linen was established through the use of beeswax and conifer resins for preservation purposes; while in ancient China, hydrophobicity was achieved through treatment with *Perilla frutescens* seed oil (Mahltig, 2005).

Textile based research has used several methods for textile functionalisation to provide durable functional properties to improve textile performance and promote textile product longevity in associated end-uses. Numerous functionalities have been imparted on textile materials using different modifying techniques that include the sol-gel process. The sol-gel process has become one of the frequently used methods for the functionalisation of textile materials due to its easy processing, low temperature treatment conditions and simpler synthesis and application processes. This method utilises hydrolysis and condensation reactions of the precursor material to produce a network of nano-colloidal particles that form on the textile through the gradual evaporation of the solvent (Berendjchi et al., 2011).

Following the functionalisation of textiles, the ability of a textile material to withstand external influences that may cause damage and limit its application has also been an area of extensive research (Berendjchi et al., 2011). Properties such as self-cleaning and antibacterial activity have been beneficial in providing protective barriers to, not just the textile material but surrounding areas, especially when the material is used as apparel or upholstery. These properties provide the opportunity to elevate standards of hygiene and reduce energy costs associated with laundering.

1.2 Rationale

Traditionally, textiles have been categorised in the low technology domain due to their primary functions, which include providing protection and aesthetic purposes. Due to intensified globalisation and associated global competition, textile manufacturers continue to compete for a significant share of the global market through the development of more technical and innovative textile products (Kathirvelu, D'Souza and Dhurai, 2008). As a result of the increasing need for highly efficient technical textiles, research continues in the pursuit to further improve existing products and associated application methods to meet changing consumer needs. Properties that are exhibited by textiles are essential as they influence its end-use. Highly functionalised textiles have the ability to provide properties dependent on the modifications applied onto the textile. The efficiency of a functionalised textile is greatly influenced by the effectiveness of the properties imparted through functionalisation. For this purpose, there has been an increase in multi-functional textile production to enhance properties of technical textiles. Multi-functional properties have also been beneficial in the widening of fields of application for textile products.

Multi-functional properties such as self-cleaning and antibacterial activity have become popular in protective clothing industries because they introduce high levels of hygiene, prevent cross-contamination and reduce bacterial degradation of textile materials. Protective clothing and associated industries continually explore techniques that provide better and reliable protective measures on textiles. The durability of such properties becomes equally important as it impacts the product performance in providing protection against external influences over a prolonged period. Recent reports and evaluations of chemicals used to functionalise textiles have been of concern due to their toxic effects of both the wearer and the environment, and as such attempts are continually been made to improve the process of functionalisation through the use of safer substances.

Cotton fabric, due to its favourable features such as comfort and softness, is among the very popular textiles used. With further modifications to include hydrophobic coatings, cotton provides dryness and cleanliness properties that would be features to include on technical textiles. As cotton and other natural fibres are constantly in competition with synthetic fibres, the application of finishes on such natural fibres has allowed cotton to compete with synthetic fibres in their fields of application (Berendjchi et al., 2013). The addition of functional properties provides the opportunity to investigate whether cotton could be used as protective clothing with the added property of more comfort. The easy application of sol-gel technology onto fabric due to the surface area of fibre, makes fabric one of the optimal substrates for its application and as such, this technology was used for the functionalisation of 100% knitted cotton.

The dual functionality of self-cleaning and antibacterial activity on cotton fabric has been an area of recent research as such properties provide the needed properties to improve cleanliness of cotton. Cotton fabric, being an ideal medium for settling and growing pathogenic bacteria because of its hydrophilic and porous structure, benefits from self-cleaning and antibacterial finishes because such finishes prevent the increase in bacterial population on the fabric through activity against bacteria while the self-cleaning properties prevent the penetration of contaminants through its repulsion properties (Berendjchi et al., 2011). The degree and durability of such properties then determine the areas to which cotton could be used as protective clothing. The ability to impart such properties to determine whether cotton can compete with other outdoor protective clothing was the subject of the research undertaken, which was part of a larger E.U. funded SAFEPROTEX project looking to produce high protective clothing for complex emergency operation using various fabric types. Cotton was used as the fabric of choice for this research to act as a model for the development of the sol-gel treatment for textile surface coating due to its reactive surface and also explore the protective properties of self-cleaning and antibacterial that could be imparted by the sol-gel process.

1.3 Aims and objectives

An increased demand for sustainable textiles has created the need for continued research focussed on the manufacture of textile materials enhanced through techniques that improve their performance and in turn their efficiency. The development of multi-functional properties has proven to be a method by which this can be achieved. The durability of such properties determines how sustainable the textile will be and determines the ability of the textile to maintain its properties when exposed to external factors such as abrasion or laundering. Researchers aim to revise current synthesis and application methods to avoid high industrial costs through the optimisation of techniques such as the sol-gel process to develop cost effective industrial processes.

Using sol-gel technology, due to simpler synthesis and application processes, the following aims and objectives were set:

- To develop a sol-gel process suitable for textile surface coating;
- To develop dual functional properties of self-cleaning and antibacterial properties on 100% knitted cotton;
- Analytical analysis of sol-gel films and sol-gel treated cotton to observe its interaction with the fibres, yarns and fabric;
- To investigate the durability of properties of sol-gel treated cotton to laundering and abrasion.

CHAPTER 2:
LITERATURE REVIEW

2.1 Introduction

Cotton, grown in countries such as the United States, China, Pakistan, India, Brazil and a few others, has been classified as one of the world's oldest fibres due to its extensive use over many years and as a commodity, holds a 60% share in the fabric market (Textile World, 2000). Its continued popularity in current textile markets has led to its high demand especially in the clothing and home furnishing industries (Cotton Incorporated, 2014). Cotton is the desired fibre for fabric and ultimately the preferred fabric in the textile industry due to it's high comfort levels as a result of easy moisture absorption and release, ability to interact with various dyes, withstand high temperatures and also because of its good durability and abrasion performances (Wakelyn et al., 2007).

This research investigated the development of sol-gel technology and its application on cotton fabric to achieve the dual functionality of self-cleaning and antibacterial activity. This literature review aims to provide an overview on cotton as a fibre, state the fundamental concepts of sol-gel technology as well as review recent achievements in multi-functionalisation of 100% knitted cotton in relation to the self-cleaning and antibacterial properties to illustrate how this fabric has been functionalised and thereby highlight the novelty of the method developed in this research.

2.2 Cotton fibre and structure

2.2.1 Cotton growth and harvesting

The cotton plant, of the genus *Gossypium*, is by nature a perennial shrub but is grown commercially as an annual crop in warm-weather regions of North and South America, India and Africa. Cotton seedlings emerge from the soil within 1 - 2 weeks after planting. Flower buds appear after 5 - 6 weeks and different blossoms grow from white (Upland cotton) or creamy yellow (Pima cotton) to dark yellow within the next 3 - 4 weeks. It takes 40 - 80 days for cotton to grow from bloom to open boll. The boll formed consists of seed and fibre. Once the boll opens, within the latter part of the 40 –

80 days, it dries and becomes the white, fluffy and clean fibre; ready for harvest as illustrated in Figure 2.1 a-g (Wakelyn et al., 2007).

Figure 2.1 Cotton seed (a) at different stages of growth from a seedling (b) to Blossom (c) to boll (d) to opening boll (e) to opened and dry bolls ready for harvest and finally harvested cotton (g) [Images a, b, c, e, g are Courtesy of Talyor Hackbarth and images d and f Courtesy of Cotton Australia)

Once matured, different methods of harvesting are used to collect the cotton crop. Harvesting of the cotton crop can be achieved through machine harvest or hand harvest. Machine harvest, as the name suggests, involves the harvesting of cotton with a machine designed for such a purpose while hand harvesting involves cotton bolls being picked one boll at a time. Due to economic factors, more than 99% of cotton harvesting in developed countries such as United States and Australia, is undertaken mechanically while developing countries still utilise the hand harvesting method. The harvested cotton may still contain cotton seed and other plant material which need to be removed through cleaning processes such as ginning (Figure 2.2). The ginning process, having two different methods, separates the fibres from the seed and plant matter. Saw-teeth gins possess teeth that pull the fibres from the seeds while roller gins pass fibres between rollers to separate the fibres from the seed. Once ginning is completed, the harvested crop is then placed into bales to preserve its quality and enable easy transportation (Wakelyn et al., 2007).

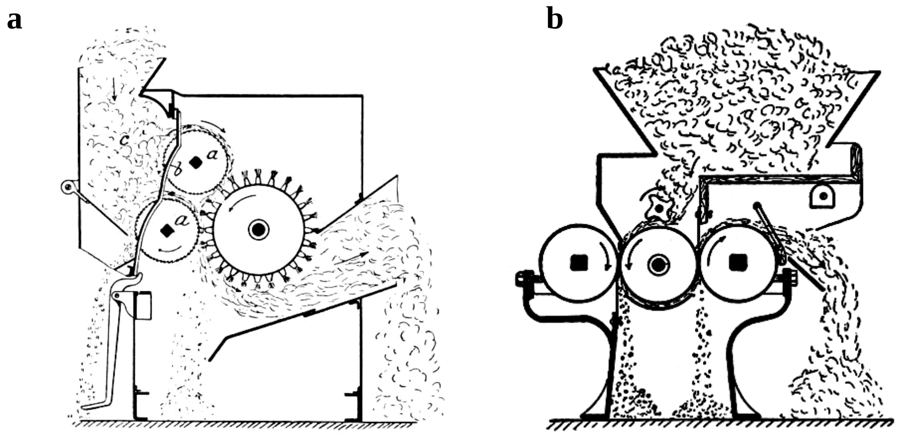


Figure 2.2 Examples of saw ginning (a) and roll ginning (b) processes (Paldiya, 2014)

2.2.2 Cotton composition

Cotton fibres on the boll are essentially single cells growing as seed hairs of the *Gossypium* plant (Carter, 1971) which undergo different stages during the growth process. Firstly, the epidermal cell elongates in a 13 - 20 day process which results in the development of the primary wall surrounding a large lumen (Figure 2.3). The fibre then undergoes thickening (15 to 55 days) that leads to a build-up of cellulose around the primary wall. This cellulosic layer constitutes the secondary wall and the tertiary wall (Figure 2.3). At the maturation stage, the formed tubular cells collapse and the kidney-shaped lumen in the middle of the cotton fibre is formed as shown in Figure 2.3 (Sen, 2001; Collop, 2008). Cotton fibres are essentially composed of 95% cellulose, 1.3% protein, 0.7% pectic substances which are oligosaccharide polymers, 0.6% waxes composed of long chain fatty acids, alcohols and resins, 1.2% ash, 0.3% total sugars and 0.8% organic acids (Wakelyn et al., 2007). The waxy layer serves as a protective barrier to prevent water penetration and microbial degradation (Wakelyn et al., 2007). For the removal of all non-cellulosic material such as the waxy layer and fats, as well as other hydrophobic materials such as the proteins, pectin and organic acids, scouring is used. Scouring agents used differ, depending on the desired treatment. Alkaline agents such as sodium hydroxide solutions have been used to remove pectins through hydrolysis reactions and waxes through saponification reactions that reduce such oils into soaps in alkaline solutions (Choudhari and Menezes, 2011; Karmakar, 1999). Conventional scouring methods are currently being replaced by environmentally friend approaches of enzymes, to eliminate the waste generated and reduce the harsh chemical effects of scouring agents used in conventional methods (Rajendran et al., 2011).

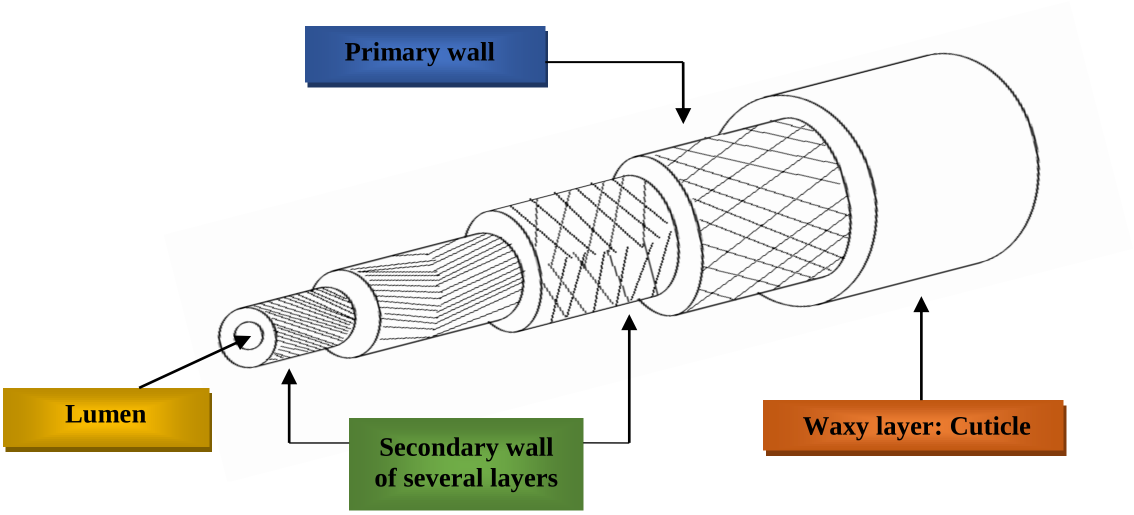


Figure 2.3 Different components of a cotton fibre

In order for cotton to be absorbent, the waxy layer needs to be removed and the hydroxyl groups of cellulose on the cotton fibres exposed. The removal of the non-cellulosic material such as the wax layer allows better access to the cellulosic groups that promote more efficient chemical processing and finishing.

2.2.3 Properties of cotton

2.2.3.1 Physical properties of cotton

Cotton fibres usually assume a creamy white, bluish white, grey or yellowish colour. The crystalline nature of cotton and the ordered alignment of polymer chains contribute to the strength of the cotton fibres (Gohl, 1981). The uneven assembly of the fibrils promotes absorption of moisture as this arrangement exposes hydroxyl groups for moisture absorption **(**Mishra, 2005). Cotton is a moderately strong fibre that does not stress easily and its inelastic and rigid nature is due to the crystalline polymer network (Gohl, 1981; Textile Fashion, 2012). Cotton has excellent resistance to degradation by heat; with fibres decomposing at high temperatures (240°C) and when exposed to sunlight, cotton does show some degradation due to UV-light which turns the fibre yellow (Textile Fashion, 2012).

2.2.3.2 Chemical properties of cotton

Cotton fibres are composed of polymeric cellulose chemically named as poly 1, 4-β-D-linked anhydroglucopyranose. The repeating unit used in the polymerisation process is shown in Figure 2.4. The degree of polymerisation, which is the number of monomeric units in a polymer chain, for cotton is estimated to be around 5,000 units of anhydroglucopyranose (Gohl, 1981).

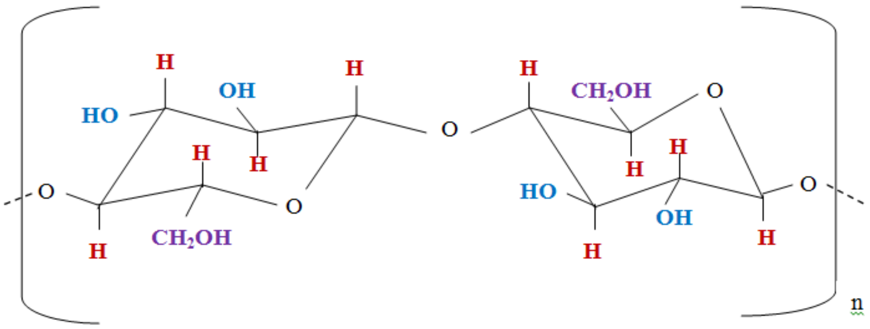


Figure 2.4 Repeating unit of cellulose referred to as a celloboise

The primary and secondary hydroxyl groups as well as β-glycosidic reactive bonds act as functional groups that allow chemical reactions to occur and therefore allow chemical treatments to be applied to the cotton fabric. Cotton fibres are readily hydrolysed at the glycosidic ether bond in acidic conditions (Figure 2.5).

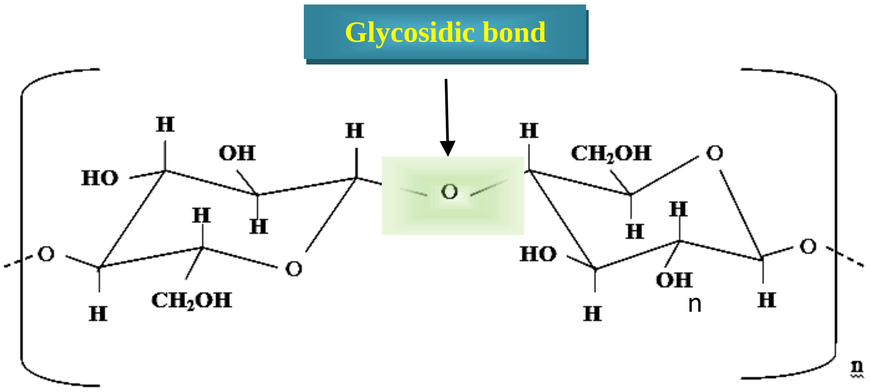


Figure 2.5 Cellulose structure illustrating the glycosidic bond

Acidic conditions, such as those used in bleaching of cotton to improve absorbance (Anand et al., 2006) have been reported to weaken the cotton fibres while in alkaline conditions, commonly used in mercerisation to improve dye affinity and fibre strength (Lacasse and Baumann, 2004), cotton fibres show better resistance because there is poor interaction between alkali polar groups and cotton polymer network (Lacasse and Baumann, 2004).

2.3 Textile surface modification

2.3.1 Non-wet processes for textile modification

Various textile surface modification techniques have been developed to apply functionality onto textiles. Such methods include non-wet processes of physical and chemical vapour depositions. These techniques involve reactions between the vaporised precursors and substrates to form solid material on substrates in a vacuum medium (Pan and Sun, 2011). Other modifying techniques that have gained popularity in the textile industry include plasma treatment. Plasma technology has been used in textile industries as a method to deposit nanocomposites to impart various functionalities to fabric (Gashti et al., 2012). The advantages of plasma treatment include the reduction of water usage and associated waste generated in wet processes. This treatment acts as a fabric pre-treatment prior to the application of finishes. Fibre surfaces become partially oxidised, due to treatment with oxygen plasma, which leads to an increase in polar groups available on the surface, such as hydroxyl groups that improves adhesion (Mahltig, 2011).

Despite these advantages, plasma treatment depends on the system to reproduce exact values of gas pressure and power input as well as the flow rate of such to ensure that results are reproducible; this means where slight variations occur, reproducibility becomes an issue. This accuracy becomes crucial in generating the reactive species to initiate plasma treatment. The high level of charge developed through of use of this technique is undesirable as it leads to other fibre defects and due to expensive equipment used and the need for high vacuum pumps, technical challenges are faced in scaling up for production processes (Sarmadi, 2013).

2.3.2 Wet processes to modify textile surfaces

The textile industry is the most energy intensive industry with the use of large amounts of chemicals and water in textile processing (Sarmadi, 2013). Although this can be problematic in terms of impacts on the environment, textile industries still utilise water based processes due to their robust ability to scale up easily, limited alteration to production lines and the relatively simple equipment used (Buyle, 2012). Techniques such as electrolyte deposition incorporate catalytic reduction of metal ions in an aqueous solution which subsequently deposit on the substrate without the use of electrical energy (Pan and Sun, 2011). The most popular, due to simplicity and low reaction temperatures, is the sol-gel technique. This method involves various application techniques in which fabric immersion is followed by padding, knife coating, transfer coating, spray, dip and padding (Wei, 2009). Most industries utilise the pad-dry-cure method because it can easily be incorporated into the continuous production line. The limitations that have been identified with the sol-gel application technique is the use of large amount of solvents and water as well as low thermal stability of textile materials, usually 200°C (Mahltig and Textor, 2008). These limitations can however be managed through the development of durable products and optimisation of the solvent system.

2.4 Sol-gel technology and its application

2.4.1 Introduction

The sol-gel process has generated great interest as a method for chemical finishing on textile materials due to the extensive possibilities for the development of new and improved products; especially in the growing technical textile market. This process is favoured due to various advantageous properties such as simplicity of procedures and low reaction temperatures that allow easy incorporation of combined additives to apply various functionalities. Through simple pad or dip coating processes, self-cleaning, antibacterial, water repellent and other finishes can be applied on fabric materials (Wei, 2009).

The sol-gel process involves the development of an inorganic network through a three step process. The initial step involves the formation of a sol. The sol comprises of colloidal suspensions, typically metal nanoparticles, in organic or aqueous solvents (Gashti et al., 2012; University of Oslo 2006; Brinker and Scherer 1990). Sols undergo the second step of gelation to form a network with trapped liquid phase. The gel that is formed from colloidal sols consists of a 3-dimensional network built from reactions of sub-colloidal particles (Gashti et al., 2012). The final step involves drying and curing to remove the trapped liquid, resulting in a porous structure (Gashti et al., 2012).

2.4.2 Sol-gel precursors

The precursors that are used to form sols usually consist of inorganic metals with surrounding ligands as shown in Table 2.1. These precursors can be of various chemical compositions, with metal alkoxides being the most commonly used (Brinker and Scherer, 1990; Turova et al., 2002).

Table 2.1 Commonly used ligands attached to precursors for sol synthesis (Turova et al., 2002)

COMMONLY USED LIGANDS			
ALKYL		**ALKOXY**	
Methyl	**$-CH_3$**	**Methoxy**	**$-OCH_3$**
Ethyl	**$-CH_2CH_3$**	**Ethoxy**	**$-OCH_2CH_3$**
***n*-propyl**	**$-CH_2CH_2CH_3$**	***n*-propoxy**	**$-OCH_2CH_2CH_3$**
***Iso*-butyl**	**$-CH_2CH(CH_3)_2$**	***Iso*-butoxy**	**$-OCH_2CH(CH_3)_2$**

Metal alkoxides are metal organic compounds that have organic ligands attached to the metal atom. The typical formula for a metal alkoxide is $M [OR]_x$ where M is the metal atom such as Si, Ti, Al, Zr and OR is the type of alkoxy group attached ($x= 1 - 4$). Organic ligands commonly used are alkoxy ligands that are formed by the removal of the proton from the hydroxyl ion by an alcohol (John and Sobata, 2010). These are commonly used precursors because of their ability to easily hydrolyse in the presence of water (Turova et al., 2002; Brinker and Scherer, 1990; Sakka, 2005). Factors such as the metal atom electronegativity, the increase of the coordination number of the metal atom, the steric hindrance of the alkoxy group and the molecular structure of the metal alkoxide affect the chemical reactivity of the metal alkoxide (Niederberger and Pinna, 2009). To achieve hybrid materials of various purposes and therefore functionality, metal alkoxides can be modified to impart various properties to the network formed. The development of hybrid molecular precursors involves organic modifications of the metal alkoxide that adds organic compounds in an inorganic network (Mammeri et al., 2005). The modified metal alkoxides used in this research were organo-alkoxysilanes of the general formula:

$$\mathbf{X\text{-}R\text{-}Si\ (OR')_3}$$

X= Non-hydrolysable organic moiety which can be either reactive or non-reactive.
R= Aryl or alkyl group
R'= Methyl, ethyl, isopropyl which is part of the alkoxy ligand

Scheme 2.1 The general formula for an organo-alkoxysilane (Materne et al., 2012)

Amongst the alkoxysilanes used in the sol-gel process, alkoxysilanes with methoxy or ethoxy groups are commonly used. These organo-functional silanes are not the most reactive but are popular for surface modification because they can be easily handled and the alcohol by-products are non-corrosive and volatile (Arkles, 2006). Organo-trialkoxysilanes are immediately miscible with water however a large number require the hydrolysis of their alkoxy groups to be miscible. For alkoxy hydrolysis to occur, alkoxy groups require molecular contact of water. This factor is among the reasons that make alkoxysilanes very difficult to hydrolyse (Plueddemann,1991). Functionalised silanes used in sol synthesis are capable of forming chemical bonds with functional groups present on the fibre surface, mostly –OH groups present on cellulosic fibres. Modified sols with cross-linking abilities such as epoxysilanes and vinylsilanes increase the adhesion of the nanosol coating to the fibre and thereby improve mechanical resistance (Brezezinski et al., 2011). These precursors, under the right conditions, undergo hydrolysis and are converted to their corresponding hydroxides.

The hydroxides of silanes are unstable and susceptible to further condensation reactions to form nanoparticles (Brezezinski et al., 2011). The sol-gel process is widely used because the composition and purity of the synthesised sols can be controlled. Other advantages include the production of hybrid materials to achieve the properties desired. The Si-C bond on a modified silane is stable against hydrolysis in aqueous media and this stability allows the incorporation of additives such as long alkyl chains to promote hydrophobicity on the treated substrates (Kickelbick, 2007; Samley et al., 2014). The critical surface tension of a substrate reflects surface properties such as wettability. Critical surface tension values lower than 20 dynes/cm have been associated with superhydrophobicity. In order to achieve such values on surfaces, certain surface coatings or finishes are required. Most hydrophobic silanes have values within the range of 20 - 30 dynes/cm and therefore become preferred precursors to achieve low critical surface tension values for hydrophobic properties (Arkles, 2006).

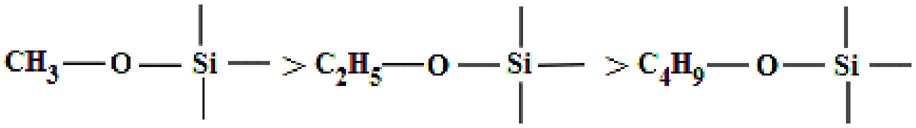
2.4.3 Hydrolysis reaction of silanes

Alkoxides are very sensitive to moisture and known to decompose in the presence of water or solvents (John and Sobata, 2010). The alkoxy groups undergo hydrolysis to form silanol species which involves the replacement of OR groups with OH groups (Scheme 2.2). This hydrolysis might occur through the use of catalysts because of low reactivity of alkoxysilanes. The silanol-contained species are highly reactive intermediates that could continue condensation reactions with themselves and promote bond formation with substrates. Catalysts that initiate hydrolysis also usually promote condensation (Arkles et al., 1992).

$$\equiv Si-OR + H_2O \rightleftharpoons \equiv Si-OH + ROH$$

Scheme 2.2 Hydrolysis reaction of alkoxide demonstrating the replacement of OR with OH groups

Acid-catalysed conditions are favoured over base-catalysed conditions as high rates of hydrolysis occur in acidic mediums when compared to basic conditions (Samley et al., 2014). One of the factors that influence hydrolysis rates could be the steric bulk of the silane. The steric bulk of the alkoxy group determines the rate of hydrolysis such that, methoxysilanes are hydrolyse at approximately 10 times faster than ethoxysilanes (Samley et al., 2014). The general trend is as shown in Scheme 2.3.



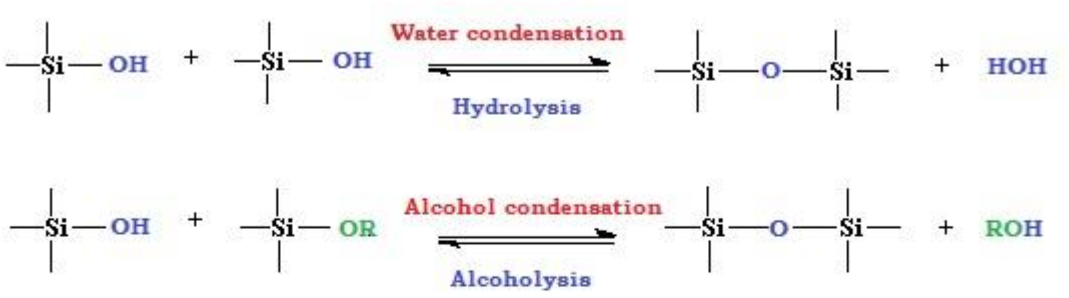
$$CH_3-O-Si- > C_2H_5-O-Si- > C_4H_9-O-Si-$$

Scheme 2.3 General trend of hydrolysis of the different type of alkoxysilanes

Increasing the organic substitution in the general trend of $Me_3SiOMe > Me_2Si\ (OMe)_2 > MeSi(OMe)_3$ enhances the hydrolysis rate. The silanol intermediates are desirable as they possess greater solubility and reactivity than their alkoxy precursors and siloxane products (Abel et al., 2006). Silanols produced are very unstable (Si-OH) and condense to form of Si-O-Si bonds (Kickelbick, 2007). Organic groups that remain stable during the sol-gel process and do not undergo hydrolysis are defined as network modifiers. Groups that react with themselves and other components are called network builders (Samley et al., 2014).

2.4.4 Condensation reaction of silanes

Silanols, being very reactive, are network builders as they react within themselves to form the silica network (Arkles, 2006). Sols with high silanol content are desired because they promote high solubility and reactivity when compared to the amount of precursors and the siloxane products (Abel et al., 2006). Continued reaction produces a complex three-dimensional structure through a process called polymerisation (John and Sobata, 2010).

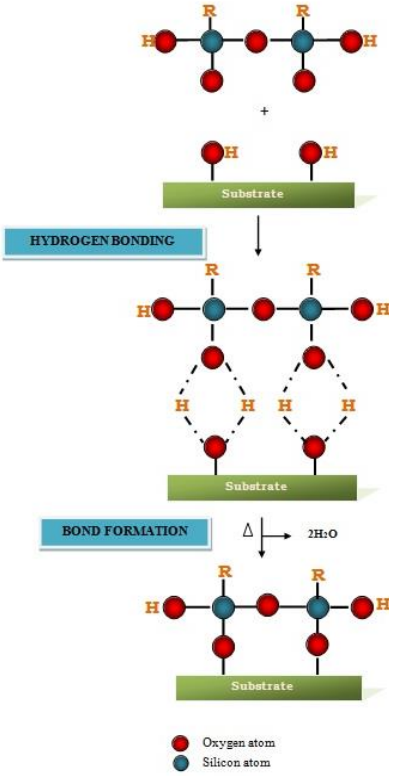


Scheme 2.4 Water and alcohol condensation reactions that occur in the sol-gel process

Catalysts that promote hydrolysis also promote condensation reactions. These two reactions occur simultaneously (Osterholtz and Pohl, 1992); in an alcohol solution, incomplete hydrolysis creates an equilibrium where there is a high number of unhydrolysed Si-OR groups. These reactions of hydrolysis and condensation lead to oligomeric intermediates with combined OR and OH groups. When excess water is added, hydrolysis can be completed and OR free species produced (Schmidt et al., 1984; Arkles, 2006). The rate of condensation is dependent on the conditions of the reaction such as pH, temperature, solvent type and presence of catalysts (Wei, 2009).

2.4.5 Sol-gel application

The continued hydrolysis and condensation reactions within the sol system lead to the production of an extensive silica network. Synthesised sols are applied on cotton fibres / fabrics typically through the dip-pad process. The textile is dipped into the sol at varied times and padded to remove excess solution. Initial bonding that occurs between the sol and fabric material is hydrogen bonding (Scheme 2.5). Drying is then carried out to allow the removal of solvent (Mahltig et al., 2005; Saleemi et al., 2013) and during the heating stages of the sol application, covalent bonding occurs between sol coating and fabric material (Scheme 2.5).



Scheme 2.5 Schematic illustration of sol synthesis and application process on cotton substrate

Padding pressures utilised during sol application are important as they influence the amount of liquor left on the textile material. The amount of liquor pick-up has an effect on the final coating that forms on the textile material. High liquor pick-up leads to an increase in the amount of coating on the textile material. A high amount of liquor pick-up causes higher amounts of water to be removed during the drying stage, resulting in low efficiency of production processes. Evaporation of large amount of water could also lead to migration of finish on the fabric and subsequently result in an uneven distribution of coating on the treated fabric. High rates of evaporation can also lead to more concentrated coating on the surface of fabrics and less penetration into the internal regions of the fabric. However, if the high pad pressure is used to achieve very low wet pick-up for fabrics, which have low absorption of treatment solution, an uneven distribution of the coating on the fibre surface could be caused as the liquid phase is discontinuous due to low volumes of liquor on the fabrics. To reduce the occurrence of uneven finish distribution on the fabric, the fabric is sufficiently saturated and excess liquid removed using defined pad pressure to ensure adequate wet-up (Schindler and Hauser, 2004). During the drying process, the nanoparticles formed through initial hydrolysis and condensation reactions cross-link to form a nanoparticle network with trapped liquid phase called a lyogel (Brezezinski et al., 2011). Further drying at elevated temperatures allows chemical bonding to occur and evaporation of the trapped liquid phase to produce a porous, cross-linked nanoparticle network called a xerogel, as shown in Figure 2.6 (Pompe et al., 2013). Through the drying process, the large capillary forces of the evaporating liquids in the porous structure occur, which can lead to cracking of the coating (Kickelbick, 2007). Drying at higher temperatures allows the removal of the residual liquid and promotes the formation of a porous coating (Brezezinski et al., 2011; Alongi et al., 2012). Improper sol synthesis and application processes lead to increased rigidity of the fabrics and cross-linking which reduce fibre motion and as a result, stiffen fabric structure (Brezezinski et al., 2011). Typically, pad applications of chemical finishes yield liquor pick-up around 70 - 100%. In order to obtain consistent chemical application, the nip pressure should be uniform across the fabric width and the fabric speed should not vary throughout the application process (Schindler and Hauser, 2004).

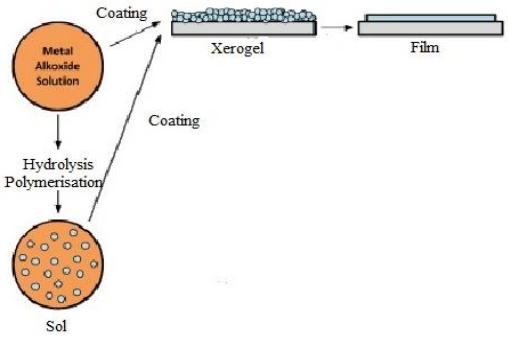
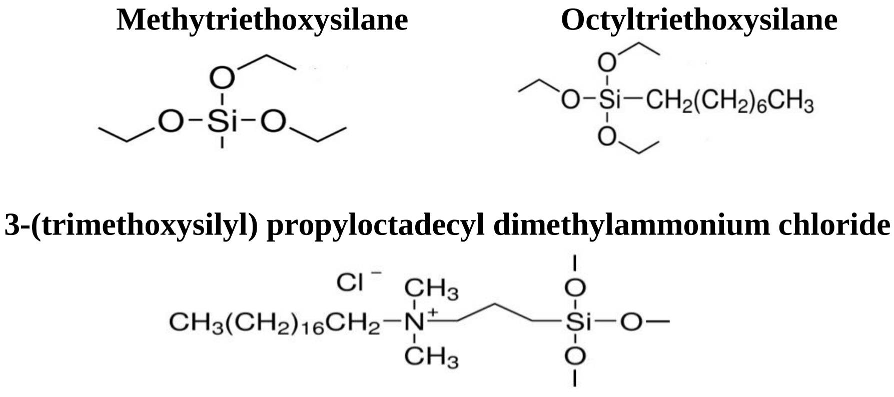


Figure 2.6 Summary of sol-gel process (Samiey et al., 2014)

2.5 Sol-gel process to achieve hydrophobicity

The use of water repellent textiles in various industries has increased, due to the vast potential of such functional textiles especially through the application of these functional properties using hydrophobic polysiloxanes (Mahltig, 2011). The sol-gel process has been the preferred method for functionalisation because of its ability to use low quantity of precursors to achieve hydrophobicity (Mahltig and Bottcher, 2003; Wei, 2009). Fluorinated silanes have been popular due to their ability to produce coatings that exhibit high water contact angles greater than 150° (Textor and Mahltig, 2010; Bae et al., 2009 ; Xue et al., 2009). Fluorine-based compounds cannot be destroyed or easily broken down and as a result, they are known to accumulate in plants, animals, water and other aspects of the environment. Continued exposure and consumption of fluorinated compounds increases this bioaccumulation. With respect to human toxicity, ingestion of plants or drinking of water with high levels of fluorides would have adverse effects on human health. Though fluorinated compounds have been used to develop textiles with superhydrophobic properties, the long term impact of the waste generated from its use has led to the development of other means of achieving the same or similar hydrophobic properties in current areas of research. Various studies have demonstrated that alkoxysilanes modified with long hydrophobic chains could be used to achieve hydrophobicity (Textor and Mahltig, 2010; Wang et al., 2010; Gao et al., 2009; Li et al., 2008). The increase in the alkyl chain length increases the hydrophobic property on treated fabric by further roughening of the surface and also reducing the critical surface tension of the treated cotton fabric sample. Hydrophobic silanes commonly used are shown in Scheme 2.6.



Methytriethoxysilane

Octyltriethoxysilane

3-(trimethoxysilyl) propyloctadecyl dimethylammonium chloride

Scheme 2.6 Structure of hydrophobic silane precursors used to impart hydrophobicity (Sigma Aldrich, 2015)

The treatment of the fabric with sols containing colloidal particles of varied sizes and composition as a result of different alignment of long alkyl chains in their polymer network, promote uneven topography of the sol-gel polymeric coating (Figure 2.7) and therefore promote high levels of hydrophobicity.

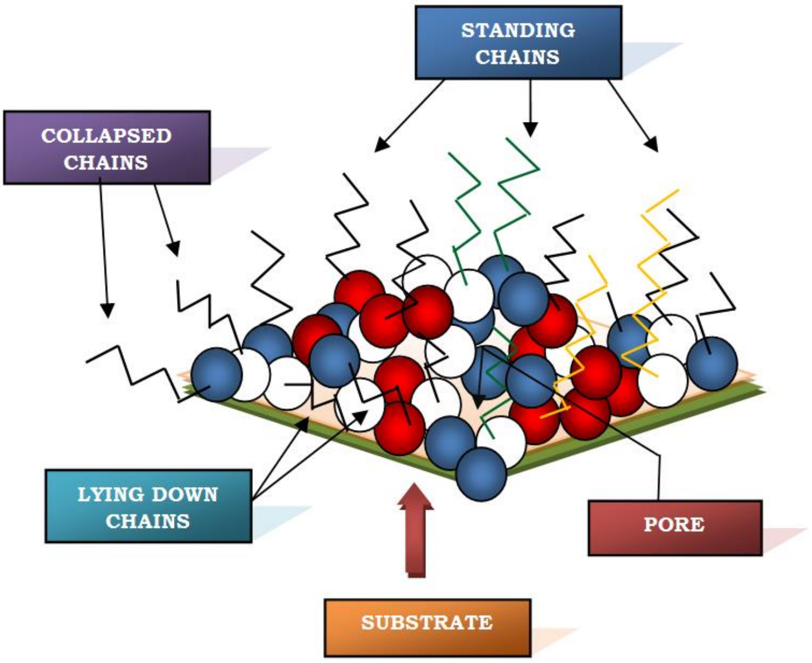


Figure 2.7 Diagram illustrating theoretic assembly of long chain alkoxysilanes on particles of sol-gel coating on a substrate.

Similar hydrophobicity acquired through the use of fluorinated sols can be achieved by treating textiles with sols containing long alkyl chains. Modified silanes such as C-8 and C-16 alkyltriethoxysilanes, where C-8 and C-16 refer to the carbon length of the alkyl group, demonstrated similar hydrophobicity to the fluorinated silane triethoxytridecafluorooctylsilane (Mahltig and Bottcher, 2003). Alkoxysilanes modified with long hydrophobic chains were therefore used in this research as precursors to achieve hydrophobicity and self–cleaning properties.

2.6 Factors affecting hydrophobic property

2.6.1 Particle size

Factors such as temperature, solvent type, pH and concentration of precursors all have an influence on the structure of particles and their dimensions (Brezezinski et al., 2011). The size of the particles formed during the polymerisation of the silane precursors plays an important role in determining sol coating adhesion to the textile fibres. Smaller particles will penetrate deeper and adhere strongly into the fabric while larger agglomerates will be easily removed from the fibre surface during washing or rubbing (Patel et al., 2014).

With larger particles however, an increase in hydrophobicity can be achieved due to increase in surface roughening (Yu et al., 2007; Bae et al., 2009). Ideal particle sizes are important as they ensure that sol-gel coatings adhere adequately to the textile. In order to achieve the controlled size of particles that promote hydrophobicity, the reaction conditions have to be considered. High levels of OH^- species promote condensation reactions that are essential for the formation of particles. An increase in alkalinity has led to an increase in the particle size of silica nanoparticles synthesised through an acceleration of condensation reactions (Arkles et al., 1992). This in turn allows rapid aggregation processes that would ultimately promote variation of particles formed on the surface (Berendjchi, Khajavi and Yazdanshenas, 2013). This variation in surface topography would aid in improving the hydrophobic property. Investigations into the influence of sol-gel particle sizes on hydrophobicity have been carried out with aims to determine an optimal particle size (Yu et al., 2007; Gao et al., 2009). Studies compared the effects of non-siloxane hydrophobic additives to synthesised silica nanoparticles and their effect on hydrophobicity. It was observed that good hydrophobicity could be achieved with silica nanoparticles of varying sizes comparable to non-siloxane based additives (Bae et al., 2009; Xue et al., 2009). With the use of the economical and low risk additives of sol-gel, hydrophobicity can be achieved and become the preferred method of functionalisation of textiles.

2.6.2 Solvent System

The solvent system used in sol synthesis is important as it promotes sol stability and homogeneity by ensuring solubility of precursors, such as modified hydrophobic additives, in aqueous solutions. The medium in which silica nanoparticles are dispersed affects the hydrophobic coatings that are applied to textile materials. The application of the sol to textile materials using organic solvents produces more repellent coatings than the use of water as the solvent.

Commonly used solvents include methanol (Xue et al., 2009) and ethanol (Mahltig and Bottcher, 2008; Messaoud et al., 2010; Fir et al., 2007; Li et al., 2008) for sol synthesis. This is because organic solvents have lower surface tensions than water that allow better wetting properties of the sol over the fibres and therefore better formation of coatings. When water is used as a solvent, there is poor solubility of hydrophobic silanes and poor coating formation with cracking (Mahltig et al., 2005). Development of a solvent system where good wetting is achieved becomes important as it ensures good solubility and coating formation.

2.7 Antibacterial finishing of textiles

2.7.1 Bacteria: definition and structure

In order to understand the antibacterial activity, it becomes important to understand the fundamental concepts of microorganisms, their definition and associated methods of combat to minimise their presence and effect on textiles. Microorganisms can be classified as either bacteria, fungi, protozoa, helminths or viruses and usually described as being either prokaryotic or eukaryotic cells. Bacteria belong to the prokaryotic family because they do not possess a nucleus and contain single chromosomes (Harvey et al., 2007). Most bacteria grow very rapidly under warmth and moisture and assume either spherical, rod or corkscrew shapes. All bacteria have a rigid cell wall that surrounds the cell membrane having a typical structure as shown in Figure 2.8. This cell wall determines the shape of the organism and makes it difficult to kill bacteria and as a result, there has been developments of more effective antibacterial methods to combat bacterial growth by targeting its cell wall. The pili are fibrous proteins that are used for cell adhesion (Jarell, 2009). In Gram positive these pili are covalently linked polymers while in Gram negative, pili are linked by non-covalent protein-protein interactions (Jarell, 2009). The flagella are organelles that are used for swimming (Jarell, 2009) while the capsule, composed of polysaccharides, encases the bacteria and mediates interactions between the bacterium and the immediate environment (Ullrich, 2009). The nucleoid carries the bacteria genome associated with genetic make-up of bacterial cell while the ribosomes provide sites for protein synthesis (Srivastava and Srivastava, 2003). The plasma membrane is a permeable barrier that holds the cell together and the cytoplasm is a dense colloidal substance that houses the ribosomes (Singh and Tomar, 2008).

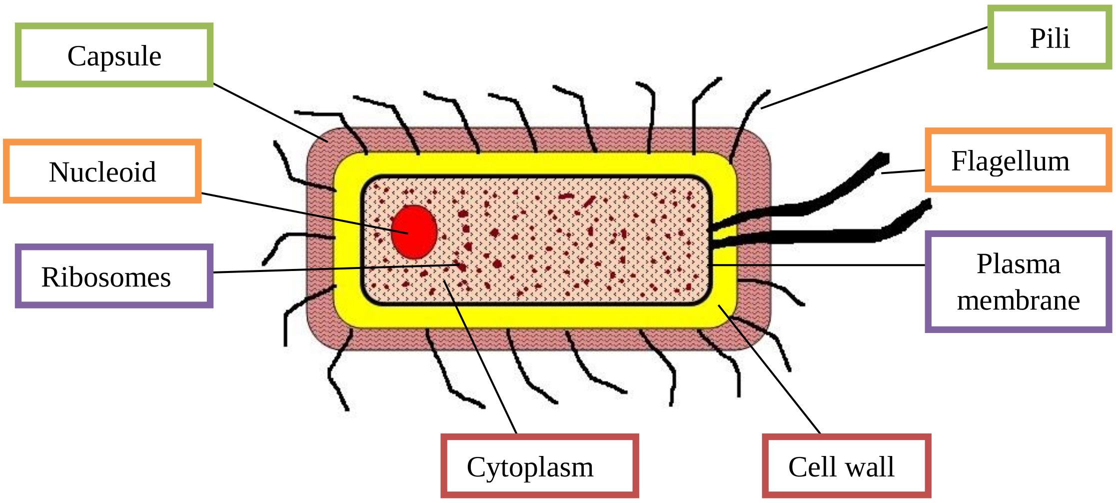


Figure 2.8 Typical bacteria structure

The cell wall of a bacterium is used to identify and therefore distinguish between different groups of bacteria. Using the cell wall, bacteria has been categorised into two distinct groups; Gram-positive or Gram-negative. Gram-positive bacteria such as *Staphylococcus aureus (S,aureus)* have cell walls that comprise of the peptidoglycan and the outer membrane while Gram-negative bacteria such as *Escherichia coli* (*E.coli*) have thick multi-layered peptidoglycan cell walls. The Gram staining technique allows the distinction to be made between Gram-positive and Gram negative. This technique involves the use of iodine to allow the crystal violet dye to fix and interact with the peptidoglycan layer of the bacteria. After rinse with 95% alcohol, a counterstain, Safranin, is then added. With Gram-positive bacteria, the purple stain of the crystal violet is retained while Gram-negative bacteria are decolourised by the solvent and assume the pink stain of the counterstain (Harvey et al., 2007). The cell wall is essential for bacterial cell survival and therefore becomes the area of interest for antibacterial agents.

2.7.2 Antibacterial agents

2.7.2.1 Types of antibacterial agents

Textiles offer the ideal medium for bacteria growth because of their large surface area that promote good bacterial adhesion, water storage properties as well as optimum temperature conditions for bacterial growth (Mahltig et al., 2010). These factors have raised the need for the development of countermeasures in the form of antibacterial finishes, to fight against bacterial degradation of textiles fibres and prevent biofouling of textiles (Mahltig et al., 2010). Such finishes aim to prevent cross-contamination and control the infestation of microbes, as well as protect the textile from deterioration, discolouration and staining (Shanmuggsundaram, 2007).

There are different types of antibacterial agents available that could be applied on textiles depending on the type of antibacterial property that is desired; usually determined by the textile’s end-use. Commonly used antibacterial agents include bleaching agents, metal-based compounds, coagulants, chlorinated aromatic compounds and quaternary ammonium compounds. Metals and metal salts can either be used in their free state or as compounds when considered as antibacterial agents. Even at low concentrations, metals are very toxic to microorganisms. Several metals such as copper, zinc and cobalt have been used as antibacterial agents, however silver is the most popular and widely used in general textiles (Gao and Cranston, 2008; Shanmuggsundaram, 2007; Chen et al., 2010). Quaternary ammonium compounds and chlorinated aromatic compounds utilise their charge to attract microorganisms and thereby act as an antibacterial agent using this method.

2.7.2.2 Mechanisms for antibacterial activity

Various methods developed have enabled the application of antibacterial agents onto textiles in order for textiles to exhibit activity. These methods are dependent on the nature of the antibacterial agent and conditions required for their effective use.

2.7.2.2.1 Controlled release/ leaching

Controlled release and leaching systems use a method employing a controlled release of antibacterial agents over time (Siepmann et al., 2012). Antibacterial agents such as silver and triclosan utilise such systems that are continually modified to achieve the ideal system for desired antibacterial delivery. Silver, for example, could be incorporated into the textile before fibres are produced into yarns and subsequently fabric (Gao and Cranston, 2008). This ensures that the silver is integrated into the textile and under moisture rich conditions, leaches to the fabric surface. The rate of leaching is influenced by the chemistry and the physical characteristic of the fibre as well as the amount of silver / metal present (Gao and Cranston, 2008; Mahltig et al., 2010) and as such, optimisation of the leaching technique would make silver and other agents effective antibacterial agents. The ion-exchange technique also uses the controlled release mechanism. In this technique, silver ions introduced through zeolite carriers incorporated in the coating, exchange silver ions with sodium ions present in moisture, under the right conditions (Gao and Cranston, 2008). Other techniques such as encapsulation utilise the control release mechanism using microspheres, as seen with antibacterial agents such as triclosan. Under the right conditions, the microspheres release the triclosan to provide antibacterial activity (Bajaj, 2002).

2.7.2.2.2 Immobilisation / non-leaching

Immobilisation or non-leaching systems involve the reaction of the antibacterial agents onto the textile fibres. Antibacterial agents such as quaternary ammonium compounds (QAC), biguanides and *N*-halamine have been bound to fabrics through covalent bonding. This bonding enables antibacterial agents such as quaternary ammonium compounds to be immobilised on the surface while other antibacterial agents such as chitosan and other coagulants have been immobilised on the surface through cross-linking to achieve non-leaching antibacterial system (Varesano et al., 2011).

2.7.2.3 Mode of action

Antibacterial agents have different modes of action, influenced by their chemical make-up. Metals and metal salts exhibit antibacterial properties through the action of binding to the intracellular proteins of bacteria and inactivating them. This inactivation disrupts the functioning of the bacteria's active enzyme centres (Bajaj, 2002). Antibacterial agents such as quaternary ammonium compounds bind to cell membranes and disrupt the lipo-polysaccharide structure of bacteria, causing cell breakdown (Shanmuggsundaram, 2007) while biguanides, being cationically charged compounds, interact with the anionic phospholipids in the microorganism cell wall which increases cell permeability and results in cell death.

Other antibacterial agents such as triclosan provide antibacterial activity by blocking lipid biosynthesis which causes cell breakdown (Williams, 2006; Shanmuggsundaram, 2007) while chitosan causes changes in the bacterial cell surface and affects cell permeability. Chitosan acts as a bacteriostatic as it inhibits bacteria growth rather than kill (Goy et al., 2009). *N*-halamine act through the oxidative properties of the N-Cl halamine bond that deactivates the microorganism. This bond, in the presence of water, produces chlorine and hydroxyl ions and forms an N-H bond. Solutions high in chlorine content act as a source for chlorine ions to regenerate this bond (Bajaj, 2002). Coagulants such as alcohols act by denaturing the protein structures while aldehydes, halogens and proxy compounds attack the cell membrane, enter the cytoplasm and affect the enzymes of microorganisms. Peroxo compounds, halogens and isothiazones are radical formers which release reactive free electrons that react with all organic structures such that the thiols in amino acids are oxidised (Shanmuggsundaram, 2007).

2.7.2.4 Antibacterial properties on textiles

Treatment of textile fabrics with antibacterial additives such as silver has occurred over the years to achieve antibacterial properties (Tomšic et al., 2009; Xing et al., 2007) due to its effective ability to deactivate the -SH group found on the bacteria enzyme (Tarimala et al., 2006). Silver, in the form of dodecanthiol-capped silver nanoparticles, has demonstrated good activity against Gram-negative bacteria such as *E.coli* (Tarimala et al., 2006). Limitations that surround leachable agents such as silver include the fluctuations in their concentrations during leaching that eventually affect efficacy and lead to coloration issues (Nischala et al., 2010). Immobilised agents such as quaternary ammonium salts like the cationic surfactant cetyltrimethyl ammonium bromide (CTAB) have shown antibacterial properties against *E.coli* and *S.aureus* that are comparable to leachable silver and also eliminate the inconsistent concentration levels that may promote bacterial resistance that are seen for leachable agents such as silver (Wang et al., 2010).

Research has identified that a combination of antibacterial additives could be utilised to improve efficacy. A combination of sodium alginate (SA) and ammonium compound of 3-(trimethoxysilyl) propyl-octadecyldimethyl ammonium chloride (TSA) colloidal solution has showed antibacterial activity against *E.coli* and *S.aureus*. (Kim et al., 2010). While biocides such as silver compounds, copper compounds and hexadecyltrimethyl- ammonium-*p*-toluolsulfonate (HTAT) have shown activity when tested against Gram-negative *Pseudomonas putida* and Gram positive *Bacillus subtilis* (Mahltig et al., 2010). Other combinations such as CTAB, octenidine and silver have exhibited activity at varying rates due to the different additives used. Combinations that possess octenidine have illustrated that this compound is a better additive due to less leaching properties when compared to CTAB and silver (Mahltig et al., 2004). It is through continued research that ideal antibacterial systems and associated properties are applied. Measures developed aim to produce treated textile fabrics that exhibit antibacterial properties that are beneficial and sustainable in textile end-uses.

Quaternary ammonium compounds have become popular antibacterial agents due to their positive charge density (Kim et al., 2010). Silanes modified with quaternary compounds and long alkyl chains provide both hydrophobic interaction and antibacterial activity. The charge on the quaternary compound attracts the cytoplasmic membrane while the long chains penetrate and therefore perforate through the membrane (Kim et al., 2010).

2.7.3 Limitations of antibacterial agents

Factors such as the simplicity of the application technique, durability of the coating and quantity of antibacterial agents are considered when antibacterial finishes are applied onto textiles. These factors are important in the determination of the efficacy of the antibacterial agent applied on the textile and, as discussed in Section 2.7.2; various methods have been used to impart an antibacterial property. Challenges faced in the use of predominantly viscous polymer based or controlled release finishes include the poor fabric handle, inconsistent activity and discolouration of the treated fabric (Mahltig et al., 2005). Other issues encountered involve the balance between high activity versus safe handling to ensure non-toxicity to humans, as well as the environment. Consumers are more aware of such environmental toxicological setbacks and in response, measures are being developed to minimise such problems. Though antibacterial agents that utilise the regeneration mechanism provide good antibacterial activity, the undesirable factors lie in the need for regenerating additives to maintain the antibacterial activity. The regeneration mode of action involves the release of an active agent that requires regeneration through substances such as bleaching agents during laundering or photochemical exposure (Bajaj, 2002) and therefore relies on such chemicals for its activity. When compared to other mechanisms, this method possesses the extra step of activation, without which, the finish would have no activity. Other agents that act using this method include photoactive TIO_2 nanosols which exhibit antibacterial properties upon exposure to UV light (Mahltig et al., 2005) while silver requires a moist / wet environment to achieve very good activity (Radeshkumar and Münstedt, 2006).

The controlled release system allows embedded antibacterial additives, such as triclosans, chitosans, biguanides and metal ions such as copper and silver, to be released at diffusion rates dependent on pore cavity size and how easily the agent can be released from such cavities and also the amount of agent i.e. the volume that is held in the cavities. This method is only as effective as the appropriate pore diameter and its degree of retention of the antibacterial agent. This becomes problematic when ideal pore diameters are not achieved and continued release of the additive leads to reduction in quantity and therefore efficacy. Antibacterial finishes with poor durability have limited end-uses. Durability becomes an important feature to include when developing antibacterial finishes especially when considering the economic and environmental impact of materials in the textile industry.

Durable coatings would influence overall chemical use as less chemicals would be used in synthesis and application processes, which subsequently would reduce the environmental impact of chemical waste and therefore make durable products more profitable in the long run. Benefits such as these have allowed non-leachable antibacterial finishes to gain popularity over the years as they lead to prolonged antibacterial properties when compared to leachable additives (Bajaj, 2002; Mahltig et al., 2005). Long chain quaternary ammonium compounds such as tetraalkylammonium trialkoxysilanes or cationic polymers have been immobilised in silica matrices to achieve these non-leachable antibacterial finishes. Such compounds exhibit antibacterial properties as the positively charged nitrogen on quaternary ammonium compounds attract the negatively charged bacterium into close proximity and long chains perforate the cell membranes (Menno and Koole, 2011). This action causes leakage of proteineous material that disrupts growth, lowers reproduction and leads to poor survival of microorganisms (Mahltig et al., 2005; Kim et al., 2010).

2.8 Multi-functional textiles

2.8.1 Recent literature highlighting dual functional textiles

Multi-functional properties become desirable when the individual properties that consist multi-functionality further improve the performance of treated fabrics. With the growing need to produce sustainable textiles, it becomes important to maintain textile quality and properties. One of the factors considered in the maintenance of textile properties is its degradation due to microbial interaction, especially in natural textiles. Textile degradation affects the longevity of treated fabric materials and as a result, measures to maintain imparted properties on treated fabrics are been developed. It has been reported that though hydrophobic surfaces reduce the binding energy at the interface between the bacterium and the hydrophobic surface, perfect protection of the surface from bacteria is not confirmed (Song et al., 2011). The incorporation of antibacterial additives to such hydrophobic surfaces has demonstrated further addition of antibacterial properties to the initial activity produced by the hydrophobic surface (Song et al., 2011; Shateri-Khalilabad and Yazdenshenas, 2010).

The combined property of hydrophobicity and antibacterial activity have been beneficial in providing a protective barrier against microbial attack and has been achieved on textile fabric using octyl-trimethoxysilane and silver particles (Shateri-Khalilabad and Yazdenshenas, 2010; Shateri-Khalilabad and Yazdenshenas, 2012; Sestak and Balogova, 2013). Through the use of hexadecyltrimethoxysilane and copper based sols, superhydrophobicity (water contact angle of approximately 150°) and antibacterial properties against both Gram-negative (*E.coli*) and Gram-positive (*S.aureus*) bacteria have been imparted on textile materials (Berendjchi et al., 2011). These precursors demonstrated that long alkyl chains and metal ions could achieve a dual functionality of water repellence and antibacterial properties. Other methods of producing multi-functional fabric for the purpose of protective clothing have been achieved through the use of diureapropyltriethoxysilane [bis(aminopropyl)-terminated polydimethylsiloxane (1000)] (PDMSU) and $^{1}H,^{1}H,^{2}H,^{2}H$-perfluorooctyltriethoxysilane (PFOTES) sol hybrid which resulted in antibacterial activity against Gram-negative *E.coli* and water contact angles of 147° (Vilcnik et al., 2009). These dual-functional textiles achieved through the pad-dry-cure method demonstrated dual functional properties; however, even with such properties on textiles, durability was not established.

2.8.2 Durability of dual functional textiles

Achieving effective antibacterial and / or hydrophobic properties is the first step of functionalising textiles. The degree of annealing to the fabric and consequently the durability of finishes on fabric samples determines whether treated fabrics are suitable for practical applications. This second characteristic necessitates the study of durability of finishes on textiles of interest. The more durable a finish is, the better the performance of the functionalised textile. With increasing performance comes increased popularity of products within consumer markets. Xue et al. (2008) and Shateri-Khalilabad and Yazdenshenas (2010) investigated the durability of their sol-gel functionalised coatings. In both instances, properties were maintained as Xue et al. (2008) observed a small reduction in water contact angle from 168° to 163° and Shateri-Kahlilabad and Yazdenshenas reported no significant changes in antibacterial activity and slight drop in water contact angle from 151° to 149°due to the incorporated epoxy to improve durability. Extensive sonication to determine when the functionalised textile became ineffective could have been carried out. Accredited laundering standards such as ISO 105-C06:2010 (Chattopadhyay et al., 2014) and AATCC 61-2003 for laundry test (Gao et al., 2009) could have been used to determine durability as it would have allow an objective assessment of obtained results as well as comparisons between related investigations. Wash fastness of functionalised textiles was also carried out by Tomšič et al. (2009). The cure temperature and application method were investigated and changes observed. Samples treated via the exhaustion method proved to be more antifungal than those treated through the pad-dry-cure method. They concluded that the efficacy of coatings applied through exhaustion method proved suitable to attain long-lasting antimicrobial results (Tomšič et al., 2009).

The growing need for efficient and shortened production times to maximise industrial output creates the need for quick and efficient processes. The sol synthesis duration of

24 hours employed in Textor and Mahltig’s research (2010) becomes a disadvantage even with the promising properties attained. Durable coatings act as a counter measure to high industrial costs as less sol synthesis and its application would be required due to low production turnovers. Textor and Mahltig (2010) demonstrated durability to abrasion using the Martindale test of involved 50,000 rub cycles for treated fabric. Hydrophobicity was measured and changes in the mechanical properties such as stiffness of fabric were identified. Future work, such as cross-linkers to improve flexibility of the coating, could have been included to determine its effect on the abrasion performance especially if there was a different application for the treated fabric.

2.9 Conclusions

The sol-gel technique can impart both hydrophobicity and antibacterial properties using inorganic and organic agents synthesised in acidic and / or alkaline conditions. Most literature reviewed incorporated fluorinated precursors to achieve high hydrophobicity for properties such as self-cleaning. This research focussed on the more environmentally friendly long alkyl chains to impart this property. Recent studies have been carried out which used these silanes and has demonstrated that the hydrophobicity achieved using halogenated silanes can also be achieved using long chain alkoxysilanes. Factors that influence the type of coating formed on cotton surfaces such as particle size and solvent system have been discussed and some correlation between solvent system and particle size and their effect on sol systems established. This highlighted the need for optimisation of the sol synthesis processes in order to achieve desirable properties on treated cotton fabric. The use of different application techniques has achieved durable antibacterial and hydrophobic properties. Though studies have tested for durability, thorough laundering using international laundering standards could be incorporated in the study of the durability of multi-functional properties for an extensive study of this property, which would highlight limitations in the application method used and identify the need for further method optimisation. This would also determine potential fields to which the treated materials are best suited as different fields would require not just different properties but different degrees of efficiency.

Previous research groups have focused more on the use of the pad-dry-cure method to apply sol-gel to the cotton fabric because this is the traditional method incorporated in production lines in the textile industry. Methods used to achieve multi-functions have involved the use of several steps as opposed to the use of “one-pot” application system to achieve durable multi-functional properties. Treatment of cotton fabric samples has also involved immersion in the sol, followed by the pad-dry cure method. The research undertaken studied the application of sol-gel onto cotton through treatment in sol solution over a period of time to determine the effect of longer impregnation time on the properties imparted on the treated cotton fabric. A “one-pot” system was also used to impart both self-cleaning and antibacterial properties.

CHAPTER 3:

HYDROPHOBIC AND SELF-CLEANING PROPERTIES OF SOL-GEL TREATED COTTON FABRIC

3.1 Introduction

A surface is characterised as hydrophobic if the water-based liquid placed on the surface forms droplets, rather than spreading and soaking into it (Arkles, 2006). The formation of droplets occur as a result of attractive forces between molecules of the liquid that prevent its separation and subsequently spreading. Once these attractive forces, referred to as cohesive forces, of water-based liquids are greater than forces associated with its interaction on the surface, the water gathers and droplets are formed. The contact angle between the liquid / solid interfaces of droplet and surface can indicate the degree of hydrophobicity of the surface (Arkles, 2006). “Although the contact angle of water on a substrate is a good indicator of the relative hydrophobicity or hydrophilicity of a substrate, it is not a good indicator of the wettability of the substrate by other liquids. Critical surface tension is associated with the wettability properties of a solid. It serves as a better predictor of the behaviour of a solid with a range of liquids” (Arkles, 2006). The increase in the critical surface tension of a given surface would decrease the contact angle because there is an increase in the adsorptive behaviour of the substrate. It is the relationship between these two factors that establishes the level of hydrophobicity of a functionalised surface and thereby textile (Arkles, 2006).

Modified alkoxysilanes with long alkyl chains have been used to apply hydrophobic properties on textile surfaces (Textor and Mahltig, 2010). These hydrophobic silanes tend to assemble in different positions in the sol-gel polymeric network due to steric hindrances, forming silica nanoparticles of varying sizes. The application of sols having such varying silica particle sizes on cotton fabric leads to the formation of sol-gel coatings of an uneven surface topography that further roughen the cotton fibre surface and subsequently results in water repellence. In this research, sols were synthesised using a combination of different alkoxysilanes to achieve hydrophobic and potentially self-cleaning properties as well as antibacterial properties on knitted cotton fabric. Silanes with different lengths of alkyl chains were used to determine their influence on the hydrophobic property of the treated cotton fabric in this chapter. Future research to establish the optimised levels of hydrophobic silanes could be carried out to achieve superhydrophobicity and very low roll-off angles for self-cleaning properties.

3.2 Materials and Equipment

3.2.1 Materials

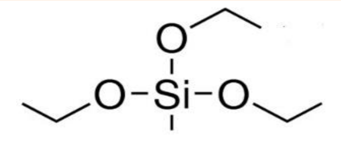
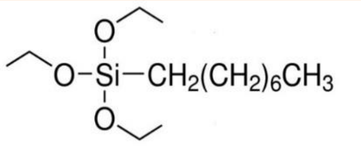
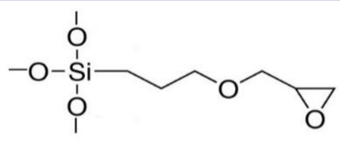
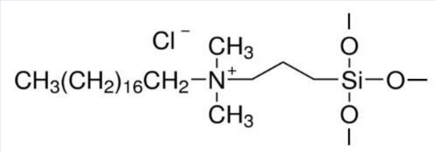
3.2.1.1 Fabric

Scoured and bleached interlock knitted fabric made from 100% cotton was supplied by Vertical Garments Ltd (Leicester, UK).

3.2.1.2 Silanes and solvents

Methyl-triethoxysilane, Octyl-triethoxysilane, 3-(trimethoxysilyl)propyloctadecyl dimethylammonium chloride, and 3- glycidopropyltrimethoxysilane were purchased from Sigma Aldrich. The structures of these silanes are shown in Table 3.1. For the purpose of this thesis, these silane presursors were abbreviated as follows: Methyl-triethoxysilane was represented as MTES, Octyl-triethoxysilane as OTES, 3-(trimethoxysilyl) propyloctadecyldimethylammoniumchlorid as QUAT and 3-glycidopropyltrimethoxysilane as GLYMO. This simplified labelling of graphs and tables throughout the thesis.

Table 3.1 Silanes used in sol synthesis and their corresponding structures (Sigma Aldrich, 2015)

Methyl-triethoxysilane (MTES) 	**Octyl-triethoxysilane (OTES)** 
3-glycidopropyltrimethoxysilane (GLYMO) 	3-(Trimethoxysilyl)propyl octadecyldimethylammoniumchloride (QUAT) 

Ethanol was purchased from Fisher Scientific. Felosan NFG (non-ionic detergent) and sodium carbonate were purchased from MP Biomedicals.

3.2.2 Equipment

3.2.2.1 Fabric Treatment: Dye machine

To ensure adequate agitation of fabric material in the sol liquor, a Datacolor Ahiba Nuance Top Speed II IR dyeing machine was used (Figure 3.1). This dye machine possesses microprocessor technology to accurately control heating and cooling functions and has circular rotating motion programme systems to provide agitation. Such systems allow reproducibility of results for multiple treatments.

Figure 3.1 Datacolor Ahiba Nuance dyeing machine used for fabric treatment (Datacolor)

Heating of samples being treated was achieved using the inbuilt infrared heating technology while a precision PT-100 probe was used to monitor and display actual temperature in dye tubes during treatment. These dye tubes are designed to create a pressured atmosphere to aid in temperature build up and stability, as well as maximum safety to prevent spillage. For cooling, cold water supply pipes were connected and circulated through the inlet and outlet system within the ahiba cavity. Programmes were written using the automated controller system that allowed parameters such as temperature, speed and treatment time to be set. This was displayed graphically on a visual display for easy monitoring throughout treatment. An automated alarm system alerts when programmes have finished.

3.2.2.2 Pad mangle

To control the liquor pick-up of the treated fabric, an Ernst Benz pad mangle was used (Figure 3.2). Liquor pick-up is controlled by passing impregnated fabric between two rollers at a defined pressure to squeeze out air and force the liquor through the fabric material (Choudhury, 2006).

Figure 3.2 Image of Ernst Benz pad mangle used for padding process

3.2.2.3 Contact angle equipment

To determine the contact angle of treated and control fabric, a CAM200 Optical Contact Angle Meter (KSV Instruments Ltd) was used (Figure 3.3).

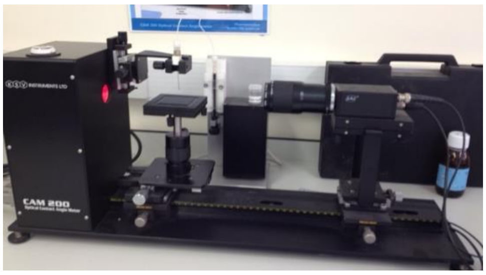


Figure 3.3 The CAM200 optical contact angle meter used for the measurement of the water contact angle

The CAM 200 uses drop shape analysis to determine static and dynamic contact angles and runs its image analysis software on WindowsTM operating systems (2000/XP). For effective measurement, the CAM 200 utilises monochromatic lighting, a high resolution CCD camera and telecentric lens to generate high quality images. Good images are required for accurate measurement of contact angles as calculations of angles are highly dependent on image quality.

3.3 Experimental

3.3.1 Fabric pre-treatment

The knitted cotton fabric, purchased from Vertical Garments Ltd (Leicester, UK) was scoured further to improve absorbency and ensure that fabric was completely clean. To achieve this, the cotton fabric was treated for 45 minutes with 1 g/L Felosan NFG and 2 g/L sodium carbonate at 100°C. After scouring, cotton fabric was rinsed three times at 60°C with distilled water including neutralisation using 1 g/L acetic acid for 15 minutes at 60°C. After rinses, fabrics were hydroextracted to remove excessive water and allowed to dry at ambient temperature overnight.

3.3.2 Sol synthesis

Sol preparation with mixed silanes

To synthesise sols, 300 mL of 50% v/v ethanol solution was stirred and adjusted to pH 3.2 with 1M hydrochloric acid. 30 mL of MTES, 5 mL of GLYMO, 10 mL of OTES and 5 mL of QUAT at their ratio of 30: 5: 10: 5 were added dropwise to the 50% v/v ethanol solution and continuously stirred (Figure 3.4). These silane values and ratios preliminarily optimised from earlier feasibility tests carried out by TEAM research at initial stages of sol development (TEAM Research Report, 2010). However, initial reactions with the ratio used resulted in a cloudy sol with unreacted silanes resting at the surface of the sol at reaction pH of 4. To improve silane reactivity in the 50% v/v ethanol solution, the pH of the solvent was adjusted within the acidic range to increase hydrolysis rate and thereby improve solubility (Arkles et al., 1992).

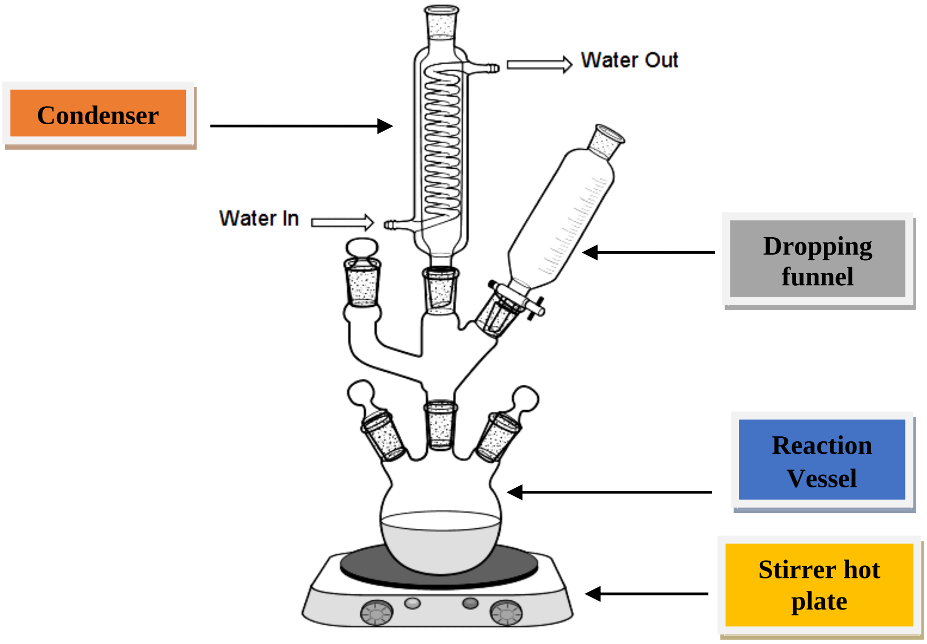


Figure 3.4 Sol synthesis reaction set-up using a cold water cooling system (condenser) to prevent loss of highly volatile chemicals such as ethanol

A clear sol would indicate that all the silanes participated in the hydrolysis reaction and formed part of the nanoparticle network that developed as the reaction proceeded. The pH was therefore varied within the range of 3 and 4. It was found that at pH 3.2, the cloudy mixture became clear after 1 hour of constant stirring. This pH value was then used for all reactions. Sol synthesis was carried out for 4 hours at room temperature. After the 4 hour reaction time, the synthesised sol became clear and colourless.

Sol preparation with individual silanes

In order to understand the contribution of the individual silanes to the properties of the sol-gel finish on the fabric, sols containing individual silanes were also prepared. For synthesis of sols containing MTES silane, 30 mL of MTES was added to 300 mL of 50% v/v ethanol solution. For the GLYMO sol, 5 mL of GLYMO was added to 300 mL of 50% v/v ethanol solution. For the OTES sol, 10 mL of OTES was added to 300 mL of 50% v/v ethanol solution and finally for the QUAT sol, 5 mL of QUAT was added to

300 mL of 50% v/v ethanol solution. Then the individual silane in 50% v/v ethanol solution was stirred for a total of 4 hours at room temperature.

3.3.3 Fabric application process

For sol application, the synthesised sol solution was applied either neat or dilute. For dilution, deionised water was used to obtain a 50% v/v sol concentration. To treat knitted cotton fabric, liquor to goods ratio of 25:1 was used. This liquor ratio provided the sufficient amount of sol required to ensure that the fabric was immersed fully during treatment over the 4 hour period. Sol, either neat or dilute, was placed in the dye tubes and pre-weighed fabric immersed in the sol and the tubes were sealed (Figure 3.5).

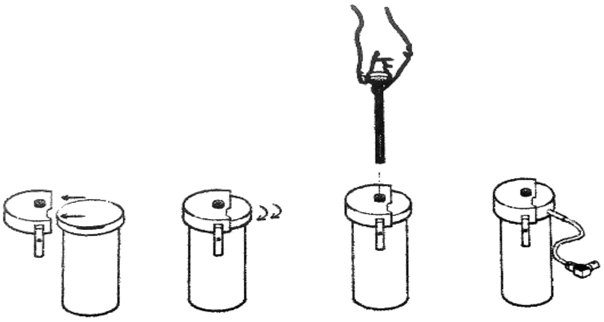


Figure 3.5 Process of sealing a dye tube of the Ahiba dye machine. The dog point on the lid was tightened using a screwdriver (Ahiba Nuance Manual,2001)

The sealed tubes were placed in the sample wheel holder of the Ahiba Nuance dye machine and pre-set programme started (Figure 3.6). To achieve 40°C during the 4 hour treatment time, the Ahiba was programmed to ramp the temperature up as quickly as possible. This ensured that the system, being heated by infrared lamps (Figure 3.6), reached 40°C from an initial starting temperature of approximately 24°C within 5 minutes. Agitation rate was set at 20 rpm for the duration of the 4 hour treatment time and tube motion and rotation was as shown in Figure 3.7.

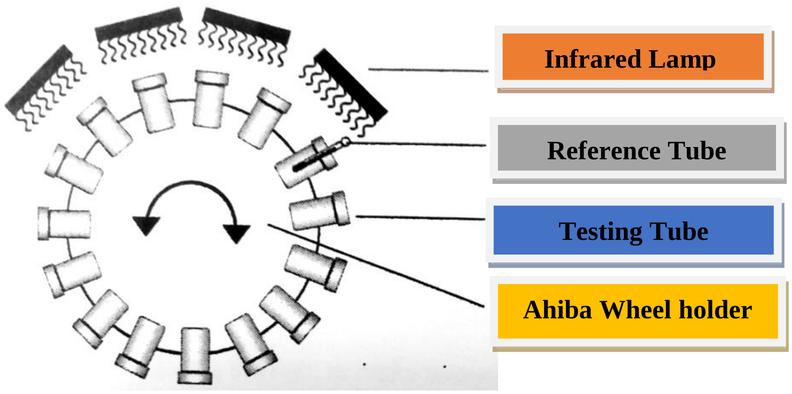


Figure 3.6 Schematic diagram of dye tubes arrangements on the wheel (Ahiba Nuance Manual, 2001).

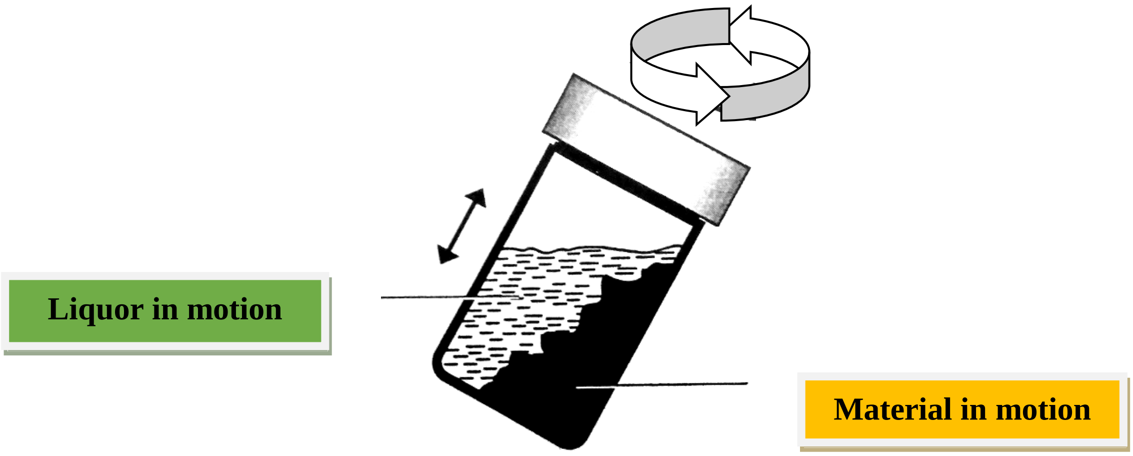


Figure 3.7 Motion of material and solution in a dye tube (Ahiba Nuance Manual, 2001)

To ensure consistent liquor pick-up, treated cotton fabric samples were passed through the pad mangle twice at a pressure of 45 kg/cm at a speed of 1 m/min or once at 15 kg/cm at speed of 1 m/min. The padded cotton fabric samples were dried at ambient temperature overnight. For further drying, the treated cotton samples were dried at 70°C for 5 minutes in a fan operated oven followed by curing at 120°C for 20 minutes to initiate covalent bonding of sol-gel coating to cotton fabric. After curing, the samples were allowed to cool overnight and rinsed in the Ahiba at ambient temperature (24°C) for 30 minutes. The rinsed cotton samples were then hydroextracted to remove excess water and dried in a fan operated oven at 40°C for 2 hours. The samples were then ready for testing of properties.

3.3.4 Hydrophobicity testing

3.3.4.1 Water Rating Number Measurement

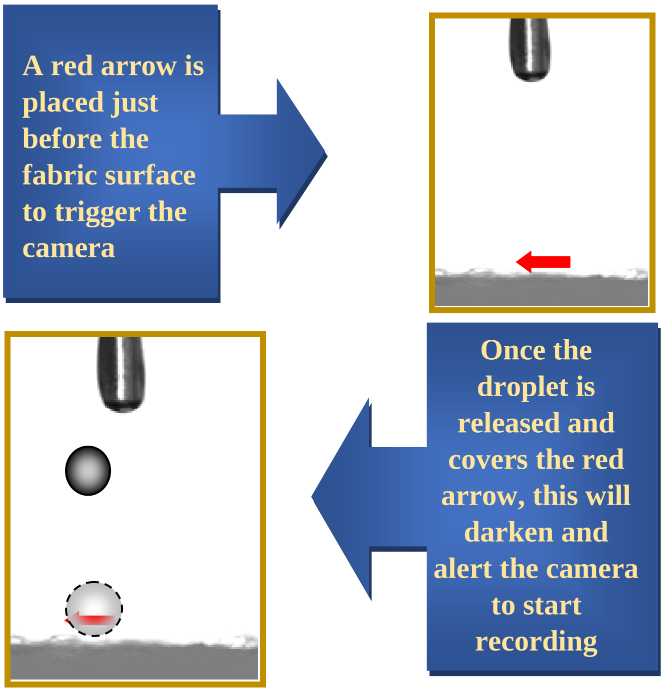
To test hydrophobicity, the Water Rating Number (WRN) hydrophobicity test method modified from the DuPont test AATCC 118-1972 was used. Testing was carried out using different concentrations of iso-propanol solutions and behaviour of droplets formed on surface observed. Table 3.2 shows the concentration of iso-propanol used and their corresponding water rating number. To determine the water rating number for a treated fabric sample, a drop of 20 µL of test solution was placed on the surface of the fabric and observed for 10 seconds. Measurements started with the lowest concentration of iso-propanol and repeated with increasing concentrations until the highest iso-propanol concentration was reached which did not wet the fabric surface. For example, if at the value of 4, the droplet was absorbed in less than 10 seconds, the WRN value for the surface on which it was placed would be 3.5.

Table 3.2 Water Rating Numbers (WRN) and their equivalent iso-propanol concentrations

Water Rating Number	Concentration of iso-propanol v/v (%)
1	2
2	5
3	10
3.5	15
4	20
4.5	25
5	30
6	40

3.3.4.2 Water Contact Angle Measurement

To calculate the water contact angle (WCA) for treated cotton fabric, images were obtained using the CAM200 Optical Contact Angle Meter. The syringe used to hold the solution for droplet deposition on the tested surface was filled with deionised water by pressing the “Fill” option setting of the CAM200 software testing system. The needle of the filled syringe was held in place and aligned within the frame and in front of the micro camera. The cotton sample was mounted and placed underneath the needle in front of the micro camera and system programmed to dispense 11 μL of deionised water on the surface of the fabric. To ensure that images were captured within a specified time, a trigger was placed on the screen that was activated once the droplet of test solution darkened the section where it was positioned; thereby triggering the camera and capturing the image (Figure 3.8).



A red arrow is placed just before the fabric surface to trigger the camera

Once the droplet is released and covers the red arrow, this will darken and alert the camera to start recording

Figure 3.8 CAM 200 images showing the dispensing mechanism used for image capture when droplet detaches from needle and drops unto fabric.

For image capture, the CAM200 software system was set to record for 1 second and 5 frames captured within that time. Once images were obtained, contact angle calculations were carried out using ImageJ software. This software required manual alignment of points to calculate the angles on the image and as such, 5 points were selected on the image and "calculate contact angle" option selected. Calculation lines were marked on the image and the angles calculated on the left and the right (Figure 3.9). The average angles were calculated and produced in a spreadsheet. To consider human error, calculation of angles was carried out 5 times on the same image and the averages obtained to serve as the final contact angle for that image.

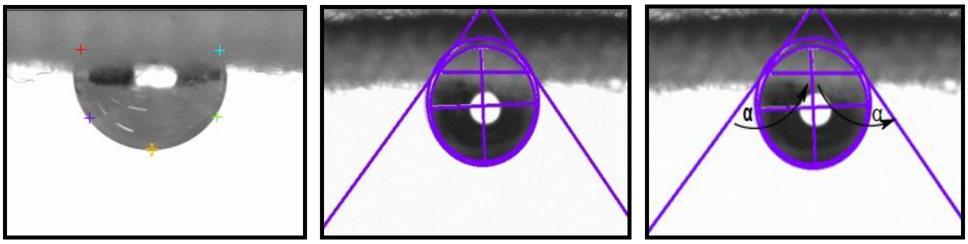


Figure 3.9 Calculation of Water Contact Angle (WCA) using ImageJ software

3.3.4.3 Roll-off Angle Measurements

ROLTEST 9-11 testing was used to determine roll-off angles of water on textile samples of interest. All roll-off angles were carried out by INOTEX (Czech Republic), a collaborative partner of the SAFE-PROTEX project using equipment shown in Figure 3.10.

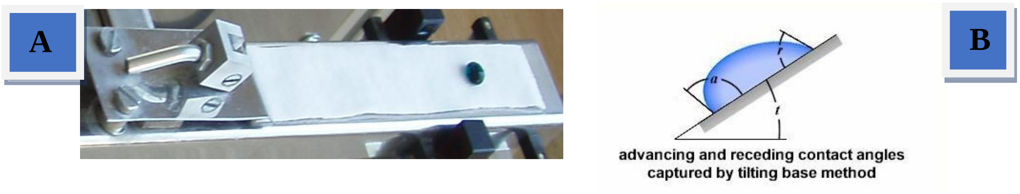


Figure 3.10 Roll-off angle sample set up (A) and theoretic roll-off angle calculation (B)

3.3.4.4 Self-cleaning measurements

Different types of water based liquids including water, milk, tea, blackberry juice and coffee were also placed on the cotton fabric to test for the fabric's self-cleaning properties. This was achieved by placing the fabric on a flat surface, dropping 20 µL of different liquids on the fabric and this was tilted at different angles to observe the rolling of droplets from the surface. The images were obtained using iPhone 4S camera and Windows photo gallery.

3.3.5 Fabric weight gain calculation

Cotton fabric was weighed using an analytical balance before and after treatment. Equation 3.1 was used to determine the percent weight gain achieved after sol-gel treatment. The cotton samples were conditioned in a fan operated oven at 25°C overnight to ensure that weight measurements were consistent.

$$Weight\ gain\ (\%) = \left[\frac{Final\ weight\ (g) - Initial\ weight\ (g)}{Initial\ weight\ (g)}\right] \times 100$$

Equation 3.1

3.4 Results and discussion

3.4.1 Silanes and their effect on hydrophobicity

To determine the influence of silane type on the hydrophobic property, sols containing MTES, GLYMO, OTES and QUAT, respectively, were synthesised as stated in Section 3.3.2 and applied onto knitted cotton fabric using the application procedures as described in Section 3.3.3. Treated cotton samples padded twice at 45 kg/cm, due to better fabric handle, were measured for their water rating numbers (WRN) as described in Section 3.3.4.1 and the results illustrated in Figure 3.11. Treated cotton samples with sols containing the OTES silane achieved a higher WRN value of 3.5 when compared to cotton samples treated with sols containing the MTES silane that achieved a WRN value of 2. Cotton samples treated with sols containing the QUAT silane achieved the highest WRN value of 4 when compared to values obtained for treated samples with sols containing OTES silane. Even at low quantities of 1.6% v/v (5mL) QUAT silane, a higher WRN value of 4 was achieved when compared to quantities of 10% v/v MTES silane and 3.3% v/v OTES silane, that achieved WRN values of 2 and 3.5, respectively. The alkyl chain length for the MTES, OTES and QUAT silanes equated to 1, 8 and 18 carbon chain length, respectively, which would influence hydrophobicity.

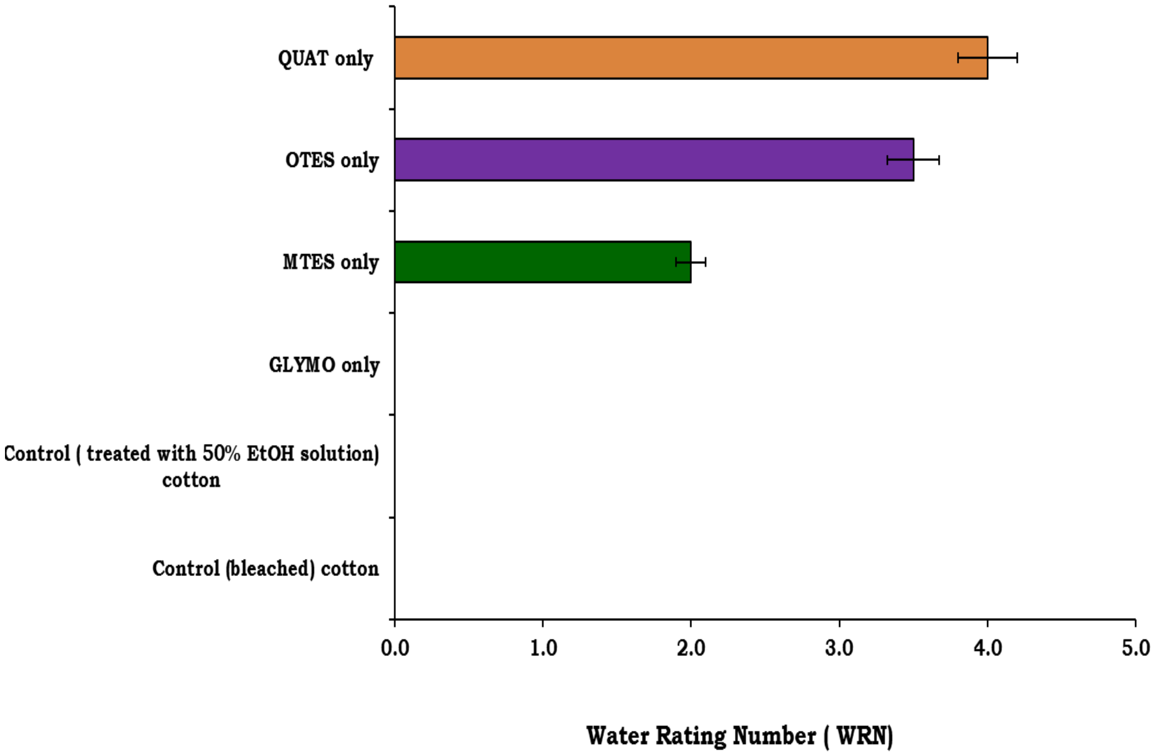


Figure 3.11 WRN values of knitted cotton treated with sols comprising of MTES, OTES and QUAT, respectively, and the control (no silane) sample treated with 50% v/v ethanol solution

The WRN values obtained were comparative to the WRN values of 4 that were achieved by Textor and Mahltig (2010) on treated cotton polyester blend fabric with silanes having carbon chain lengths within the range of 6 to 16. Though the results are similar, Textor and Mahltig utilised 15% v/v hydrophobic silane while this research was able to achieve WRN values of 4 with QUAT silane added at 1.68% v/v in 50% ethanol as opposed to the 95% ethanol solution used in the study by Textor and Mahltig (2010). This demonstrated that the developed treatment method was able to impart hydrophobic properties using very low precursor quantities and also illustrated that the alkyl chain length did play a part in imparting the hydrophobic property. From the results, an increase in alkyl chain length increased the hydrophobic property of the treated cotton samples. This confirmed the reviewed literature in Section 2.5 that identified long hydrophobic alkyl chains as means to provide and therefore produce hydrophobic surfaces. Long alkyl chains are composed of unreactive carbon and hydrogen atoms that can not interact with water based liquids, leading to the repulsion of water based liquids, and subsequently, the hydrophobic property. The hydrophobic sol-gel coating with varying sizes of particles and aggregates on individual fibres could create nano- or micro-scale roughness on fibre surfaces. The nano- or micro-rough coating on the uneven morphology of knitted cotton fabric could simulate the rough surface of the lotus leaf that achieves the superhydrophobic surface.

The control samples, which included the bleached knitted cotton and cotton fabric treated with 50% v/v ethanol solution, were also tested for any hydrophobic properties. This was to determine whether the sol-gel coating was the only contributing factor to achieve the hydrophobic property. As shown in Figure 3.11 no hydrophobicity was seen for these samples. It was also observed that the cotton fabric sample treated with sols containing GLYMO silane did not exhibit any hydrophobic properties. This could have been as a result of no hydrophobic components to repel water, as the GLYMO silane possesses an epoxy group that forms hydroxyl groups upon ring opening (Carey, 2001). These hydroxyl groups would interact with the hydroxyl groups of water based liquids, thereby creating a hydrophilic surface.

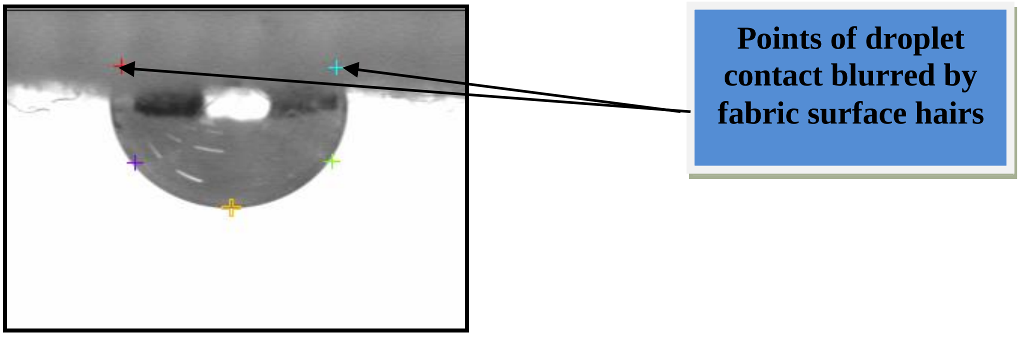
The topography of a surface, its composition and critical tension play a major role in its behaviour towards certain liquids i.e. its ability to absorb or repel (Bhusan et al., 2009). As discussed in Section 2.4.2, the hydrophobic silanes have critical surface tension values between 20-30 dynes/cm. Silanes used in sol synthesis had critical surface tension values that fell within this range and as these values are lower than the threshold of 45 dynes/cm needed to decrease absorptive properties, water repellence was imparted

(Arkles, 2006; Mittal, 2009). Achieving low critical surface tensions would have contributed to achieving repellence and as such, was observed on the fabric sample treated with the sol solution containing the hydrophobic silanes. The WRN values for the treated fabric samples were only indicative of hydrophobicity. In order to obtain a quantitative measure of hydrophobicity, the water contact angles (WCA) were measured (Table 3.3). Comparisons of the two testing methods for determination of hydrophobicity were carried out to establish the correlations between WRN values and WCA values. Another beneficial aspect for such comparisons would be determining whether WRN values, if corresponding to water contact angles, could be used to predict possible WCA values. WRN measurements would then act as an indicative tool to determine hydrophobic properties without carrying out the WCA analysis. Table 3.3 showed that WCA increases with increasing WRN value.

Table 3.3 Water Rating Numbers (WRN) and Water Contact Angles (WCA) of knitted cotton fabric treated with different individual silanes of MTES, OTES and QUAT, respectively. The bleached cotton was used as a control sample

Fabric samples	WRN	WCA (°) (measured at 1 second)
Control (bleached) cotton	0	0.0 (±0.0)
MTES only	2	120.0 (±1.1)
OTES only	3.5	129.0 (±12.7)
QUAT only	4	133.2 (±6.8)

The results illustrated that with an increase in alkyl chain length, there was an increase in WCA values. The standard deviation values obtained for WCA values indicated that there was a wide variation between the values of angles measured for each fabric sample. These variations, caused by the surface hairiness of the fabric material, made it difficult to determine a clear point of contact between droplet and surface as shown in Figure 3.12, as it was difficult to clearly define the baseline on the image and points of selection for angle calculation were carried out manually. This increased the occurrence of human error upon selection of points and thereby affected the degree of accuracy. Different fabric types could be used to remove surface hairiness and improve contact angle measurements.



Points of droplet contact blurred by fabric surface hairs

Figure 3.12 Image demonstrating the points selected for determination of the baseline for WCA value calculation using ImageJ

The influence of the type of surface on water contact angle values has been widely investigated. Studies have discovered that the surface roughness and its associated microscopic variations create barriers that are not considered by the Young's equation used for angle calculations. Theoretical equations developed by Young do not consider such surface topography as calculations of water contact angles are based on a flat surface and as a result surface roughness not considered; this however would influence and subsequently contribute to value variation (Yuan and Lee, 2013). Further testing could be carried out to determine WCA and WRN values of the sol-gel coating on smooth surface rather than on the fabric. This would help determine the coating's WCA and WRN values and how these values are influenced by the fabric surface of the knitted cotton.

3.4.2 Base formulation and hydrophobicity

The base formulation utilised the 30: 5: 10: 5 ratio of MTES: GLYMO: OTES: QUAT for sol synthesis as described in Section 3.3.2. Knitted cotton fabric was treated with the synthesised sol through processes as described in Section 3.3.3 and treated samples tested for their hydrophobicity and self-cleaning properties as described in Section 3.3.4. Table 3.4 showed the WRN values and average WCA values of samples treated with base sol solution. It was found that WRN values obtained for cotton samples treated with such sols were the same as those obtained for samples treated with sol containing QUAT only. This indicated that the long alkyl chains on QUAT contributed in achieving the hydrophobic property. When samples were tested for their WCA values however, it was observed that though the WRN values were the same, the samples treated with the base sol had higher WCA values of 142.5° as opposed to 133.2° seen for the individual QUAT sol. This revealed that the combination of silanes with different alkyl chain length was beneficial in increasing the hydrophobic property.

Table 3.4 Average % weight gain, average WRN values and average WCA values of samples treated with optimised sol solution. Samples were padded twice at 45 kg/cm at 1m^2/min

Sample	Pad pressure (kg/cm twice)	Weight Gain (%)	WRN	WCA (°)
100% sol-gel treated Knitted cotton	45 (twice)	7.1	4	144.2
	45 (twice)	7.1	4	142.9
	45 (twice)	7.1	4	142.5
Average (std. dev)		7.1 (± 0.0)	4 (±0.0)	142.5 (±0.9)

Ozcelik et al. (2008) stated that “touching a fabric is the first action that buyers perform in order to evaluate the fabric quality to choose a suitable fabric for garments and estimate the performance of the fabric for the end use”. The highest pad pressure of 45 kg/cm achievable on the pad mangle in the lab was used to control the liquor pick-up by removing excessive sol from the fabric for low amount of coating on the fabric. The low amount of coating, with a reasonable percent weight gain of 7%, on the treated cotton which equated to approximately 0.68g of silane on the surface for higher pad pressure of 45 kg/cm. For treated cotton samples that were padded at 15kg/cm, approximately 0.84g was added on fabric after sol-gel treatment. The low weight gain at high pressure resulted in little change to the fabric's handle, which could be confirmed by rubbing the fabric between fingers to determine any changes. The benefits of maintaining the fabric handle similar to the control cotton provides the opportunity to apply the treated cotton to its existent fields, such as clothing, as a technical textile with the added property of hydrophobicity. Achieving high WCA and WRN values even with low sol quantities becomes economical as less sol would be needed to achieve hydrophobic properties and thus reduce chemical quantities and their associated costs. Alkoxysilanes and their organic substituent, how much of the surface they cover, the amount of unreacted groups of the silanes and their distribution as well as their orientation on the surface, influences the hydrophobic property on the surface (Mittal, 2009). These factors are therefore considered during the development of hydrophobic surfaces. Sol-gel coatings that incorporate hydrophobic silanes in their network influence water repellence (Yuan and Lee, 2013; Textor and Mahltig, 2010; Gupta and Gulrajani, 2014). Measures such as the use of silanes with longer chains could be used to achieve higher WCA values. The use of hexadecyltrimethoxysilane achieved WCA values with 143-152° (Xu et al., 2012) and 140 °(Gao et al., 2009). Optimisation of application processes could achieve higher WCA values for superhydrophobicity and subsequently improved self-cleaning properties.

3.4.3 Sol-gel treatment and self-cleaning properties

The self-cleaning property has gained popularity due to its potential to eliminate the need for large volumes of laundering (Ornes, 2012; Anthony, 2011; Zheng, Gao and Jiang, 2007). Considerable investigations in the use of TiO_2 to achieve self-cleaning properties on textiles have been carried out and have been well documented in literature (Nazari et al., 2011; Jiang et al., 2011; Pakdel and Daoud, 2013; Xu et al., 2014, Xin and Daoud, 2004). Even with positive results, however, there are limitations in the need of UV for photocatalysis to occur before self-cleaning properties can be exhibited. This has led to the development of alternative approaches to achieve self-cleaning. Low roll-off angles and their abilitty to impart self-cleaning properties has been demonstrated by nature's botantical lotus leaf (Forbes, 2008; BBC News, 2011). This leaf has a waxy surface that imparts hydrophobic properties which allow water droplets to form and easily roll off the surface.

The ability of water droplets to roll off is due to the waxy microstructures of surface roughness which are smaller in size when compared to dirt particles present of the surface. This difference in size reduces interfacial and adhesion forces between dirt particle and leaf surface. The self-cleaning property of the botanical leaf occurs when the rolling water droplets roll off and come into contact with the dirt particle on the waxy surface. As adhesion between the dirt particle and leaf surface is less than adhesion between water and particle, the dirt particle is captured by the rolling droplet and removed from the surface (Gulrajani, 2006). Achieving low roll-off angles ensures that water droplets roll off easily and therefore remove dirt and any other contaminants present on such a surface (Bhusan et al., 2009). This phenomenon consistutes self-cleaning properties.

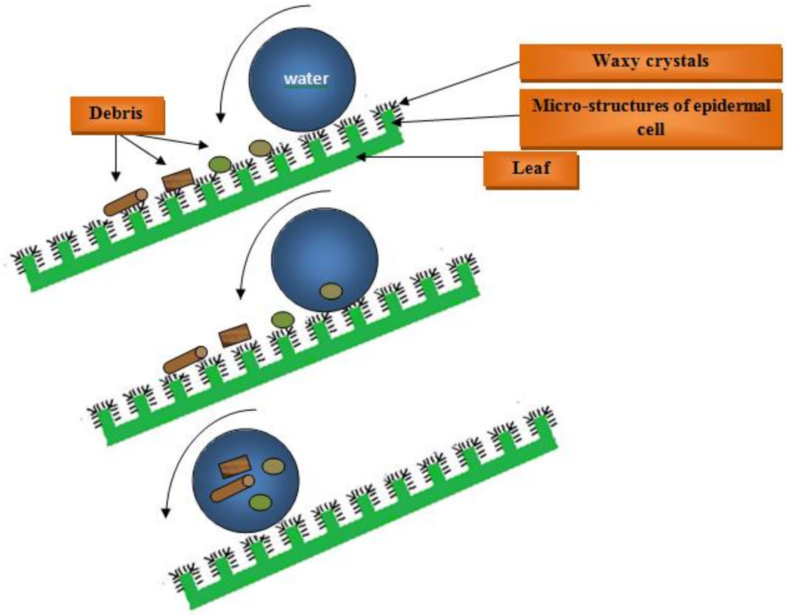


Figure 3.13 Schematic showing how debris and other contaminants are removed off the surface of the botanical lotus leaf, demonstrating its self-cleaning properties

This research focussed on achieving self-cleaning properties through the application of hydrophobic properties on cotton fabric. Roll-off angles measured for treated knitted cotton padded twice at 45 kg/cm are illustrated in Table 3.5.

Table 3.5 Roll-off angles for 100% knitted cotton treated with sol synthesised using base formulation for sol synthesis

SAMPLE TYPE	**ROLL OFF ANGLE (°)**
Control (bleached) cotton	absorbed
Treated knitted cotton with base sol	16.5 (±0.2)

A roll-off angle of approximately 16° was attained for the sol-gel treated cotton samples. Though this value was higher than 6° achieved by the lotus leaf, the treated cotton demonstrated that water droplets could easily roll off the surface. Optimisation to reduce angles to as low as 6° could be carried out to further improve the self-cleaning properties of the treated samples. Increasing the contact angle would reduce the roll-off angle because as the contact of droplets on surface reduces, the easier it rolls off such a surface.

In order to study the self-cleaning property and how roll-off angles assist with this, the treated fabrics were tested further with other liquids. Different water based liquids were used because of their varying surface tensions, staining ability and their influence on self-cleaning properties as discussed in Section 3.4.1. Water based liquids such milk, blackberry juice, tea, coffee and water itself were used to test this property and results shown in Figure 3.14. Treated cotton samples with different amounts of GLYMO were used in the study of abrasion performance and thus, a representative sample containing less GLYMO was tested for its self-cleaning properties.

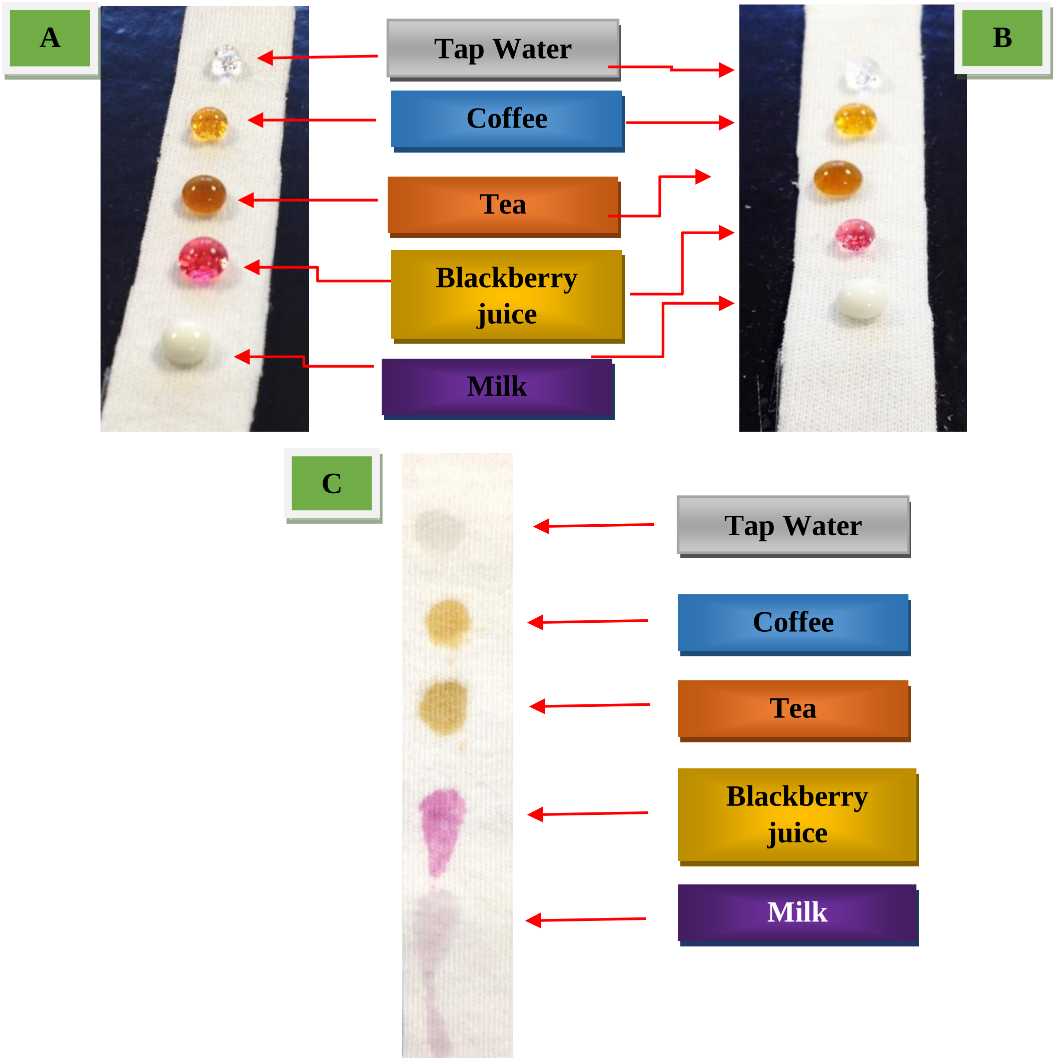


Figure 3.14 Different water based liquid behaviour (Blackberry juice, milk. tea, coffee and water) on untreated cotton fabric (c) and cotton fabric treated with base sol formulation containing 5 mL of GLYMO (A) or 2.5 mL of GLYMO (B) following by padding twice at 45 kg/cm

Liquids with different surface tensions would require different properties on the surface for their repulsion and subsequently the ability of such liquids to form droplets and roll off the surface. From Figure 3.14, It was seen that all the different liquids formed droplets on the treated knitted cotton surface. This demonstrated that the treated cotton samples with both full (5mL) and half (2.5mL) amount of GLYMO cross-linker could repel water based liquids. This repulsion led to bead formation of the water based liquids on the surface of the treated cotton fabric. The variation in amount of GLYMO cross-linker was for the investiagtion of its influence on the abrasion propertes of the treated cotton, which is discussed further in Chapter 5. When these water based liquids were dropped on the control (bleached) cotton, the liquids were immediately absorbed by the surface of the cotton fabric (Figure 3.14c). Bead formation of liquid on surfaces is a good indication that these droplets can roll off the surface under the right angle. To determine whether these droplets could roll off the hydrophobic surface of the treated cotton, the treated fabric samples were placed on a flat surface and tilted (Figure 3.15).

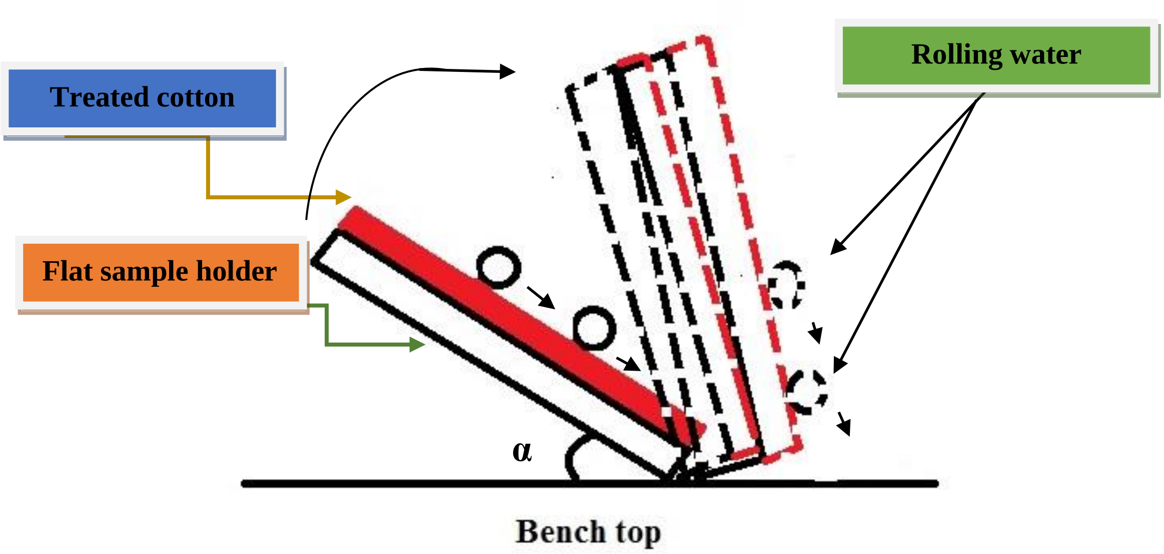


Figure 3.15 Diagram demonstrating tilting of treated cotton fabric after the treated cotton was attached to flat surface using adhesive tape

When tilting of the treated cotton fabric samples reached a certain angle, droplets of the different liquids started rolling off the surface of the treated cotton sample. Blackberry juice, water, and coffee easily rolled off the treated cotton fabric with no trace liquid on the surface, however, residual milk and tea droplets remained on the surface even when the treated sample was tilted approximately 90°. This indicated that such liquids would not completely roll off the treated surface. The self-cleaning property that is demonstrated by the botanical lotus leaf involved the rolling off of water droplets that collected any dirt or contaminants in its path. To determine whether this property could be achieved on the treated cotton samples, rinse water was applied to the surface of the cotton surface that had residual droplets. It was found that most of the residual liquids could be rinsed off the surface with water. Complete removal of trace liquid could be achieved by wiping of the surface with tissue paper (Figure 3.16 (b)). This test was able to demonstrate the degree of self-cleaning imparted by the sol-gel treatment using the methods defined in Sections 3.3.2 and 3.3.3. From these results, further development of the sol application could be carried out in order to demonstrate better self-cleaning properties. The hydrophobicity could be improved as this influences water behavior on treated surfaces and therefore how easily they roll off such surfaces (Choi et al., 2009; Xiu, 2009).

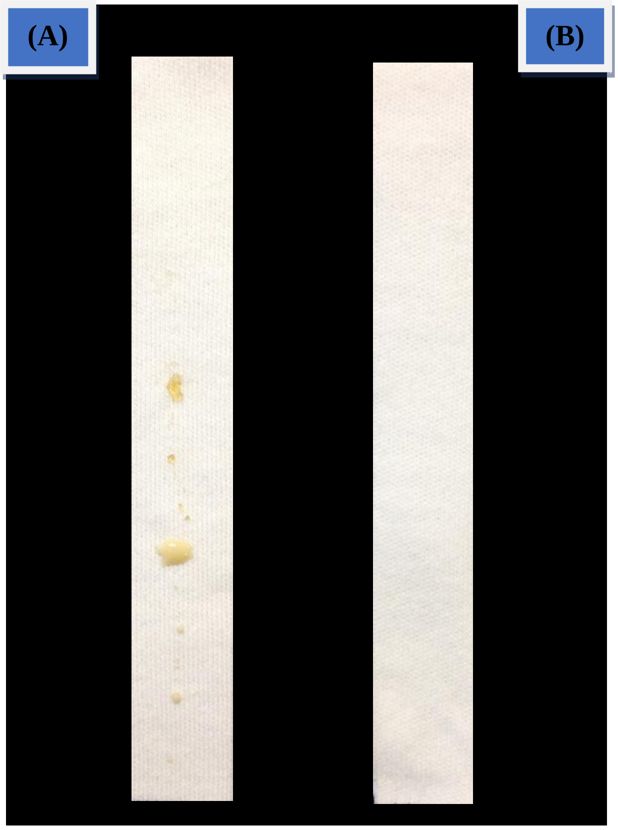


Figure 3.16 Self-cleaning properties of treated cotton fabric after liquid droplets have rolled off (A) and after deionised water rinse (B)

3.5 Conclusions

The sol-gel formulation was developed to achieve the dual functionality of hydrophobic and antibacterial properties for finishing cotton fabrics. The mixture of silanes used in the formulation included Methyl-triethoxysilane (MTES), 3-glycidopropyltrimethoxysilane Octyl-triethoxysilane (OTES) and 3-(trimethoxysilyl) propyloctadecyl dimethylammonium chloride (QUAT) at their ratio of 30: 5:10: 5 mL. The initial formulation developed produced cloudy sols with thin layers of unreacted silanes. To achieve homogenous and clear sols, investigations of pH of the 50% v/v ethanol solution and its influence on silane hydrolysis was carried out. This was because the HCl used to adjust the pH acted as a catalyst to initiate hydrolysis of the Si-OR to Si-OH, resulting in the increased solubility of silanes in the 50% v/v ethanol solution; without the application of heat. It was found that at pH 3.2, the mixture of all hydrophobic silanes became clear after the 4 hour reaction, indicating that silanes were fully hydrolysed.

Homogenous and clear sol could be uniformly applied on to cotton fabrics. As opposed to the conventional dip and pad application process currently used in sol-gel application, the application process developed in this research involved the immersion of cotton samples in sol solution under agitation for 4 hours at 40°C. This application process could allow cotton fibres to be directly involved in the sol hydrolysis and condensation and cross-linking to form the gel polymer network on the fibre surface. This application process improved the durability of sol-gel coating applied on cotton fabric. Treated cotton samples that were padded at 45 kg/cm retained cotton fabric handle.

The influence of individual silanes with various lengths of alkyl chains on the hydrophobic property of cotton fabric was investigated. Water contact angles of 120° 129°and 133° and water rating numbers of 2, 3.5 and 4 were obtained for MTES, OTES and QUAT, respectively. It was observed that with increase in alkyl chain length on the hydrophobic silanes, there was an increase in hydrophobicity.

Hydrophobic properties on cotton fabrics were achieved using the base formulation using the hydrophobic silanes of MTES, OTES and QUAT at the ratio of 30: 10: 5mL. Their WCA values of 142° and WRN values of 4 were achieved. Using low silane concentrations leads to the use of less chemicals and as a result, reduction in production costs. The treated cotton samples also achieved roll-off angle of 16°. This roll-off angle demonstrated that water droplets could easily roll off the surface of the treated cotton surface at a tilt of 16°. This feature was likened to the lotus leaf effect associated with self-cleaning. The different water based liquids (coffee, tea, blackberry juice, milk and water itself) dropped on the treated cotton fabric could easily roll off the surface except milk, which left very small residual traces on the fabric. The residual milk traces could be rinsed off with water without staining. This demonstrated the extent of self-cleaning properties imparted by the sol-gel treatment. Further manipulation of the sol and incorporation of longer chains could be used to achieve superhydrophobicity and thereby reduce roll-off angles to improve the self-cleaning properties. The cost of silanes used fall within the range of £40-200 for approximately under 1L. Though this may seem costly, such expenses could be accommodated in bulk purchases especially at industrial levels. Further tests focused on silane quantities and impact on properties could be investigated to ensure that cost of process makes the end product commercially viable.

CHAPTER 4:

ANTIBACTERIAL PROPERTY OF SOL-GEL TREATED COTTON FABRIC

4.1 Introduction

The current change in the social-economic society has expanded the end-uses of textiles from apparels up to technical textiles (Zanoaga and Tanasa, 2014). Consumers are now increasingly aware of the hygienic lifestyle which has led to the rising necessity and expectation for textile finishes with antibacterial properties (Kumar and Krishnaveni, 2011). Moreover, the use of cellulose fibres has increased over recent years mainly due to its eco-friendly, biodegradable, economical and hydrophilic nature. These features have resulted in its application not only to its traditional textile products but also in diversified outdoor and indoor-applications (Yin et al., 2012). With the increasing possibilities of end-uses, the common problem seen for natural fibres such as cotton is that “cellulose fibres also provide a convenient media for growing micro-organisms, because of their large surface areas and the ability to retain moisture along with other basic requirements such as nutrients, oxygen and appropriate temperature” (Yin et al., 2012). To combat this feature, recent studies have investigated the use of antibacterial finishes to provide protective barriers for cellulose fibres and therefore textiles (Slater, 2003). Antibacterial finishes are applied on textile materials such as cotton to prevent and control microbial infestation, proliferation and cross-contamination as well as reduce odours and stain formation, fibre degradation and overall deterioration of the textile (Zanoaga and Tanasa, 2014).

The optimal benefit of antibacterial agents is to not only destroy unwanted microorganisms but also satisfy the safety needs towards humans and the environment; and therefore ensure that toxicity levels are below the minimum criterion (Zanoaga and Tanasa, 2014). Antibacterial finish composition and structure disrupt microbial behaviour. This disruption either leads to inhibition of microbial growth, referred to as bacteriostasis, or death of microorganisms, usually termed as microbicidal (Murphy, 2004). The mode of action of an antibacterial agent is vital as it helps to establish its efficacy as an agent and therefore determines the ideal environment in which it is best applicable (Anderson et al., 2012; Zanoaga and Tanasa, 2014). Another important aspect that determines the effectiveness of an antibacterial agent includes the method of interaction with microbes; that is, the mechanism employed to ensure that there is contact with microorganisms to execute its mode of action (Murphy, 2004; Russell, 2002). Various antibacterial agents and their mode of action have been discussed in Chapter 2 and benefits of the use of immobilised antibacterial agents stated. The non-migratory feature of antibacterial agents such as 3-(trimethoxysilyl) propyloctadecyl dimethylammonium chloride (QUAT) enables finishes applied on textile to exhibit a durable and prolonged barrier against bacterial interactions (Gouveia, 2010; Paul, 2015); a feature that has been employed by the Aegis technology developed by Devan Chemicals (Devan Chemicals, 2013). The positive charge present on the nitrogen of the QUAT (Figure 4.1) attracts the microorganisms to its long hydrophobic chains which aid in cell disruption (Devan Chemicals, 2013; Jiang et al., 2005).

To produce the antibacterial property of the dual functionality of self-cleaning and antibacterial properties on cotton fabric, a quaternary ammonium compound, chemically modified to include a silane component, was used. This modified silane has been referred to as QUAT in previous chapters and will also be referred to as such in this chapter. The QUAT silane is the 3-(trimethoxysilyl)propyloctadecyl dimethylammonium chloride silane used in sol synthesis, using the base formulation discussed in Chapter 3. The QUAT silane was used as the antibacterial agent in this research due to its non-migratory nature and easy incorporation into the sol system. The alkoxysilane extension attached to the quaternary ammonium compound would undergo hydrolysis and condensation reactions and also react further with other hydrolysed silanes in the formulation to produce a sol-gel network incorporating the quaternary ammonium compound. This network, through further condensation reactions with cotton fabric, would immobilise the QUAT on the cotton fabric. 100% knitted cotton fabric samples treated using sols of this nature were tested for their antibacterial property and findings will be discussed in this chapter.

4.2 Materials and Equipment

4.2.1 Materials

Microorganism

ATCC 6538 *Staphylococcus aureus*

Chemicals

Oxoid CM0003 Nutrient Agar and Oxoid CM0001 Nutrient Broth were used to make nutrient agar plates and nutrient broth, respectively. Potassium phosphate (KH_2PO_4) was used to prepare 3.4% w/v buffer solution and the pH was adjusted with 5% w/v Sodium hydroxide solution (NaOH) to pH 7.2.

4.2.2 Equipment

An easySpiral PRO Automatic Spiral Plater was used to plate inoculum onto Petri dishes. Dixon ST18 Portable Gas Autoclave was used for sterilisation. A New Brunswick Innova 44 shaking Incubator was used for incubation and a Thermo Scientific Heλios Gamma UV/ Vis Spectrophotometer was used to determine the concentration of the inoculum. A Mettler Toledo pH meter was used to measure the pH of the buffer solution.

4.3 Determination of the Antimicrobial Activity of Antimicrobial Agents under Dynamic Contact Conditions

4.3.1 Principle of ASTM E 2149-10: Standard Test Method

This antibacterial test method has been designed to evaluate the antimicrobial activity of non-leaching, antimicrobial-treated specimens under dynamic contact conditions (ASTM International, 2013). The antimicrobial activity of a substrate-bound, non-leaching antimicrobial agent is dependent upon direct contact of microbes with the antibacterial agent (ASTM International, 2013). This test measures the antibacterial activity of a treated sample by shaking samples of immobilised surface-bound materials in a known concentrated bacterial suspension for 1hour contact time. This dynamic shake test was developed to overcome difficulties that would be faced using the standard antibacterial test methods. With hydrophobic specimens, the challenge is to ensure routine quality control and screening testing and also adequate contact between treated surface and inoculum (ASTM International, 2013).

The ASTM E 2149-10 test method enables the evaluation of the antibacterial activity for different types of treated substrates with a wide range of micro-organisms. This test is versatile and allows investigations such as the effects of contaminations from substances such as hard water, proteins, blood, serum, various chemicals and other contaminants (ASTM International, 2013). Factors such as the metabolic state of the bacterial species need to be considered when testing the efficacy of antibacterial agents. This is because the metabolic state of the bacteria can influence the effectiveness of certain antimicrobial agents (Tang et al., 2002). Life cycles (Figure 4.1) of micro-organisms are important in the study of antibacterial agents as the different stages of such cycles may alter the bacterium's susceptibility to particular antimicrobial agents.

To ensure that such factors are eliminated from the testing method, this test method employs 1 hour contact time in a buffer solution that causes metabolic stasis in the bacteria population. Metabolic stasis of the bacterium or the stationary phase of its growth pattern is the area of no change / stagnancy in bacteria population (Figure 4.1). A consistent bacterial population allows for more accuracy in the evaluation of the antibacterial agent and its activity against a bacterium of choice (Tang et al., 2002) and therefore reproducibility of results. By maintaining the bacterial population, the activity of the antibacterial agent can be determined accurately as the concentration of the bacteria would be determined and maintained within a narrow concentration (ASTM International, 2013).

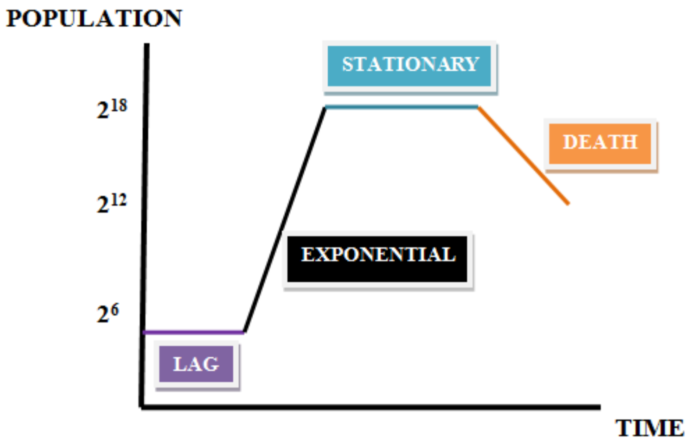


Figure 4.1 Different growth stages of a typical bacterium as a factor of time

4.3.2 Fabric sample Preparation

The cotton fabric samples (treated and untreated) were cut into small sections (approximately 1cm by 1cm) and weighed to obtain a total weight of 0.2 g. This weight was used as opposed to the 2 g stated in the testing standard to ensure that the amount of samples could be obtained from the same fabric samples, which was limited by size. The weighed fabric samples were then placed in standard autoclave bags that were sealed by applying heat. These bags were placed in an autoclaved sample holder and autoclaved at 121°C for 15 minutes. The autoclaved samples were then allowed to dry because the bags were wet from the steam. Dried bags were then unpacked and placed in the buffer solution media used for testing.

4.3.3 Preparation of agar plates and testing media

To prepare the agar plates, 28 g of Oxoid nutrient agar was placed in 1 L of distilled water. The resultant agar solution was sterilised by autoclaving. After autoclaving, the sterilised agar solution was poured into Petri dishes and allowed to set in close proximity to a flame to ensure that surrounding air was sterile (Figure 4.2). Once dried, agar plates were refrigerated to prevent any bacterial growth that also acted as a measure to preserve the plates.

Figure 4.2 Preparation of agar plates in sterilised air surroundings

The Oxoid nutrient broth was used as a medium for bacterial culture growth. To prepare this broth, 13 g of nutrient agar was placed in 1 L of distilled water and solution autoclaved. 9 mL of this solution was aseptically placed in autoclaved universal bottles. The buffer solution needed for testing was prepared using 34 g potassium phosphate (KH_2PO_4) added to 1 L of distilled water as below. 34 g of KH_2PO_4 was added to 500 mL of distilled water and the pH of the solution was adjusted to 7.2 using 5% w/v of sodium hydroxide (NaOH) solution. After pH adjustment, 500 mL of distilled water was added to ensure the volume was 1 L. This adjustment was made to ensure that metabolic stasis could be achieved and as a preservative measure, the solution was stored at 4°C. For use, 1 mL of the bulk buffer solution was placed in 800 mL of distilled water and 9.8 mL of this solution dispensed in 20 mL universal bottles.

For antibacterial evaluation of treated knitted cotton, the ASTM E 2149-10 test method was followed and a few modifications made to account for smaller fabric sample size as mentioned in Section 4.3.2. To grow the bacteria, a bead of Gram-positive ATCC 6538 *Staphylococcus aureus* (*S.aureus*) was placed in 10 mL of nutrient broth, incubated at 37°C and agitated for 24 hours at 120 rpm. As per standard method, the culture was diluted in buffer solution until the solution had an absorbance measurement of 0.28 ±0.02 at 475 nm when measured spectrophotometrically. The concentration of the culture at this absorbance has been equated to 1.5 - 3.0 x 10^8 CFU/mL. Bacterial culture solution was diluted with buffer solution to yield a concentration of 1.5 - 3.0 x 10^5 CFU/mL using the serial dilution method (Figure 4.3).

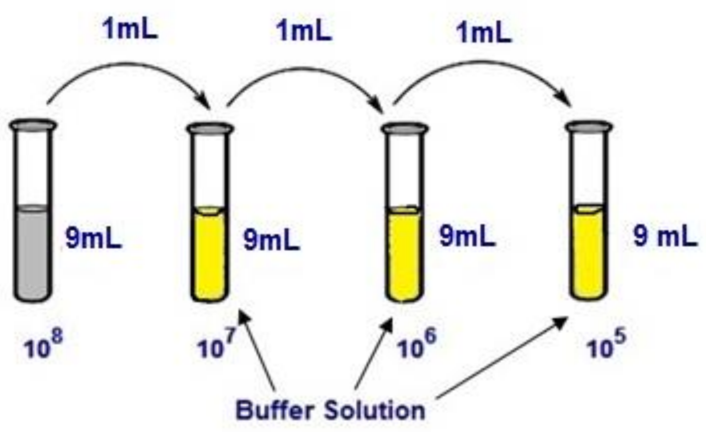


Figure 4.3 Serial dilution method used to obtain final culture concentration to inoculate treated and untreated cotton samples

To eliminate the influence of the nutrient broth as a source of nutrients that may cause an increase in bacterial population, further modifications were made to the testing method. The culture prepared was centrifuged to separate the bacteria from the nutrient broth solution. The bacterial pellet produced was redissolved in buffer solution and the desired concentration determined using the dilution method.

4.3.4 Testing of fabric samples

Knitted cotton fabric samples treated as described in Section 3.3.3 were also tested for their antibacterial property. Alongside this testing, control samples consisting of untreated cotton, referred to as control (bleached) cotton, and buffer solution without fabric were also testing to determine their effect on any antibacterial properties. To test for the antibacterial property, 0.2 g of autoclaved control and treated cotton fabric was added to 9.8 mL of the diluted inoculum (conc. 1.5 - 3.0 x 10^5 CFU/mL) and mixed using a VMR bench vortex mixer for 60 seconds. Samples were then placed in the incubator and shaken at 120 rpm at 37°C for 1 hour and 24 hours.

4.3.5 Determination of bacterial colonies after incubation using the spiral plating method

4.3.5.1 Principle of technique

This method of plating (Figure 4.4) uses a controlled dispenser mechanism governed by micro processing systems that allows deposition of a liquid onto the surface of a rotating agar plate. This method plates bacterial suspensions of approximately 400 - 400,000 CFU/mL on 100 mm agar plates and eliminates all intermediate dilutions and ensures rapid bacterial counting through direct plating.

Figure 4.4 Spiral plating equipment (Topac Inc. 2002)

The operating process of the spiral plater dispenses inoculated solution using a logarithmically decreasing volume plating method that dispenses inoculated solution on the surface of a rotating plate as the sample plating tube moves from the centre of the plate outwards (Figure 4.6 (b)). This is referred to as an Archimedes spiral plating method (Figure 4.5). The volume of inoculum plated is calibrated and known at each point on the petri dish. The bacterial concentration on the inoculated plate is determined by dividing the number of colonies on the plate by the volume dispensed in the same sector of the petri dish (Interscience, 2010).

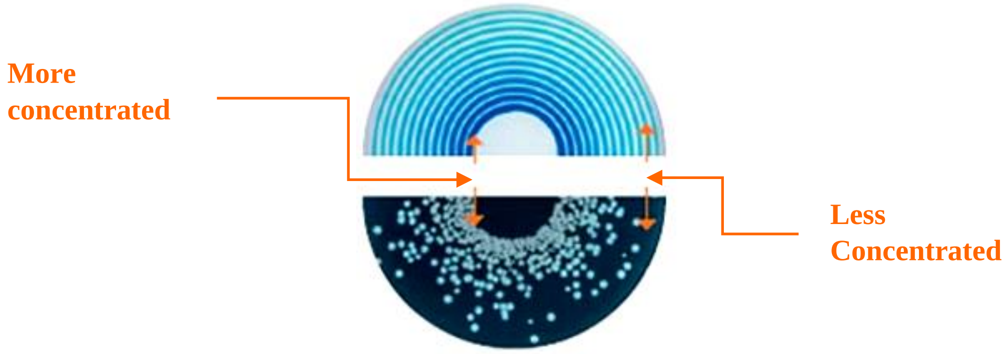


Figure 4.5 Archimedes spiral plating method (Interscience,2010)

4.3.5.2 Spiral plating technique

Sample plating was carried out at 0 hour, 1 hour and 24 hours incubation time. Treated cotton and control cotton samples and buffer solution plated at 0 hour were not incubated. To determine antibacterial activity over a period of contact time, control and treated cotton samples were incubated at 37°C for 1 hour and 24 hours. Both control and treated cotton samples where plated using the spiral plating method. Each sample was vortexed for 1 minute and solution poured into sample holder of the spiral plater. For sample solution plating, the spiral plater picked up 50 µL of solution and plated it within 25 seconds (Figure 4.6).

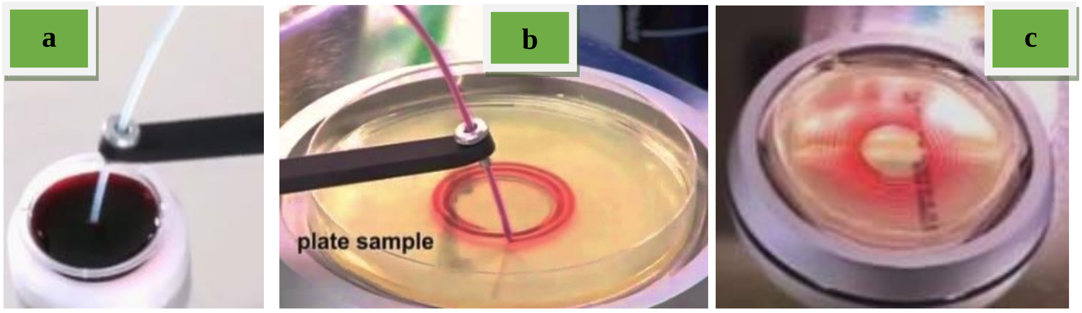


Figure 4.6 Spiral plating using easySpiralPRO which includes sample pick up (a), sample plating (b) and plated sample (c) (Interscience, 2014)

Between repeat plating of the same sample, rinsing was carried out to ensure that there was no cross-contamination between samples (Figure 4.7). To ensure this, a cleaning method was incorporated in the automated programme used. To clean, the “disinfect” button on the control panel was pressed and cleaning carried out using 70% v/v ethanol. The 70% v/v ethanol solution was used as a disinfectant and the sterilised distilled water used as the diluent as well as the rinsing solution after disinfection (Figure 4.7).

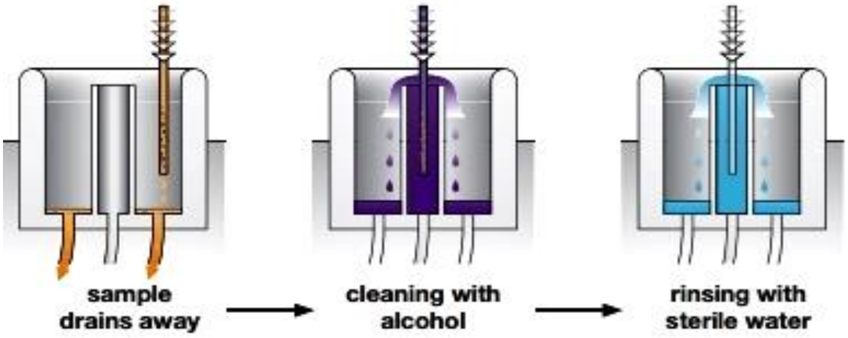


Figure 4.7 Cleaning procedure for the easySpiral PRO which begins with drain away of the sample, followed by disinfectant wash and rinsing with sterile water (Interscience, 2014)

Plated samples were placed in microbial incubation containers and incubated for 24 hours at 37°C to allow bacterial growth. Once incubation was complete, incubated samples were then evaluated and bacterial colonies counted to determine bacterial concentration and subsequently the activity of the antibacterial agent against the bacteria. To calculate the number of colony forming units for a plated sample, the inoculated agar plate was placed on the sample grid that divided the plate into 6 sections as per spiral plating procedure (Figure 4.8).

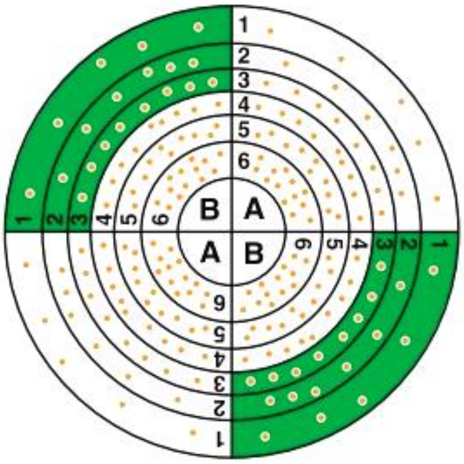


Figure 4.8 Method of bacterial colony counting using the spiral plater. Green areas indicate the sections used to count the 20 colonies needed for the calculation of CFU/mL (Interscience, 2014)

The method of calculation involved the counting of colonies from the outer edge towards the centre (highlighted green in Figure 4.8) using a graduated sample grid. Colonies were counted in either opposite sections of A or B. A minimum of 20 colonies were counted from the outer sector i.e. 1, inwards. If 20 colonies could not be counted in this sector, counting of colonies continued into sector 2 until 20 colonies were counted as described by Interscience counting procedure. If more colonies were present in the sector, after 20 colonies were counted, all colonies in that sector were counted. Once complete, the opposite sectors were also counted and values obtained were added.

To ensure accuracy, only sections with clearly defined individual colonies were used. Sector 1 - 6, as shown in Figure 4.8, correspond to different dilutions as the spiral plater dispenses the inoculum on the agar plate (Table 4.1). Once 20 or more colonies were counted from the outer to inner, the sum of colonies in opposite sections was added and the sector number in which the 20th colony was found was noted. These two numbers were then used to calculate the CFU/mL values of the sample. Each sector (1-6) had a constant by which the number of colonies was divided by (Table 4.1).

Table 4.1 Spiral plating constants values to calculate CFU/mL for inoculated samples.

Section	Constant	Dilution factor
1	1.00	10^6
2	2.58	10^5
3	5.07	10^4
4	9.00	10^3
5	15.21	10^2
6	25.00	10^1
Complete petri dish	50.00	50.00

The total number of colonies counted were divided by the section constant and multiplied by the dilution factor (Table 4.1). This calculation determined the CFU/mL of the solution plated at 0 hour, after 1 and 24 hours incubation. The CFU/mL values were then converted to Log values using the Log10 function in the excel package. These log values were used to calculate the Log reductions and therefore illustrate any antibacterial activity of the cotton samples being tested.

4.4 Results and discussion

4.4.1 Antibacterial property of fabric samples treated with sols containing individual silanes

For determination of any antibacterial property for sol-gel treated cotton fabric, testing was carried out on samples treated with sols synthesised using individual silanes MTES, GLYMO, OTES and QUAT, respectively. From the results shown in Figure 4.9, it was found that cotton fabric samples treated with sols containing the QUAT alkoxysilane showed antibacterial activity against *S.aureus* at log reduction in CFU/mL of 0.58 and 0.69 after incubation time of 1 hour and 24 hours, respectively. When compared to cotton samples treated with sols containing hydrophobic silanes, MTES and OTES, antibacterial activity at a log reduction in CFU/mL of approximately 0.24 and 0.40, respectively, was detected after 24 hours incubation time.

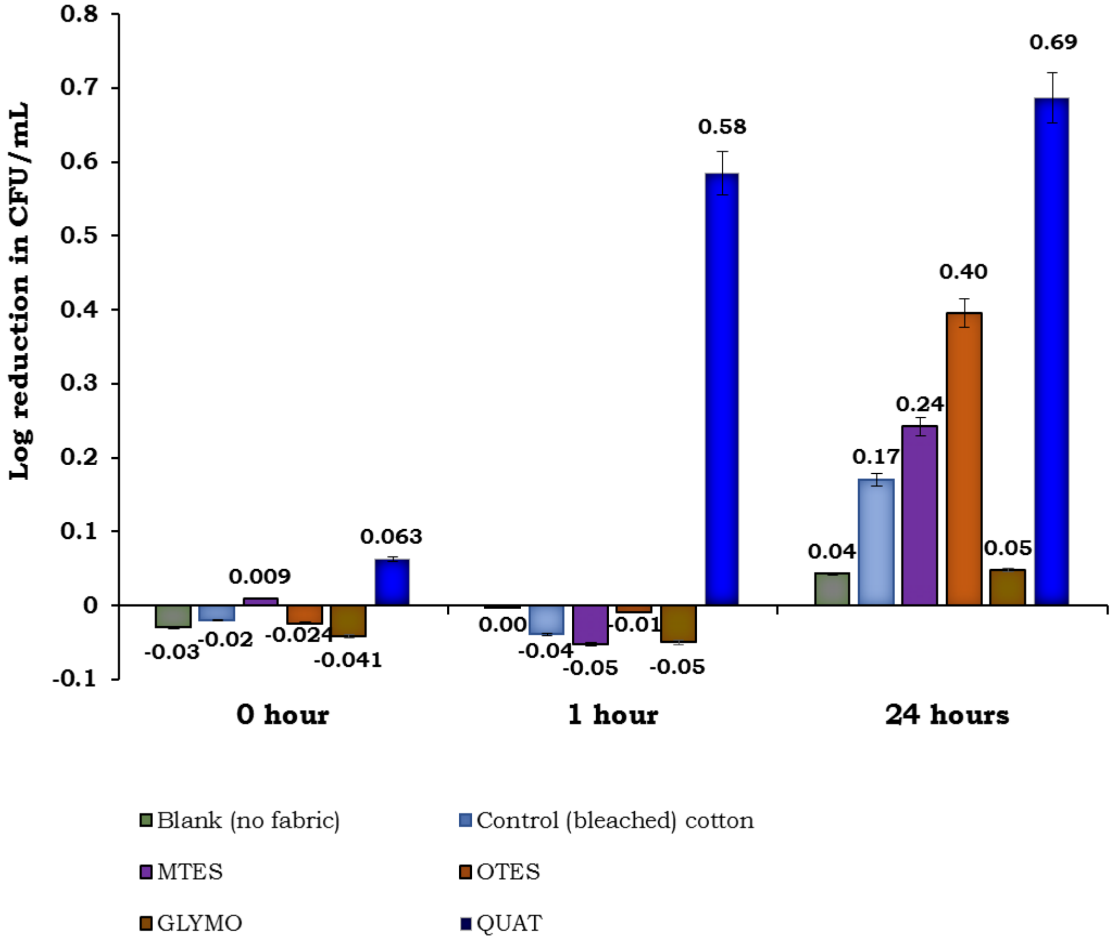


Figure 4.9 Antibacterial activity of knitted cotton samples treated with sols synthesised using different silane composition against *S.aureus* at different incubation times

This antibacterial activity was due to hydrophobic chains that has been reported to aid in cell disruption (Devan Chemicals, 2013; Monticello, 2010). The antibacterial activity observed was not as high as the activity exhibited by samples treated with sol containing the QUAT alkoxysilane because the MTES and OTES silanes did not possess the positive charge that is found on the QUAT alkoxysilane. This positive charge inactivates the bacterium cell membrane, which leads to inhibition and death of the microbe (Monticello, 2010; Erdem and Sanli 2008; Abel et al., 2002; Ramachandran et al., 2004). It can be deduced that the continued attraction between the cell membrane and the nitrogen charge on the anitbacterial agent, keeps the bacteria in close proximity for further disruption through perforation of cells by the hydrophobic chains. The low activity detected for the control samples could be the result of bacterial death due to lack of nutrients. The slight antibacterial activity observed for control samples of blank and control (bleached) cotton oculd be due to bacterial death as a result of lack of nutrients.

4.4.2 Antibacterial property of fabric samples treated with sols synthesised using base formulation

The antibacterial activity of cotton treated with sol synthesised using the base formulation of silane composition MTES: GLYMO: OTES: QUAT using ratio quantities of 300: 5: 10: 5 mL was tested against ATCC 6538 *S.aureus*. The results obtained are shown in Figure 4.10.

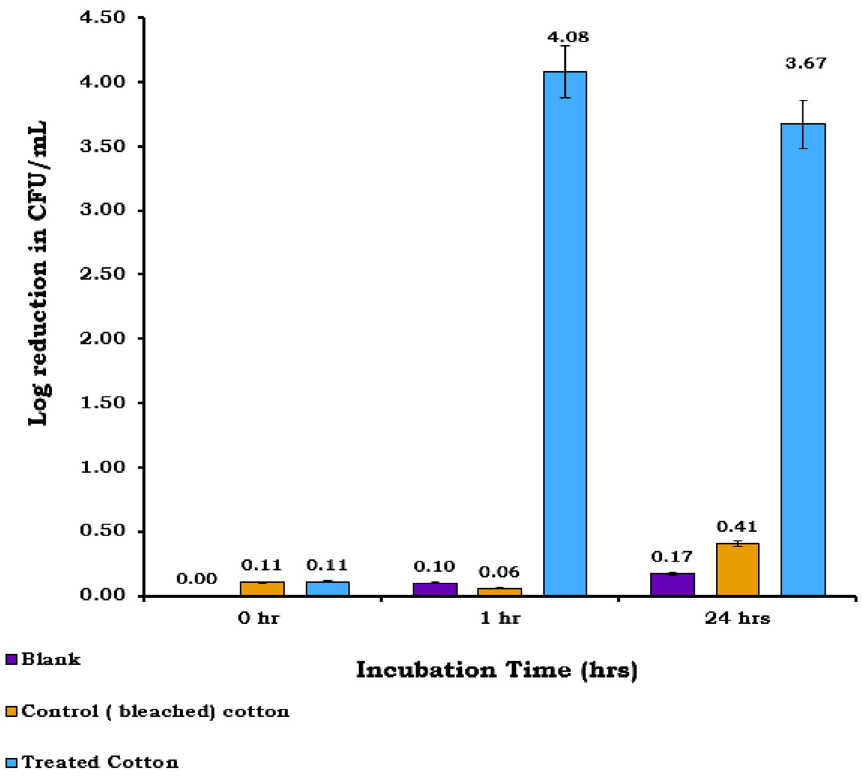


Figure 4.10 Antibacterial activity of cotton sample treated with sol synthesised using base formulation and padded twice at 45 kg/cm. Activity was measured against *S.aureus* after no incubation (0 hour), 1hour incubation and 24 hour incubation

A high log reduction in CFU/mL of 4.08 and 3.67 was observed for treated samples after 1 hour and 24 hours incubation time, respectively. When converted to percentages for comparative purposes, 99.99% activity after 1 hour and 24 hours incubation was achieved. This percentage was comparable to percentage reduction (after 24 hour incubation) of 99.99% achieved by the commercial Aegis AEM 5700 quaternary compund antibacterial agent applied on cotton socks (Annis, 2012) and approximately 99.99% activity against *S.aureus* using QUAT as an antibacterial agent achieved by Onar et al. (2011) and Kim et al. (2010). A slight log reduction for control samples was also observed as seen in results obtained in Figure 4.9; further analysis into the cause of this effect could be carried out to determine at what point the reduction in bacterial population was detected for control samples. This analysis could also be carried out to determine the point at which activity is reduced for treated cotton samples.

The log reduction values obtained for cotton fabric treated with sols containing the combined silanes were higher than those obtained for cotton samples treated with individual silanes as discussed in Section 4.4.1. This was due to the combined effect of the QUAT with its charge and the other hydrophobic silanes of MTES and OTES. The increase in silane content in the ethanolic solution resulted in a more complex and concentrated sol. Silane concentration for the individual sols of MTES, GLYMO, OTES and QUAT were 10% v/v, 1.67% v/v, 3.33% v/v and 1.67% v/v, respectively. The base formulation consisted of all four silanes and would therefore have a total concentration of 16.67% v/v. The increase in the silane content results in more reactions and therefore different alignment of the silanes in the network. The Aegis technology developed by Devan chemicals demonstrated that the hydrophobic chains on the QUAT caused cell disruption and therefore an antibacterial property due to the chain's ability to perforate cell membranes (White, Monticello and Clarke, 2007). The addition of the other hydrophobic silanes such as MTES and OTES may have added further means of perforation that may have increased the log reduction in CFU/mL after 1 hour from 0.6 of QUAT only (Figure 4.9) to 4 for the combination of QUAT and other silanes as shown in Figure 4.10. Another contributing factor that would lead to the increase in activity may be due to the inclusion of the GLYMO silane that promotes cross-linking.

The epoxy silane, GLYMO, promotes cross-linking via its epoxy ring opening and subsequent reactions with surrounding reactive groups (Vengadaesvaran et al., 2014; UNEP PUBLICATIONS, 2004; Carey, 2001; Horr and Reynolds, 1997; Reigel et al., 1998). This cross-linking would result in better bonding of the coating to the fabric surface and ensured that the post treatment rinse did not result in the loss of coating on the surface of the treated fabric sample. With more coating present on the surface and subsequently more QUAT, higher activity would be expected. The QUAT, being an organic compound with the cationic nitrogen atom (Figure 4.11), works as a surface-active agent that attracts negatively charged cell surfaces and breaks down the cell wall of such cells; causing bacterial content leakage, denaturing of essential cell proteins and eventually cell death (Snow, 2012; Monticello, 2010). More QUAT would result in more positive charges for this cell disruption and therefore activity.

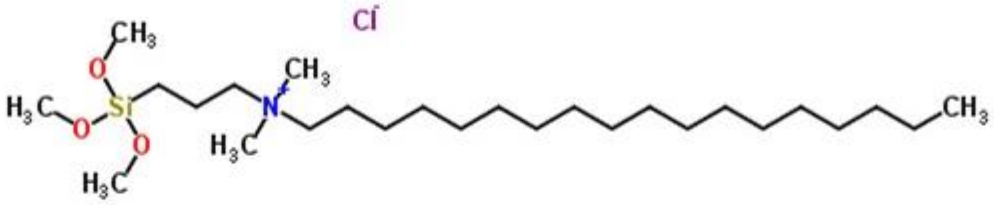
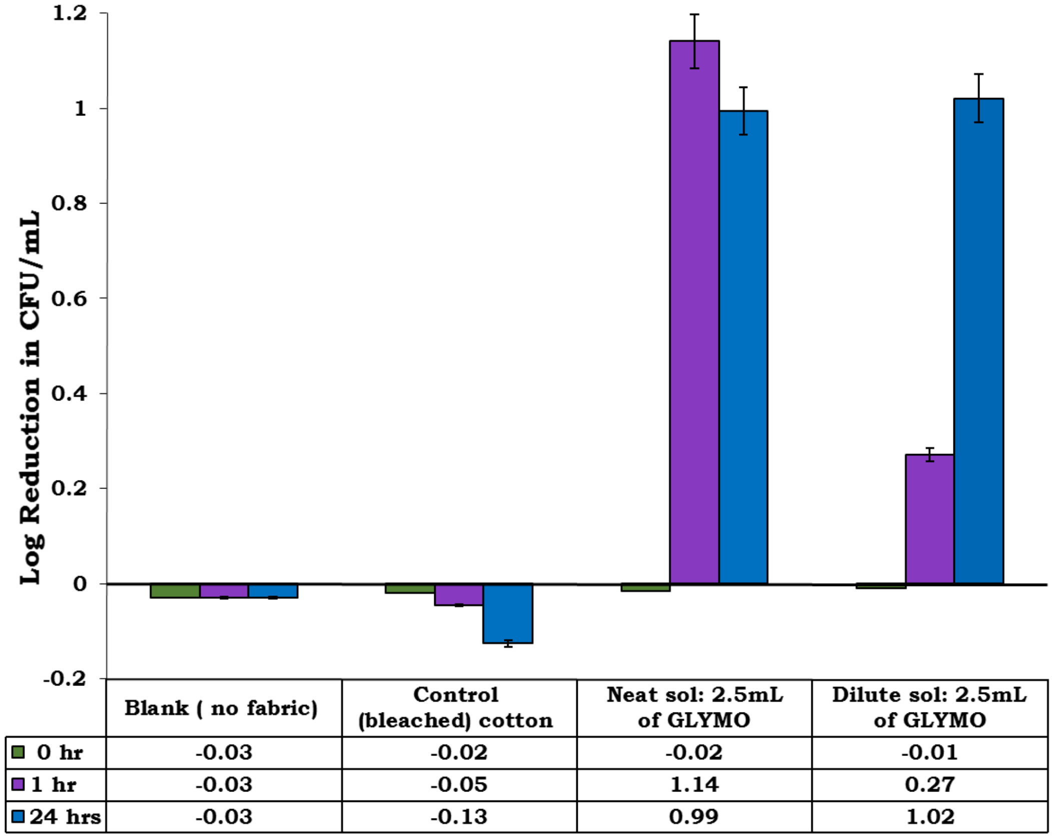


Figure 4.11 Structure of QUAT used in the sol synthesis to treat knitted cotton (CHEMSPIDER, 2015)

The formulation was modified by reducing the amount of cross-linker in order to improve the abrasion performance of the treated cotton fabric samples as discussed in Chapter 5. The fabric samples treated with this sol containing half (2.5 mL) amount of GLYMO silane, both neat and diluted were tested for their antibacterial activity and results are shown in Figure 4.12. It should be noted that the same amount of QUAT i.e. 5 mL, was used in both the neat and diluted sol used for fabric treatment. The results obtained demonstrated that the antibacterial activity reduced from the log reduction in CFU/mL of 4 for the samples treated with the 5 mL of GLYMO (5 mL v/v) to the log reduction in CFU/mL of 1 for samples treated with sols containing the 2.5 mL of the cross-linker after 1 hour incubation and from log reduction in CFU/mL of 3 to 0.99 after 24 hours incubation. This demonstrated that the cross-linker influenced the coating formed on the fabric surface. Further testing can be carried out to find how each silane influences the coating formed for further understanding the network formed and how this network affects the QUAT function which imparts its antibacterial action.



	Blank (no fabric)	Control (bleached) cotton	Neat sol: 2.5mL of GLYMO	Dilute sol: 2.5mL of GLYMO
🟩 0 hr	-0.03	-0.02	-0.02	-0.01
🟪 1 hr	-0.03	-0.05	1.14	0.27
🟦 24 hrs	-0.03	-0.13	0.99	1.02

Figure 4.12 Antibacterial activity of cotton fabric treated with neat and dilute sol containing 2.5 mL and 5mL of GLYMO synthesised using base formulation

The standard test method required testing of treated samples to be carried out for the incubation duration of 1 hour. Testing after this time duration was carried out to determine whether the antibacterial activity could still be measured after continued interaction with the inoculated solution. Such testing for longer periods would help to demonstrate how effective the antibacterial agent was and therefore determine the type of industry to which it could be applicable. This is why a 24 hour incubation time was used. Other test methods such as the ASTM E2180-07 standard test method could be used to test the antibacterial properties and assess whether similar results can be obtained. ASTM E2180-07 is designed to determine the effectiveness of antibacterial agents that are included in hydrophobic or polymeric surfaces. This method differs from the ASTM E2149-10 as it involves the use of an agar slurry inoculum that ensures good contact between the micro-organism and the treated hydrophobic surfaces (ASTM International, 2013). Modifications to the ASTM E2149-10 test method could be carried out to incorporate different testing times as it is designed to test for immobilised antibacterial agents. Tests such as the JIS L1902:2002 testing for antibacterial activity and efficacy on textile products attempts to simulate antibacterial properties when samples are exposed to bacteria by dry contact. Such tests could be useful in determine the antibacterial agent's performance in real life scenarios.

4.5 Conclusions

An antibacterial finish was successfully applied on 100% knitted cotton through the use of the QUAT silane in the sol-gel treatment process. Analysis of cotton fabric samples treated with sols synthesised using the base formulation demonstrated that this antibacterial effect was due to the combined effect of the cationic nitrogen atom on the QUAT and hydrophobic alkyl chains. The cationic nitrogen atom on the QUAT attracts negatively charged cell surfaces and breaks down their cell wall, causing bacterial content leakage and denaturing of essential cell proteins and eventually cell death while the hydrophobic alkyl chains cause cell preforation. The addition of other hydrophobic silanes improved this antibacterial property. The sol-gel coating applied on cotton fabrics was able to achieve a log reduction in CFU/mL of approximately 3 against the bacterium *S.aureus* after 24 hour incubation. It was found that a reduction in the amount of cross-linker GLYMO used in the sol formulation decreased the activity to log reduction in CFU/mL of 1. This indicated that the cross-linker did affect the durability of sol-gel coating as well as antibacterial property on the cotton fabric.

Further analysis against other types of bacteria such as E. coli would illustrate the effectiveness of the antibacterial coating applied on knitted cotton. Activity against a wide range of bacteria would be beneficial for the finish as it would allow application into various areas. The ability to exhibit antibacterial activity even after 1 hour incubation demonstrated that any contaminant that may be present on the surface of the treated material would still experience antibacterial activity and be combatted.

CHAPTER 5:

MECHANICAL PROPERTIES OF SOL-GEL TREATED COTTON FABRIC

5.1 Introduction

The application of finishes onto textile fabrics aims primarily to improve the material's performance by the introduction of additional functionalities. During the modification or treatment process, attempts are made to ensure that the original mechanical properties of the modified textile fabric are maintained and, where possible, improved. This is important in the processing of textile fabrics because textile properties play a vital role and therefore influence the areas in which they are used. Retaining the original mechanical properties is advantageous as modified textile materials can still be applicable in their end-uses and with chemical modifications, be applied in other fields.

Akaydin and Can (2010) identified that the abrasion resistance and pilling performance of fabric samples were amongst the most important properties to consider when looking at the mechanical performance of the textile fabric. Various factors such as fabric construction, yarn spinning systems and finish applications would affect the abrasion resistance and pilling performance of the textile material. As such, these factors are considered during textile construction and textile treatment so that the final textile product exhibits sufficient resistance to abrasion and pilling for intended its end-uses.

This chapter aims to find and discuss the effects of the sol application on the mechanical properties of 100% knitted cotton fabric. Testing and evaluation of the abrasion performance of the treated cotton fabrics were carried out and observations were made to determine whether properties were reduced, maintained, or improved by the sol-gel treatment. Comparisons were made between sols synthesised using different silane precursors and sols synthesised using the base formulation at different concentrations. The burst strength of the treated knitted cotton fabrics was also tested and compared with the untreated cotton samples to observe any changes in this property.

5.2 Materials and Equipment

5.2.1 Fabrics

Control cotton fabric

Scoured and bleached interlock knitted fabric made from 100% cotton and supplied by Vertical Garments Ltd (Leicester, UK). This fabric was used as control fabric for the purpose of testing and fabric for sol-gel treatment.

Treated cotton fabric

Scoured knitted cotton fabric was treated with sols synthesised as described in Section 3.3.2 consisting of individual silanes of MTES, GLYMO, OTES and QUAT, respectively, and sols synthesised using the base formulation with full (5 mL) and half (2.5mL) amounts of GLYMO cross-linker, respectively. Application of sols on control cotton fabric was as described in Section 3.3.3. Two different pad pressures of 15 kg/cm at 1 m^2/min (once) and 45 kg/cm at 1 m^2/min (twice) were used and their influence on mechanical properties were observed.

5.2.2 Equipment

To evaluate the mechanical properties of the sol-gel treated cotton fabrics, a James H. Heal Martindale abrasion tester [serial number 103247] and James H. Heal & Sons Truburst burst tester (Halifax England) (Figure 5.1) were used to undertake abrasion and burst testing, respectively.

Figure 5.1 Image of James H. Heal Martindale (a) and James H. Heal & Sons Truburst burst tester (b) used for abrasion and burst strength testing, respectively (James Heal, 2014)

5.3 Experimental

5.3.1 Abrasion testing

5.3.1.1 Principle of technique

“The resistance of a fabric against the force of friction is known as the abrasion resistance. In general, pilling is a fabric defect observed as small fibre balls or a group consisting of intervened fibres that are attached to the fabric surface by one or more fibres” (Akaydin and Can, 2010). Akaydin and Can (2010) stated that knitted fabrics have low abrasion resistance and pilling performance due to the low twist yarn and slack construction of the textile.

The principle that governs abrasion testing as stated by the ASTM International standard (2013) involves subjecting specimens to a rubbing motion in the form of a geometric figure. This motion begins with a straight line that becomes a gradually widening ellipse, which eventually forms a straight line in the opposite direction. This motion is repeated, under known conditions of pressure and abrasive action. These carefully defined parameters, within the testing method, enable reproducibility of the rubbing effect. “abrasion resistance” (often stated in terms of the number of cycles on a specified machine, using a specified technique to produce a specified degree or amount of abrasion) and “durability” (defined as the ability to withstand deterioration or wearing out in use, including the effects of abrasion) are frequently related” (ASTM International, 2013).

The testing of textiles’ resistance to abrasion contributes to the analysis of wear performance or durability of textiles as experienced in the actual use. The type of the abradant used, abradant behaviour during abrasion, fabric tension and pressure between the abradant and the test specimen (ASTM International, 2013) can affect fabric resistance to abrasion. It then becomes important to consider such factors when testing for abrasion performance.

5.3.1.2 Sample preparation

Before testing, the reference abradant, which was plain woven wool in this research, and felt pad were mounted on four testing areas on the Martindale and weights placed to ensure no creases or ridges. The rings to hold the abradant in place were screwed on and the station was ready for sample loading. Cotton samples to be tested were cut into standard sizes using a circular template of defined diameter. These cut samples were placed in the Martindale sample holder face down and secured in place as shown in Figure 5.2.

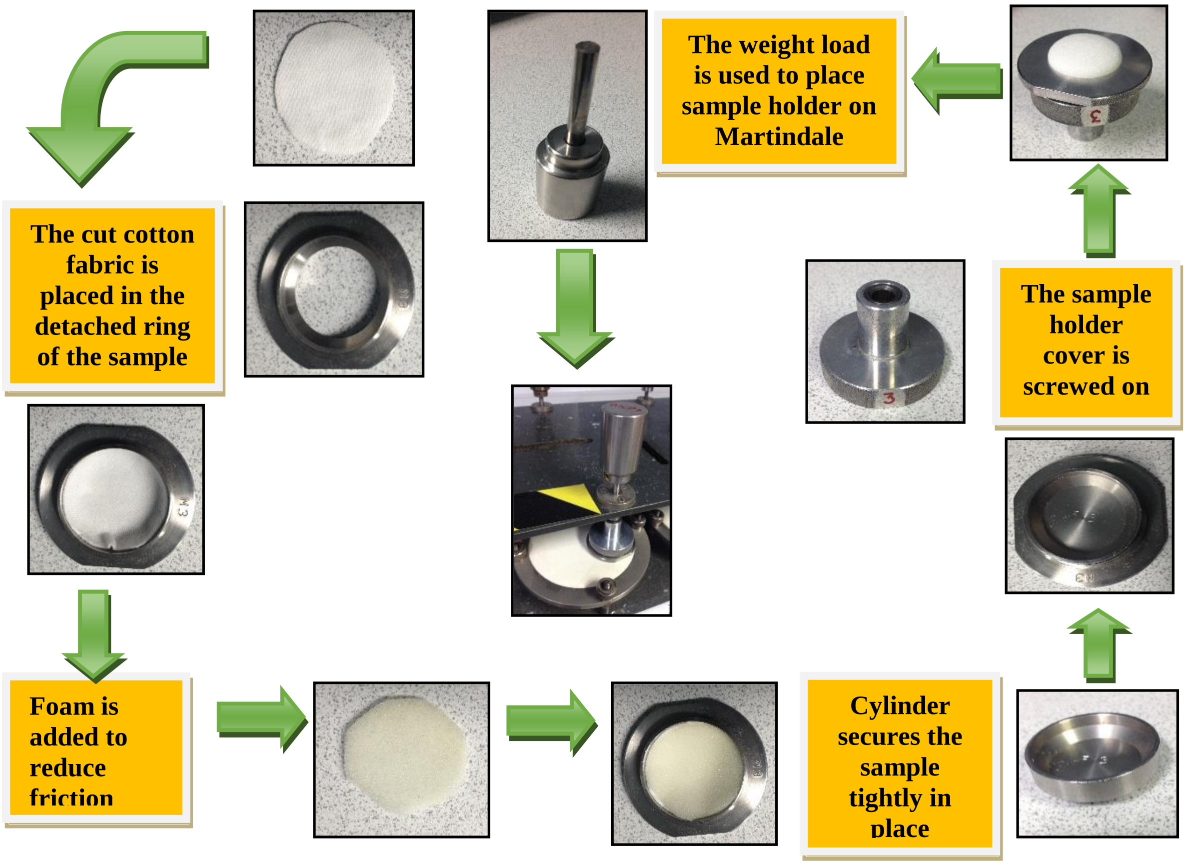


Figure 5.2 Schematic showing sample preparation for abrasion testing.

5.3.1.3 Testing and evaluation

Following the BS EN ISO 12947:1998 testing method, the prepared cotton samples were placed under defined load and rubbed against a standard plain woven abradant at regular intervals. 9 KPa was used as the weight load for abrasion testing and revolutions set to run at 1,000 intervals. Testing continued until cotton fibre breakdown. Abraded cotton samples were inspected using inspection parameters are shown in Table 5.1. Pilling evaluation was carried out using the BS EN ISO 12945-1:2001 grading system which used grade values of 1 to 5 where 1 signified severe pilling and 5 demonstrated little to no pilling. Hairiness, fibre breakage and holes were recorded at each inspection interval to determine point of abrasion failure.

Table 5.1 Inspection parameters for abrasion testing (BS EN ISO 12945-1:2001)

NUMBER OF CYCLES	INSPECTION INTERVALS
< 5,000	Every 1,000
5,000 to 19,999	Every 2,000
20,000 to 39,999	Every 5,000
> 40,000	Every 10,000

5.3.2 Burst testing

5.3.2.1 Principle of technique

Unlike woven fabrics, tensile strength measurements using conventional test methods cannot be used on knitted fabrics. This is because knitted fabrics do not have definite directions of weft and warp that are found in woven fabrics and as such, an alternative method to measure fabric strength was developed; which is referred to as burst strength (Kiron, 2014). The burst strength testing method operates by applying pressure in all directions of the fabric at the same time, using pneumatic diaphragm burst tester. The challenge faced with using diaphragm burst testing includes limits in extension that can be given to the sample, owing to the fact that the rubber diaphragm has to stretch to the same amount (Hussain, 2010). The Truburst system attempts to reduce this limitation by using a high acceleration linear potentiometer, to measure the distention up to 70 mm (±0.5%) on larger dome assemblies. Distention is the ballooning effect that occurs as the fabric specimen is tested under pressure application. The microprocessor incorporated in the Truburst allows proportional control to provide linear pressure increase, which allows bursting within a specified time. This control ensures repeatability of test parameters and elimination of variables in testing (Hussain, 2010).

5.3.2.2 Testing and Evaluation

For burst strength testing, distention was set to 70 mm and diaphragm pressure to 20 KPa. This was the required pressure to raise the free surface of the diaphragm. The Perspex diaphragm was placed on the Truburst and dome assembly released to secure and create vacuum to build pressure. The clamped diaphragm was inflated using pressure displaced at 95 mL/min to determine the pressure required to expand the diaphragm to the set distention height. Once measured, the dome was released and cotton samples placed on top of the Perspex diaphragm. The dome was then activated to clamp samples in place and diaphragm was expanded to the point when the cotton sample ruptured. The pressure at which this rapture occurred was recorded. To determine the burst strength, equation 5.1 was used. The difference between the pressure required to inflate the diaphragm and the total pressure required to rupture the specimen was the burst strength; which is measured in units of pressure.

$$Burst\ strength = Mean\ Burst\ pressure\ - Diaphragm\ pressure$$

Equation 5.1

5.4 Results and discussion

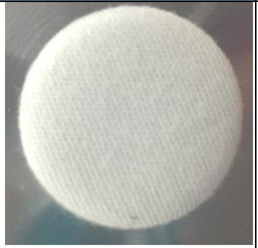
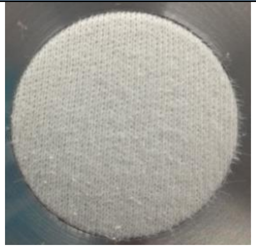
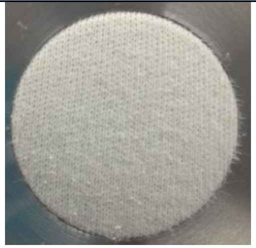
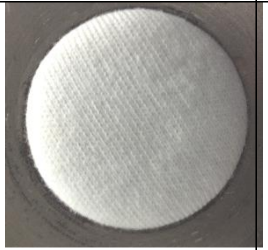
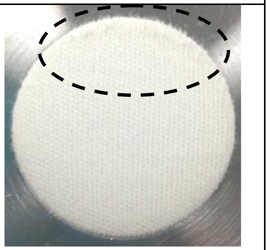
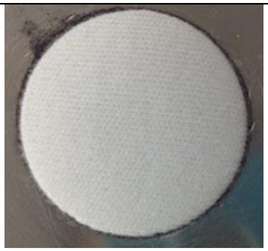
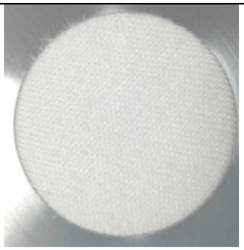
5.4.1 The influence of different silane composition on abrasion property

To understand the influence of silanes on the abrasion performance, knitted cotton samples were treated with sols of different silane compositions. After sol-gel treatment, treated cotton fabric samples were either passed through pad pressures of 45 kg/cm twice or 15 kg/cm once, as described in Section 3.3.3. The effect of these two pad pressures on the abrasion performance was also investigated

5.4.1.1 Sol with MTES alkoxysilane only and its influence on abrasion performance

Sols synthesised with the MTES alkoxysilane were prepared and applied onto cotton fabric as described in Section 3.3.3 and abrasion testing carried out as described in Sections 5.3.1.2 and 5.3.1.3. Results in Table 5.2 show that after the initial 5,000 revolutions, there was little or no pilling of Grade 4 and no hairiness for the abraded treated cotton surface while the control (bleached) cotton had severe pilling of Grade 1 with high amounts of surface hairiness. These results indicated that sol-gel application improved the abrasion performance of the treated cotton by providing a protective barrier against pilling. Further abrasion testing was carried out to determine the extent to which the sol-gel coating provided this protective property against pilling, hairiness and fibre damage. After 10,000 revolutions, most of the pill balls that formed on the control (bleached) cotton were removed however some hairiness was still observed. For the treated cotton samples, no hairiness or pilling was seen. This trend of constant hairiness on the control cotton fabric and anti-pilling properties on the treated cotton samples was observed as samples were subjected to more revolutions until fibre breakage. From the results shown in Table 5.2, it was found that the treated cotton fabric samples padded once of 15 kg/cm once achieved higher revolutions than the treated fabric samples padded twice at 45 kg/cm.

Table 5.2 Abrasion test results for cotton fabric treated with sol containing MTES alkoxysilane only and their Water Rating Numbers (WRN)

Sample type	Pad pressure (kg/cm)	Before Abrasion	Abrasion				
			After 5,000	After 10,000	After 15,000	After 20,000	After 25,000
Control (bleached) cotton	N/A	 WRN value: <1	 WRN value: <1	 WRN value: <1	 WRN value: <1	 WRN value: <1	 WRN value: <1
Sol-gel treated cotton fabric	45 kg/cm (twice)	 WRN value: 2	 WRN value: 1	 WRN value: <1	 WRN value: <1	 WRN value:<1	 WRN value: <1
	15 kg/cm (once)	 WRN value: 2	 WRN value: 1	 WRN value: <1	 WRN value: <1	 WRN value: <1	 WRN value:<1

As highlighted with the graduated circle in Table 5.2, fibre breakage and thereby abrasion failure was seen after 20,000 revolutions for the treated samples padded twice at 45 kg/cm while the treated samples padded once at 15 kg/cm had fibres still intact and showed no damage. This difference in abrasion performance between the two pad pressures could be due to the amount of coating on the treated cotton fabric. Lower pad pressures result in a higher amount of coating on the fibre surface while the higher pad pressure removes excessive sol, to achieve a lower liquor pick-up, which results in lower amount of coating on the surface.

After 20,000 revolutions, further broken threads and holes were seen for the treated cotton fabric samples padded twice at 45 kg/cm. However, the treated cotton sample passed through lower pad pressure of 15 kg/cm (once) were able to withstand abrasion up to 30,000 revolutions, before broken threads and holes were observed (Figure 5.3). With reference to control (bleached) cotton, this cotton sample achieved 55,000 revolutions before there was fibre breakage or holes in the abraded cotton sample (Figure 5.4). These results showed that the abrasion performance of the cotton fabric was reduced by application of the sol-gel coating containing MTES only.

Figure 5.3 Abraded cotton sample treated with MTES only sol and padded once at pad pressure 15 kg/cm after 30,000 revolutions

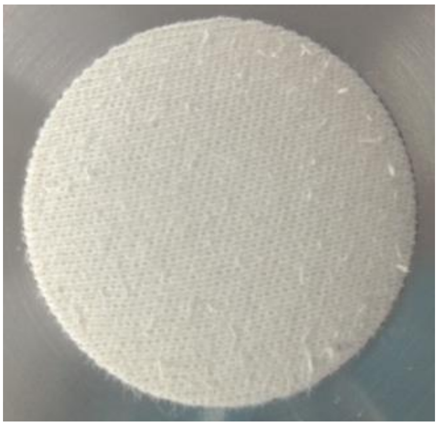


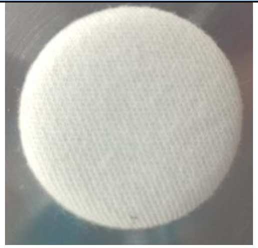
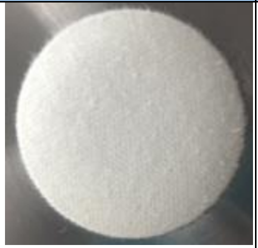
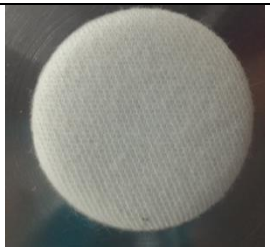
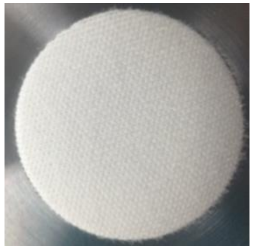
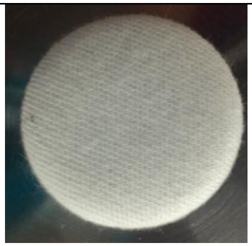
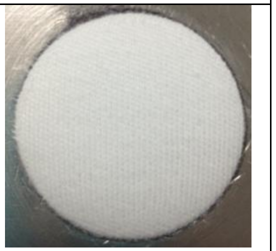
Figure 5.4 Abraded control (bleached) cotton after 55,000 revolutions

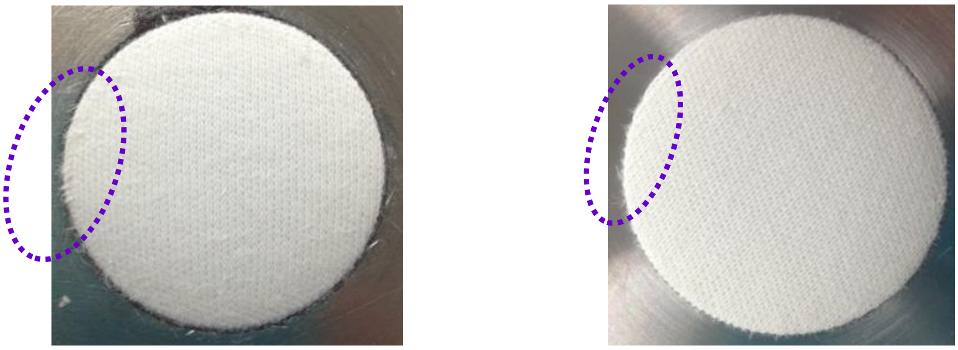
Cotton samples treated with sol containing MTES achieved WRN values of 2 (Table 5.2), showing that the short hydrophobic methyl chain on the alkoxysilane was able to impart some hydrophobicity. This hydrophobic property was reduced to a WRN value of 1 after the first 5,000 revolutions after which, no WRN values could be measured. The reduction in WRN values indicated that the sol-gel coating was not strongly bound to the surface of the treated cotton fabric, resulting in the removal from the surface during abrasion testing.

5.4.1.2 Sol with MTES and GLYMO alkoxysilanes and its influence on abrasion performance

The abrasion performance of cotton fabric samples treated with sol containing GLYMO and MTES alkoxysilanes was carried out to observe its effect on abrasion performance. Results in Table 5.3 showed that treated cotton fabric samples padded twice at 45 kg/cm achieved 30,000 revolutions while treated cotton fabric samples padded once at 15 kg/cm achieved 35,000 revolutions as shown in Figure 5.5. This improved abrasion performance, when compared to results in Table 5.2, could be due to the presence of GLYMO cross-linker. GLYMO has been reported to improve formation of coatings because of its ability to improve flexibility (Mahltig and Textor, 2008). These results demonstrated that abrasion performance for cotton fabric treated with sols containing MTES and GLYMO was improved when compared to samples treated with sols containing MTES only.

Table 5.3 Abrasion test results for cotton treated with sol containing MTES and GLYMO alkoxysilanes and their Water Rating Numbers (WRN)

Sample type	Pad pressure (kg/cm)	Before Abrasion	Abrasion				
			After 5,000	After 10,000	After 15,000	After 20,000	After 25,000
Control (bleached) Cotton	N/A	 WRN value: <1	 WRN value: <1	 WRN value: <1	 WRN value: <1	 WRN value: <1	 WRN value: <1
Sol-gel treated cotton fabric	45 kg/cm (twice)	 WRN value: <1	 WRN value: <1	 WRN value: <1	 WRN value: <1	 WRN value: <1	 WRN value: <1
	15 kg/cm (once)	 WRN value: <1	 WRN value: <1	 WRN value: <1	 WRN value: <1	 WRN value: <1	 WRN value: <1



MTES and GLYMO (45 kg/cm)
After 30,000 revolutions

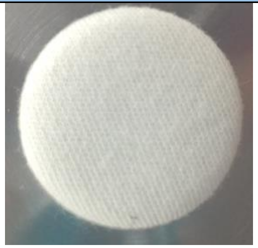
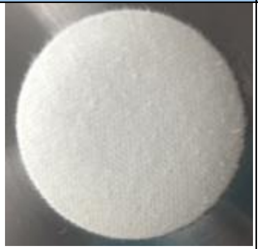
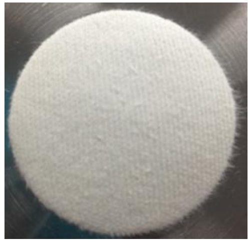
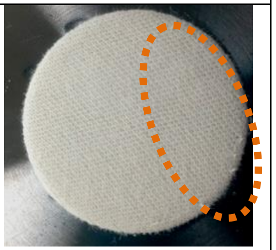
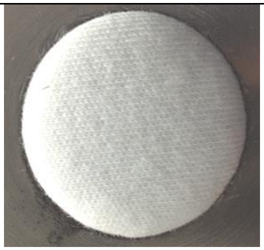
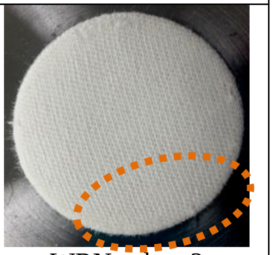
MTESand GLYMO (15 kg/cm)
After 35,000 revolutions

Figure 5.5 Images of abraded treated cotton samples treated with sol containing MTES and GLYMO alkoxysilanes

5.4.1.3 Sol with MTES, GLYMO and OTES alkoxysilanes and its influence on abrasion performance

The hydrophobic alkoxysilane OTES was added to the mixture of MTES and GLYMO alkoxysilane for cotton fabric sol-gel treatment. Table 5.4 shows the abrasion test results for cotton fabric treated with sol containing MTES, GLYMO and OTES alkoxysilanes and their Water Rating Numbers (WRN). It was found that cotton samples treated with sols of this composition and padded once at 15 kg/cm and padded twice at 45 kg/cm achieved 25,000 revolutions. When these results were compared to results shown in Table 5.3 and Figure 5.5, a reduction in abrasion performance was seen. The presence of higher molecular silanes such as OTES has been reported to increase hardness and plasticity of the coatings formed (Wienhold and Westerwelle, 2006; Mahltig and Textor, 2008) and may have influenced the sol-gel coating performance against abrasion. This is because long organic chains reduce the connectivity of the inorganic network that forms during hydrolysis and condensation reactions. This is referred to as nano-segregation that reduces mechanical strength of the sol-gel coating (Latella et al., 2012). Thick and rigid coatings are limited in their ability to withstand stress and are therefore highly susceptible to abrasion failure. Further evaluation of the type of coating and how it affects the movement of yarns would be an area of research to improve abrasion resistance.

Table 5.4 Abrasion test results for cotton treated with sol containing MTES, GLYMO and OTES alkoxysilanes and their Water Rating Numbers (WRN)

Sample type	Pad pressure (kg/cm)	Before Abrasion	Abrasion				
			After 5,000	After 10,000	After 15,000	After 20,000	After 25,000
Control (bleached) Cotton	N/A	 WRN value: <1	 WRN value: <1	 WRN value: <1	 WRN value: <1	 WRN value: <1	 WRN value: <1
Sol-gel treated cotton fabric	45 kg/cm (twice)	 WRN value: 4	 WRN value: 3.5	 WRN value: 3	 WRN value: 3	 WRN value: 3	 WRN value:3
	15 kg/cm (once)	 WRN value: 4	 WRN value: 3.5	 WRN value: 3	 WRN value: 3	 WRN value: 3	 WRN value: 3

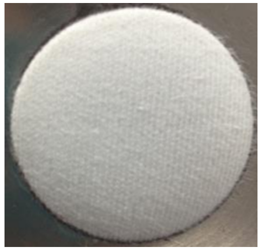
WRN values increase from 2 to 4 was observed with the introduction of the hydrophobic OTES silane. This was due to the 8 carbon alkyl chain on the silane that aids in providing hydrophobic properties. It was also observed that the WRN values reduced to 3.5 and 3 between 5,000 and 10,000 revolutions. The WRN values remained constant with continued abrasion. The retention of the hydrophobic property could be due to the cross-linker that may have improved the bonding of sol-gel coating with the fibres of the cotton.

5.4.2 Base formulation for sol synthesis and its effect on abrasion property

The base formulation for sol synthesis included MTES, GLYMO, OTES and QUAT silanes in the ratio of 30: 5: 10: 5 mL. Cotton fabric samples were treated with sols of this silane composition and tested for abrasion performance. Results in Table 5.5 illustrated that the control (bleached) cotton sample had very severe pilling after the initial 5,000 revolutions after which most of these pills were removed and the sample remained intact even after 15,000 revolutions. Treated cotton samples showed resistance to pilling as no pilling was seen after the first 5,000 revolutions but failed abrasion testing at 15,000 revolutions. When compared to earlier results, it was seen that abrasion performance was reduced. This could have been due to the addition of the higher molecular QUAT silane that may have affected the coating formed.

Treated cotton samples padded once at 15 kg/cm performed better than those padded twice at 45 kg/cm. This was due to more sol-gel coating on the surface of the treated cotton sample as a weight gain of 9.3% was achieved for samples padded at 15 kg/cm while a weight gain of 7.1% was achieved for treated cotton samples padded twice at 45 kg/cm. Though treated cotton fabrics failed abrasion at the 15,000 revolutions, treated padded once at 15 kg/cm remained intact while treated cotton samples padded at 45 kg/cm demonstrated severe breakage that resulted in cotton sample ripping off the sample holder.

Table 5.5 Abrasion results for cotton treated with sol containing MTES, GLYMO, OTES and QUAT alkoxysilanes and their Water Rating Numbers (WRN)

Sample ID	**Sol-gel treatment**	**Before Abrasion**	**Abrasion**		
			After 5,000	**After 10,000**	**After 15,000**
Control (bleached) cotton	No treatment	 WRN value: <1	 WRN value: <1	 WRN value: <1	 WRN value: <1
Sol-gel treated cotton fabric	Sample was treated with sol-gel and padded twice at 45 kg/cm	 WRN value: 4	 WRN value: 3.5	 WRN value: 3	 WRN value: 3
	Sample was treated with sol-gel and padded once at 15 kg/cm	 WRN value: 4	 WRN value: 3	 WRN value: 3	 WRN value: 3

The hydrophobic properties of the treated cotton samples were measured as abrasion testing progressed, to determine the effect of constant rubbing on this property. Slight reduction in WRN values from the initial value of 4 to 3.5 for treated samples padded at 45 kg/cm and from 4 to 3 for treated samples padded once at 15 kg/cm. This demonstrated that hydrophobic properties on the treated cotton samples were maintained and therefore durable to abrasion. These results also demonstrated that most of sol-gel coating was firmly attached to the surface of the individual cotton fibres while loosely bound sol-gel coating removed resulted in the slight reduction in the WRN values.

5.4.3 Optimisation of base formulation for sol synthesis and its influence on abrasion performance

From the results discussed in Sections 5.4.1 and 5.4.2, it was found that the silane composition of sol synthesised affected the abrasion performance of the treated fabric sample. In attempts to improve the abrasion resistance of the treated cotton fabric, the concentration of the sol and its effects on the abrasion performance of the treated fabric sample were investigated. The initial sol solution was diluted with deionised water using 1:1 ratio and applied on the cotton fabrics, to observe any changes in the abrasion performance of the treated sample.

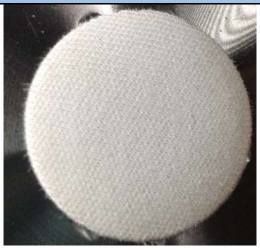
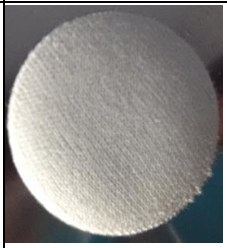
The results in Table 5.6 showed that fibre breakage and holes occurred after 22,000 revolutions, with the initial signs seen at 20,000 revolutions. This demonstrated that with a reduction in sol concentration, a further 5,000 revolutions could be achieved for samples treated with the diluted sol, when compared to the concentrated sol illustrated in Table 5.5. Hydrophobicity testing showed that WRN values for unabraded samples decreased from 4 to 3. This reduction and its continued decrease was as a result of a lower concentration of sol applied on the cotton fabric material.

Table 5.6 Abrasion results of treated cotton samples treated with diluted sol synthesised using base formulation and padded once at 15 kg/cm (once) and twice at 45kg/cm

Sample ID	After 5,000	After 10,000	After 15,000	After 20,000
Treated cotton (15 kg/cm once)	 WRN value: 3	 WRN value: 3	 WRN value: 3	 WRN value: 2
Treated cotton (45 kg/cm twice)	 WRN value: 3	 WRN value: 2	 WRN value: 2	 WRN value: 2

To observe the influence of the cross-linker, the GLYMO silane was reduced from 5 mL to 2.5 mL in the sol composition and abrasion performance tested for cotton samples treated with resultant sols synthesised. The results obtained are shown in Table 5.7.Reducing the amount of cross-linker did not achieve higher revolutions to demonstrate It was observed that the treated cotton samples padded at 45 kg/cm achieved 20,000 revolutions while the treated cotton samples padded once at 15 kg/cm demonstrated a reduction in abrasion performance as 15,000 revolutions were achieved. These results, when compared to results in Table 5.6, demonstrated that cotton samples treated with diluted sols containing 5 mL of GLYMO and sols synthesised with neat sols containing 2.5mL GLYMO achieved the same abrasion performance. To investigate whether the pH of the 50% v/v ethanol solution would affect the abrasion properties of the cotton, abrasion testing was carried out of cotton fabric treated with 50% v/v ethanol solution at pH 3.2 for 4 hours and padded once at 15 kg/cm and twice 45 kg/cm as described in Section 3.3. The results obtained are shown in Figure 5.6.

Table 5.7 Abrasion results of cotton samples treated with neat sol synthesised using 2.5 mL of GLYMO in base formulation

Sample ID	After 5,000	After 10,000	After 15,000	After 20,000
Treated cotton (15 kg/cm once)	 WRN value: 3	 WRN value: 2	 WRN value: 2	FAIL
Treated cotton (45 kg/cm twice)	 WRN value: 3	 WRN value: 2	 WRN value: 2	 WRN value: 2

50% v/v ETOH Treatment Padded once at 15 kg/cm

50% v/vETOH Treatment Padded twice at 45 kg/cm

Figure 5.6 Abrasion results of cotton samples treated with 50% v/v ethanol solution with no silanes adjusted to pH 3.2 after 1,000 revolutions

Figure 5.6 showed that only 1,000 revolutions could be achieved for cotton samples treated with 50% v/v acidic ethanol solution. This demonstrated that the acidic solution affected the abrasion performance of treated cotton sample as it could only withstand

1,000 revolutions before fibre breakage. The abraded samples were observed under the SEM and illustrated at different magnifications as shown in Figure 5.7.

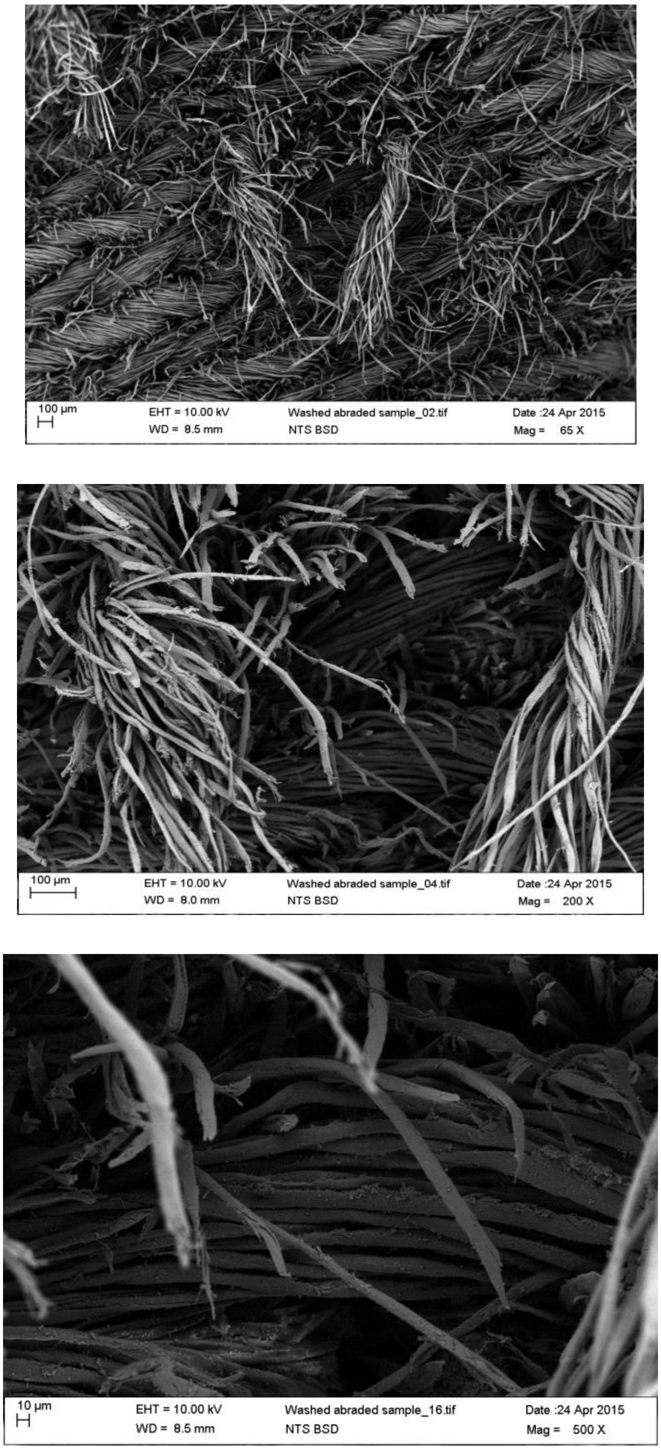


Figure 5.7 SEM of cotton samples treated with 50% v/v ethanol solution with no silanes adjusted to pH 3.2 after 1,000 revolutions

It was seen that yarns were broken off the knit structure at points of abrasion failure. This result also showed that the sol-gel treatment was able to restore some abrasion resistance after its application on cotton fabric in acidic conditions and therefore with reference to results discussed earlier, varying the silane composition restored the abrasion performance. It should also be noted that improvements in abrasion after dilution of sols, as seen in Table 5.6, could have been due to an increase in pH. As water was used for dilution, this would have changed the acidic pH of the sol (at approximately pH 3 after sol synthesis) because of its higher pH value of 7.

5.4.4 Sol-gel treated cotton fabric and its burst strength performance

Burst strength testing of knitted cotton fabric enables a multi-directional tensile test that identifies failure in the direction of least resistance to evaluate the fabric's physical strength and fibre bond (Hussain, 2010). Burst testing was tested on a representative selection of samples to see the effect of the different sol types on the cotton's strength. Testing was carried out on samples treated with the acidic 50% v/v ethanol solution, without silanes, to determine whether the pH affected the burst strength of the cotton fabric. Results obtained are shown in Figure 5.8.

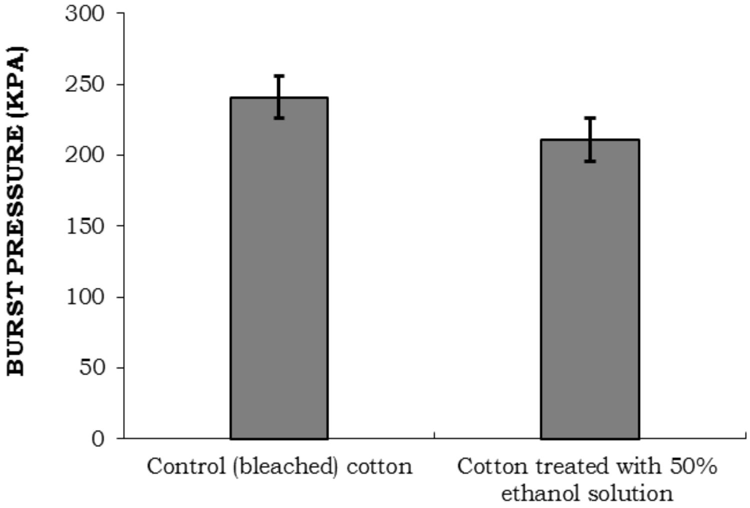


Figure 5.8 Burst testing results of control (bleached) cotton and cotton fabric treated with 50% v/v ethanol solution without silanes

From results in Figure 5.8, some reduction in strength was observed as burst pressure decreased from 241 to 211 KPa. Effect of pH, when compared to abrasion performance was not as significant as there was a slight reduction in strength. This demonstrated that cotton samples treated with sols at low pH resulted in treated cotton samples that could not withstand prolonged application of stress, as applied by abrasion testing, but demonstrated a slight reduction in strength.

To observe the influence of the sol-gel coating on burst strength, further testing was carried out on cotton samples treated with sols synthesised using the base formulation that involved silanes added to 50% v/v ethanol solution. These treated samples were padded once at 15 kg/cm and twice at 45 kg/cm. Burst strength test results are shown in Figure 5.9.

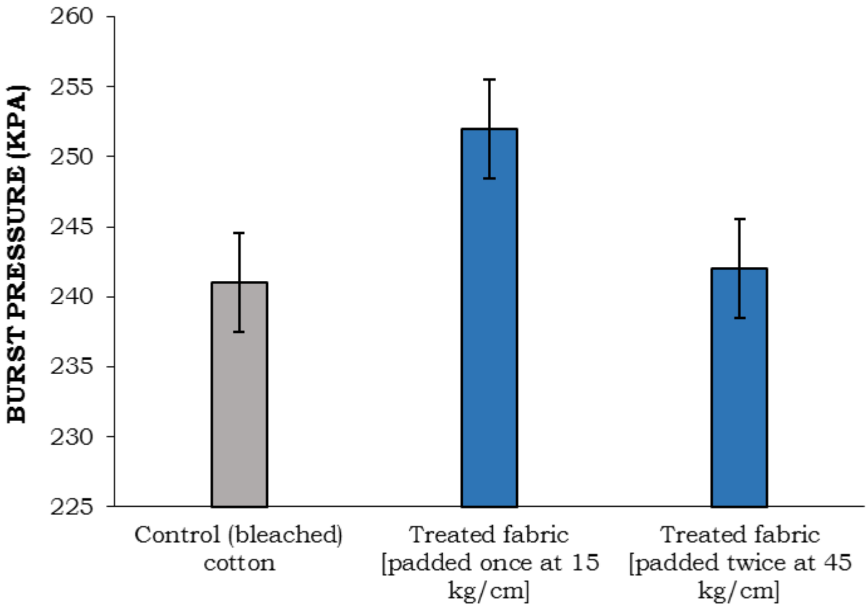


Figure 5.9 Burst testing results for cotton samples treated with sols synthesised using the base formulation padded once at 15 kg/cm and twice at 45 kg/cm

Treated cotton fabric padded twice at 45 kg/cm achieved burst pressure of 242 KPa while treated cotton fabric padded once at 15 kg/cm achieved burst pressure of 252 KPa. Treated cotton samples padded at 45 kg/cm achieved the same burst pressure as achieved for control knitted fabric while treated cotton samples padded once at 15 kg/cm demonstrated an improvement in fabric strength. These results demonstrated that the burst strength was restored after sol-gel treatment as seen for the treated sample padded at 45 kg/cm and improved further with more coating, as seen in results obtained for the treated cotton samples padded once at 15 kg/cm.

The effect of sol concentration and amount of cross-linker on abrasion performance has been discussed in Section 5.4.3 to determine whether sol concentration and reduction in amount of cross-linker affected burst strength, burst testing was also carried out on cotton samples treated with diluted sols synthesised using the base formulation, containing 5 mL of GLYMO and cotton samples treated with sols containing the 2.5 mL of GLYMO and results shown in Figure 5.10.

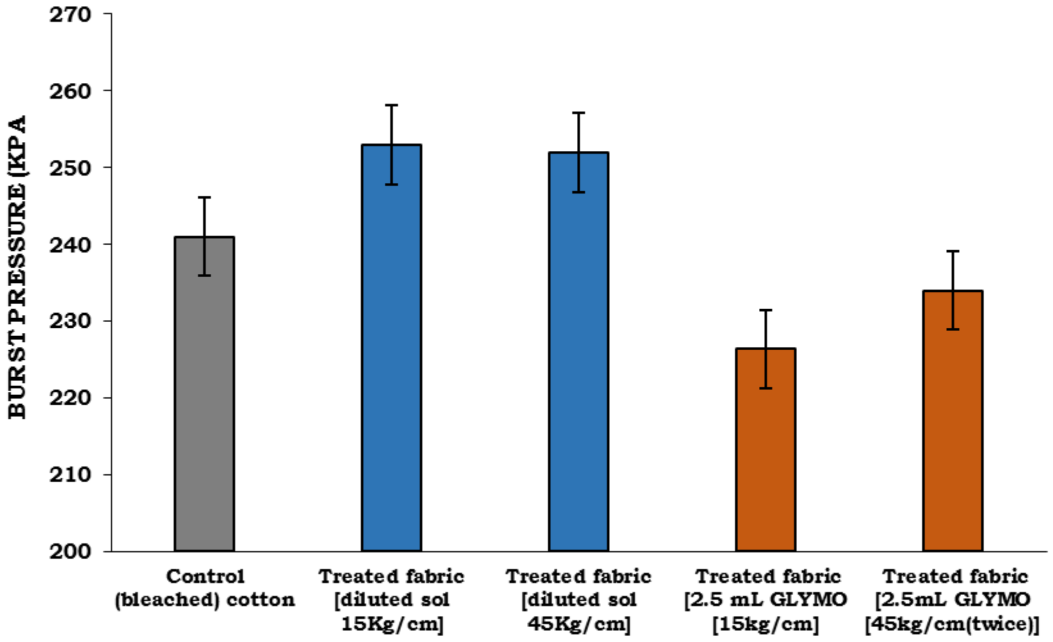


Figure 5.10 Burst testing results for cotton samples treated with diluted sol containing 5mL of GLYMO and neat sol containing 2.5 mL of GLYMO padded once at 15 kg/cm and padded twice at 45 kg/cm

From the results in 5.10, cotton samples treated with sols synthesised using the base formulation that was diluted to a 1:1, demonstrated similar burst pressures values of 252

KPa and 253 KPa for pad pressure of 45 kg/cm and 15 kg/cm, respectively. This demonstrated that with sol dilutions, burst strength was improved to values obtained for the neat sol applied on cotton fabric and padded once at 15 kg/cm , as shown in Figure 5.8. Cotton samples, treated with sols synthesised using base formulation containing 2.5 mL of GLYMO, achieved burst pressure results of 226 KPa when treated samples padded once at 15 kg/cm, and 234 KPa for treated samples padded twice at 45 kg/cm. These results demonstrated that reduction in GLYMO led to a small reduction in burst strength.

5.5 Conclusions

Abrasive forces could damage sections of fibre material from fabric surfaces, affecting its associated resistance to stress, which then leads to fibre breakage. This subsequently results in the loss of fabric tensile strength. For this reason, the abrasion resistance of the textile material becomes one of the limiting factors in product life cycles (Mahltig and Textor, 2008) and therefore plays a major role in the textile usage (Parsons, 2006). Another limiting factor faced by knitted fabrics includes pilling caused by frequent abrasion and rubbing. Untreated knitted cotton fabrics demonstrated severe pilling of Grade 1 with the high amounts of surface hairiness, after 5,000 revolutions of abrasion testing. If garments are made of this knitted cotton fabric, they may be discarded by wearers at the stage when severe pilling appears, even though the pilling could be removed by further abrasion or rubbing during use. The sol-gel treatment was able to improve the pilling properties of knitted cotton fabrics. It was found that there was no pilling observed even after 25,000 revolutions for the samples treated with sols, even sols containing MTES alkoxysilane only. This demonstrated that the sol-gel coating provided additional anti-pilling properties to the intended dual funnctionality of hydrophobic and antibacterial properties.

A reduction in abrasion resistance was found for the cotton samples treated with sol solution, when compared abrasion performance of to the untreated cotton fabric. This is because the acidic nature of the 50% v/v ethanol solution, used for sol synthesis, drastically reduced the abrasion performance of cotton fabric treated in the ethanol solution for the 4 hour treatement period. However, the introduction of silanes in this solution restored the abrasion performance differently, depending on the combination of silanes used. These results demonstrated that where prolonged resistance to abrasion was required, further optimisation of pH levels and duration of fabirc treatment. Water dilution of sols synthesised demonstrated an improvement in abrasion performaance, however this dilution led to a reduction in hydrophobic properties. The acidic pH is required to hydrolyse the ethoxy groups on the silanes to produce the crucial silanol groups that enable reactions between the sol-gel coating and the reactive groups on the cotton fibres to occur. The more acidic the medium, the higher the rates of hydrolysis and therefore formation of the silanol groups. Optimisation studies could be carried out to determine the treatment time required to ensure sufficient reaction between sol solution and cotton fabric.

The abrasion performance of the sol-gel treated cotton samples padded at 15 kg/cm was better than the treated cotton samples padded at 45 kg/cm. This was attributed to the thicker sol-gel coating that could be present on the treated samples padded at lower pressure due to more sol-gel coating on the surface. However, the thicker coating did reduce fabric handle, which could be demonstrated through touch, and good breathability properties. The treated cotton samples padded at higher pressure would be desirable as fabric handle was maintained for cotton samples. Textile end-uses that require high resistance to abrasion would require further optimisation of the current sol-gel treatment method to further improve the abrasion performance of the treated cotton fabric. The sol-gel application method developed demonstrated that this treatment process was able to restore some abrasion resistance for cotton samples treated in the acidic conditions. It also demonstrated that the burst strength was not adversely affect by the sol-gel coating and in some cases, a slight improvement seen.

CHAPTER 6:

ANALYTICAL ANALYSIS OF SOL-GEL TREATED COTTON FABRIC

6.1 Introduction

Analytical techniques provide the means of studying intricate chemical and physical properties of textile surfaces. These techniques give further information on how finishes such as sol-gel applied on fabric material affect textile surface topography (Patel et al., 2014). To understand the topographical and chemical characteristics of sol-gel treated textile surfaces, spectroscopy techniques such as Scanning Electron Microscopy-Energy-dispersive X-ray (SEM-EDX) and Attenuated Total Reflectance / Fourier Transform-Infra-red (ATR / FT-IR) have been widely used (Fischer et al., 2008). SEM-EDX allows analysis of surfaces at various magnifications coupled with the EDX elemental analysis while FT-IR analysis has been used to identify types of bonding that are present on textile surfaces. Several analyses were carried out on treated cotton fabric samples using ATR / FT-IR to determine the type of bonding that was present on the treated surface. Further investigations were also carried out using this technique to determine the type of bonding that occurred during the formation (drying and curing) of the sol-gel film and sol-gel coating on the cotton fabric. SEM-EDX analysis was able to illustrate the sol-gel coating applied on the treated textile material and the changes to the surface topography. EDX analysis was used to identify the elemental composition of the coating on the treated cotton samples. Other techniques such as fabric moisture management were used to measure moisture management and breathability properties of treated cotton fabrics. Through these techniques, knowledge on the behaviour of sol-gel on the knitted cotton surfaces was acquired.

6.2 Materials and Equipment

6.2.1 Textile fabric

Control (bleached) cotton: Bleached and scoured cotton from Vertical Garments (Leicester)

Treated cotton samples: Control (bleached) cotton samples were treated as described in Section 3.3.2 using MTES, GLYMO, OTES and QUAT silanes in 50% v/v ethanol solution (pH 3.2).

6.2.2 Equipment

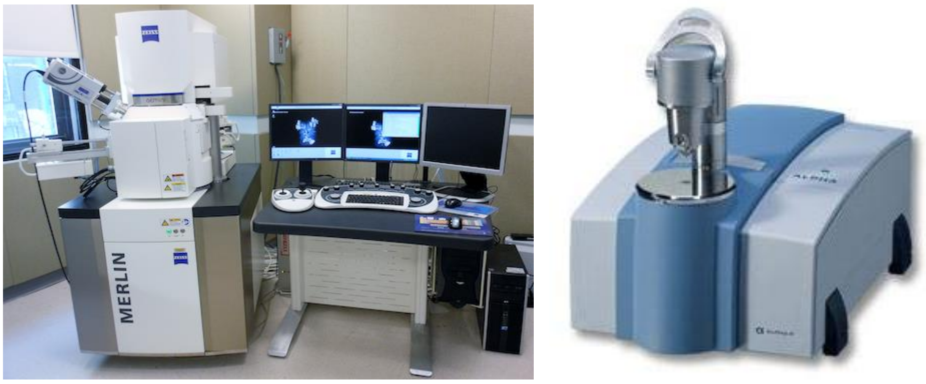


Figure 6.1 A Carl Zeiss SEM / EDX equipment (Image courtesy of New York University – Department of Chemistry, 2012) and a Bruker Platinum-ATR alpha equipment for ATR / FT-IR analysis (Bruker Corporation, 2016)

SEM-EDX and ATR / FT-IR analyses were carried out using the Carl Zeiss SEM / EDX and Bruker Platinum-ATR alpha, respectively.

6.3 Experimental

6.3.1 Fabric treatment

For analytical analysis, knitted cotton was treated with sol-gel as described in Section 3.3.2 and summarised in Section 6.2.1. Cured fabric samples were rinsed in deionised water for 30 minutes at 20 rpm in the Ahiba Nuance. This was carried out at room temperature to remove any unreacted sol-gel. Rinsed samples were then hydroextracted to remove excess water and allowed to dry at 25°C overnight.

6.3.2 Sol-gel film formation

To form the sol-gel film for analytical analysis, sol solution was poured into watch glasses and allowed to dry overnight (Figure 6.2). The dried sol-gel films were then dried further at 70°C for 5 minutes followed by curing at 120°C for 20 minutes. This was carried out to ensure that the sol-gel film formed was processed as described in the methods for cotton fabric treatment. The sol-gel films were then placed onto the aluminium stubs for SEM analysis.

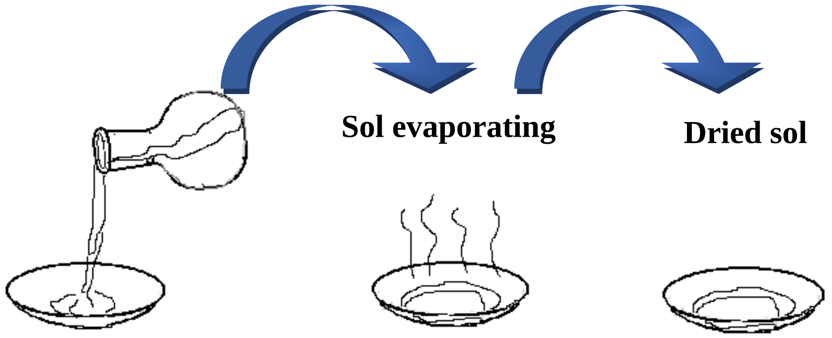


Figure 6.2 Schematic diagram showing the method to produce sol-gel film for SEM and ATR / FT-IR analysis

6.3.3 Scanning Electron Microscopy (SEM) analysis

6.3.3.1 Principle of Technique

Scanning Electron Microscopy (SEM) is an analytical technique that uses a highly convergent beam of electrons focussed on the surface of a sample to provide a three - dimensional appearance of the surface at varied magnifications; it also provides the means to observe the surface morphology of textiles (Gashti et al., 2012). The measurement of signals produced, as a result of electron interaction with surface molecules, is converted into the image. With SEM analysis, there is a need to ensure sample compatibility with the SEM system requirements. This is essential for successful analysis as it allows reduction in backscattering and unnecessary charge up caused by electrons that may lead to poor imaging as a result of abnormal contrast and image deformation (Li, 2005). The limitations that develop as a result of back scattering and over excitation include poor imaging and restrictions in examining widen regions on surface being analysed. In such instances, measures are taken to ensure that the samples being analysed are electrically conductive and able to withstand the high vacuum systems. Gold coating during sample preparation can be used to ensure that back scattering and over excitation are avoided and has been incorporated in SEM sample analysis (Li, 2005). To achieve good SEM imaging, cotton samples were gold coated to ensure that images captured had the best resolution and sharpness. SEM microscopy is the preferred method for surface analysis as opposed to optical microscopy due to better depth of fields and smaller wavelengths achieved by electrons in SEM. Such wavelengths lead to improved image resolution and therefore better images (Wittke, 2008; Li, 2005). The schematic of how this is achieved is shown in Figure 6.3. The electron column operates through the production of a stable electron beam that is controlled through the different lens. These lens control levels of the beam size, current and shape of the elctron beam, to ensure that the right composition of the electron beam is produced on the sample (Figure 6.3).

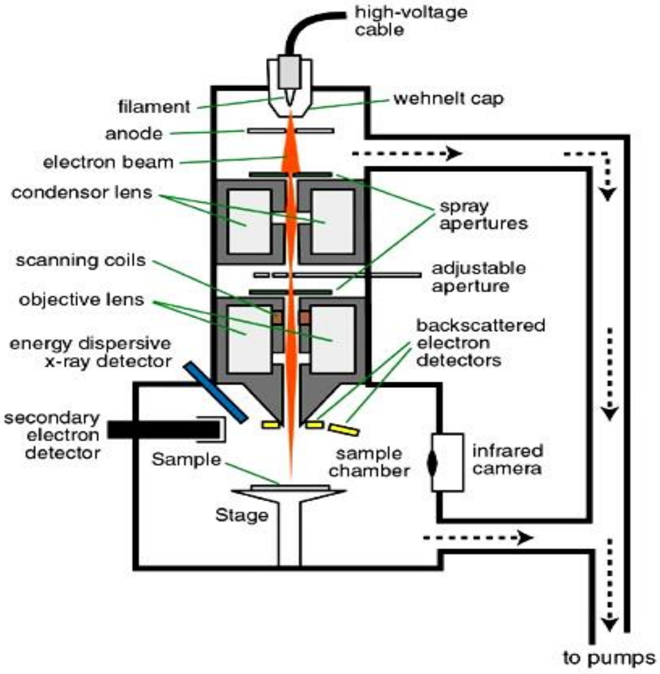


Figure 6.3 SEM schematic showing mechanism of how the equipment generates electrons and how these electrons are focussed on the sample being analysed. (Wittke, 2008)

For the system to work, a vacuum is used to enable the free movement of electrons.This is because electrons cannot move freely in air as air, being an insulator, does not have free electrons to transfer motion of electrons through it or promote what is referred to as conductivity. The vacuum needed to transfer electrons from source to sample is produced by the removal of air using a combination of mechanical and diffusion pumps. Electron guns used to produce electrons for an electron beam, are comprised of cathode materials. The beam produced, being divergent after passing through the anode plate, is re-focussed and controlled when passed through the condensor and objective lens (Wittke, 2008). The condensor lens control the amount of beam current that is passed down the rest of the column while the objective lens are then used to re-focus the beam after its passage through the adjustable aperture. This objective lens ensures that the electron beam is focussed onto the sample and controls the final size and position of this beam. Scanning coils in the column are essential for beam rastering over the sample (Wittke, 2008). This beam and its interaction with the sample allows image formation. The focussed electron beam that collides with the sample surface, undergoes some transformations. The beam can either pass through the sample atoms without collision, or the beam can collide with the electrons from the sample atoms to create secondary electrons or collide with the nucleus of the sample atom to produce backscattered electrons (Evans Analytical, 2015). These transformations are then measured by the detectors of the electron column. SEM equipment also incorporate an EDX spectrometer as shown in Figure 6.3. This detector measures the energy dispersive X-rays that are characteristic and unique to different elements,which is represented by the elemental spectra for surfaces. SEM coupled with EDX analysis, being inexpensive, provides a quick identification of the elemental composition of the surface topography (Wittke, 2008).

6.3.3.2 Methodology

6.3.3.2.1 SEM analysis of cotton fabric materials

Cotton fabric samples were cut into 1 cm x 1 cm sections, which were suitable sizes for the SEM aluminium stubs (Figure 6.4 (b)). To hold the samples in place, a circular two-faced adhesive (as placed on stubs in Figure 6.4 (b)) was placed on the circular SEM specimen stubs followed by the cotton sample. The aluminium stubs were then placed on the carousel sample holder (Figure 6.4).

Figure 6.4 Examples of carousel sample holders without adhesive tape (a) (E. Fjeld Company, 2003) and SEM aluminium stubs and adhesive tape (b) (Emresolutions, 2014) used to hold samples for SEM analysis

Before the samples were anlaysed, the samples were placed in the gold coater. To gold coat, a vacuum was applied until 10^{-1} Torr was achieved. Argon gas was then introduced into the chamber and a discharge produced to achieve a reading of electromagnetic force of 1 kV and electric charge of 40 mAmp. This discharge allows argon ions to form and reach the gold cathode in the chamber. These argon ions knocked off gold ions that deposited on the fabric sample (Figure 6.5).

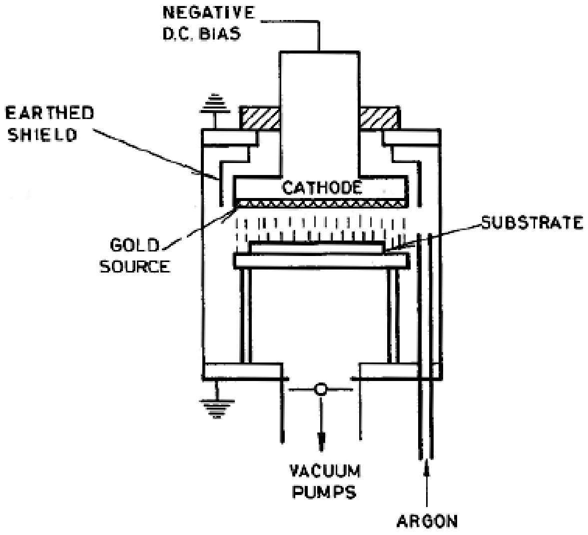


Figure 6.5 Schematic diagram illustrating the components of equipment used in gold coating (Williams, 2011; with permission from springer)

After coating, these samples were placed on the carousel holder (Figure 6.4 (a)) and placed in the SEM vacuum chamber. The equipment was allowed to pressurise and set, accelerating voltage was set at 10.00kV and sample height at 0.8mm to ensure adequate excitation for imaging. High definition beam technology of the Carl Zeiss was used for imaging of the surface of control and treated cotton samples. The Imaging was carried out at varying magnifications to demonstrate the changes due to sol-gel treatment.

6.3.3.2.2 Procedure for EDX analysis on cotton samples

For EDX analysis, Inca software was used. A still image was captured from the cotton sample in the pressured chamber after SEM analysis and the section of interest selected using the ‘point of interest’ option on samples prior to gold coated. The ‘point of interest’ options included a broader selection or individual spot analysis for elemental analysis. Once the area for elemental analysis was selected, the system automatically ran an elemental analysis of the selected area and spectra produced.

6.3.4 Attenuated Total Reflectance / Fourier Transform-Infra-red (ATR / FT-IR) analysis

6.3.4.1 Principle of ATR / FT-IR technique

Fourier Transform-Infra Red is the study of the interaction of infrared light with matter (Smith, 2011). This analysis is represented as an infrared spectrum plot of the measured light intensity versus a property of light; which in FT-IR analysis is the wavelength, represented as the wavenumber. The wavenumber indicates the number of wave cycles per unit length. When a sample interacts with a beam of infrared light, its molecules vibrate and it is these vibrations that are interpreted by the detectors and plotted on IR spectra. Most infrared spectra are plotted between the wavelength range of 4000 to 400 cm^{-1}. On such spectra, different peaks represent the composition of the sample being analysed (Smith, 2011).

Attenuated Total Reflectance / Fourier Transform-Infra-red (ATR / FT-IR) was the analytical technique used to identify the type of bonding present on treated surfaces of knitted cotton fabric. ATR / FT-IR was preferred over transmission FT-IR due to its ability to generate qualitative and quantitative analysis of the samples with little or no sample preparation. In contrast, conventional FT-IR analysis by transmission involves sample preparation by dilution with IR transparent salt to prevent total absorption of bands in the infrared spectrum while ATR / FT-IR analysis eliminates this dilution. The elimination of lengthy sample preparation allows for faster sample analysis and therefore quicker production of results. ATR sampling operates through the use of very thin sampling path length and a deeper penetration of the IR beam into the sample (PIKE Technologies, 2015). The IR beam is directed into a crystal of a relatively higher refractive index which is crucial in generating ATR spectra as it influences the critical angle that has to be exceeded for complete ATR to occur (Figure 6.6).

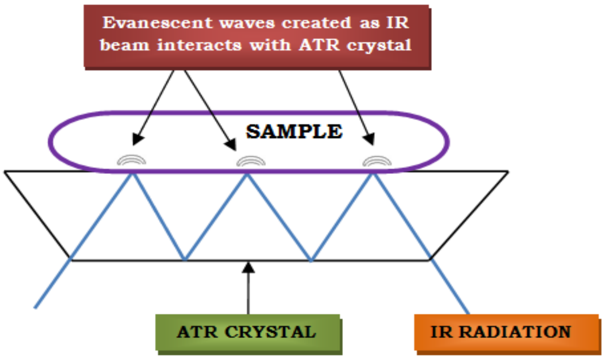


Figure 6.6 Graphical representation of an ATR reflectance and the evanescent wave involved in analysis.

The IR beam reflects from the internal crystal surface and creates an evanescent wave (Figure 6.6) which radiates into the sample. There are different types of ATR crystals available for use. The ATR/FT-IR crystal used for analysis was diamond; in this research. In order for successful analysis, the sample must be in close contact with the crystal as the evanescent wave only extends to 0.5 - 5µm (Perkin Elmer, 2005). Part of the energy that this evanescent wave produces is absorbed by the sample and the reflected radiation returned to the detector. The radiation detected is then translated into spectra, over a specified wavelength range (Perkin Elmer, 2005).

6.3.4.2 Methodology

For ATR / FT-IR analysis, fabric and sol-gel films were mounted onto the crystal and pressure applied as per equipment design as shown in Figure 6.1. Using the OPUS programme, measurement parameters were set to run over wavelength range of the 4000 - 400 cm^{-1}at a resolution of 2 cm^{-1}. The number of scans was set at 50 scans for improved accuracy. The background was run using “measure background” option prior to sample analysis. Cotton material without sol-gel was used as background. This resulted in simpler spectra that avoided overlapping of peaks of interest. For ATR / FT-IR analysis of treated cotton samples, the “measure sample” option was selected to run scans and spectrum was produced on the Opus system. For peak identification, the automated “peak selection” option was used that populated wave numbers on corresponding peaks.

6.3.5 Moisture management analysis

Testing was carried out by the collaborative partners INOTEX (Czech Republic).

6.4 Results and Discussions

6.4.1 SEM imaging of sol-gel films

The type of sol-gel films formed using sols synthesised using the base formulation were studied using SEM analysis. Sol preparation was carried out as described in Section 3.3.2. The synthesised sols were stirred for 4 hours at 40°C to simulate the 4 hour treatment that was used in cotton fabric treatment. These sols were placed on watch glasses and allowed to dry overnight. Further drying was carried out for 5 minutes at 70°C and curing for 20 minutes at 120°C. SEM analysis was carried out on dried sol-gel films and dried + cured sol-gel films to determine whether curing did influence the final film formed. The results obtained are shown in Figures 6.7 and 6.8, respectively.

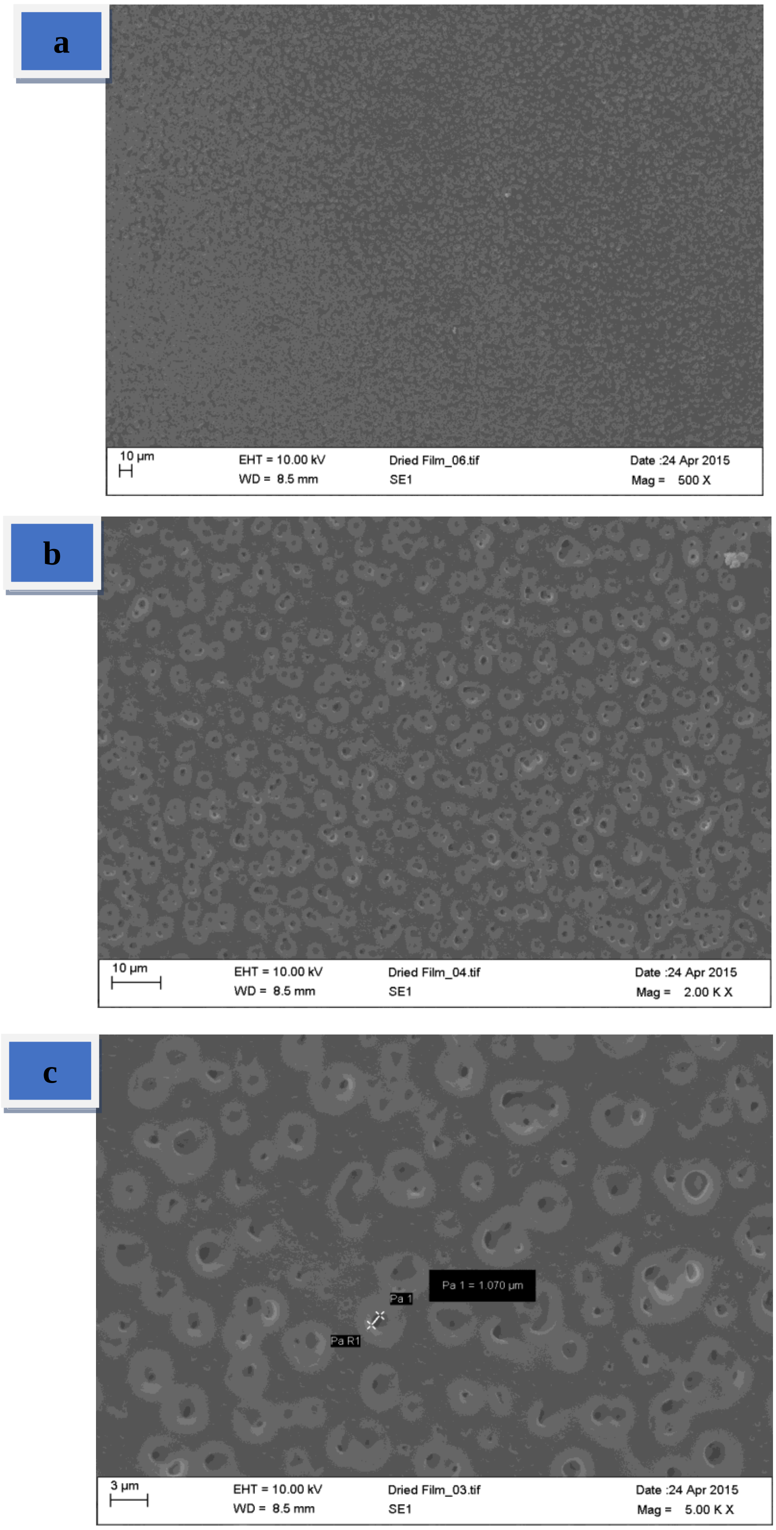


Figure 6.7 SEM images of sol-gel film dried at room temperature captured at 500x (a), 2000x (b) and 5,000x (c) magnification

Images in Figure 6.7 show the porous nature assumed by the of sol-gel film after drying at ambient temperature; confirmed to be pores as the black adhesive used to attach the film could be seen in the images. It is through the hydrolysis and condensation reactions that sol-gel films with trapped liquid phase are formed. During evaporation and application of heat, solvent and moisture evaporation from such gels, leads to the formation of pores in the film. It was also observed that these pores were of varying sizes as illustrated in Figure 6.7(c). This porous structure may have contributed to the good moisture management results illustrated in Section 6.4.4. The thickness of the sol-gel film was also measured as shown in Figure 6.8.

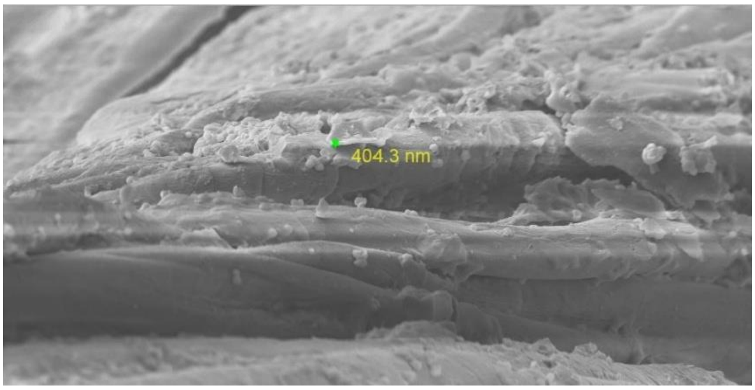


Figure 6.8 SEM images demonstrating the thickness of the sol-gel film formed on the treated cotton at 2000x magnification

To determine whether any further changes occurred to the sol-gel film, the air-dried sol-gel films were dried for 5 minutes at 70°C and cured for 20 minutes at 120°C. SEM was carried out and the results shown in Figure 6.9. Curing the dried sol-gel film samples resulted in more pore formation as illustrated in Figure 6.9. This occurred due to further evaporation and therefore removal of any formed or trapped water that may not have evaporated during ambient drying. At higher temperatures, trapped liquid was to escape from the pores in sol-gel film (Brezezinski et al., 2011). A lower magnification of the cured film (Figure 6.9 (a)) illustrated agglomerates of sol-gel particles that form due to the continued polymerisation reactions between neighbouring particles in the sol, which precipitated out of solution due to their size. Further illustrations are discussed in Section 6.4.2.

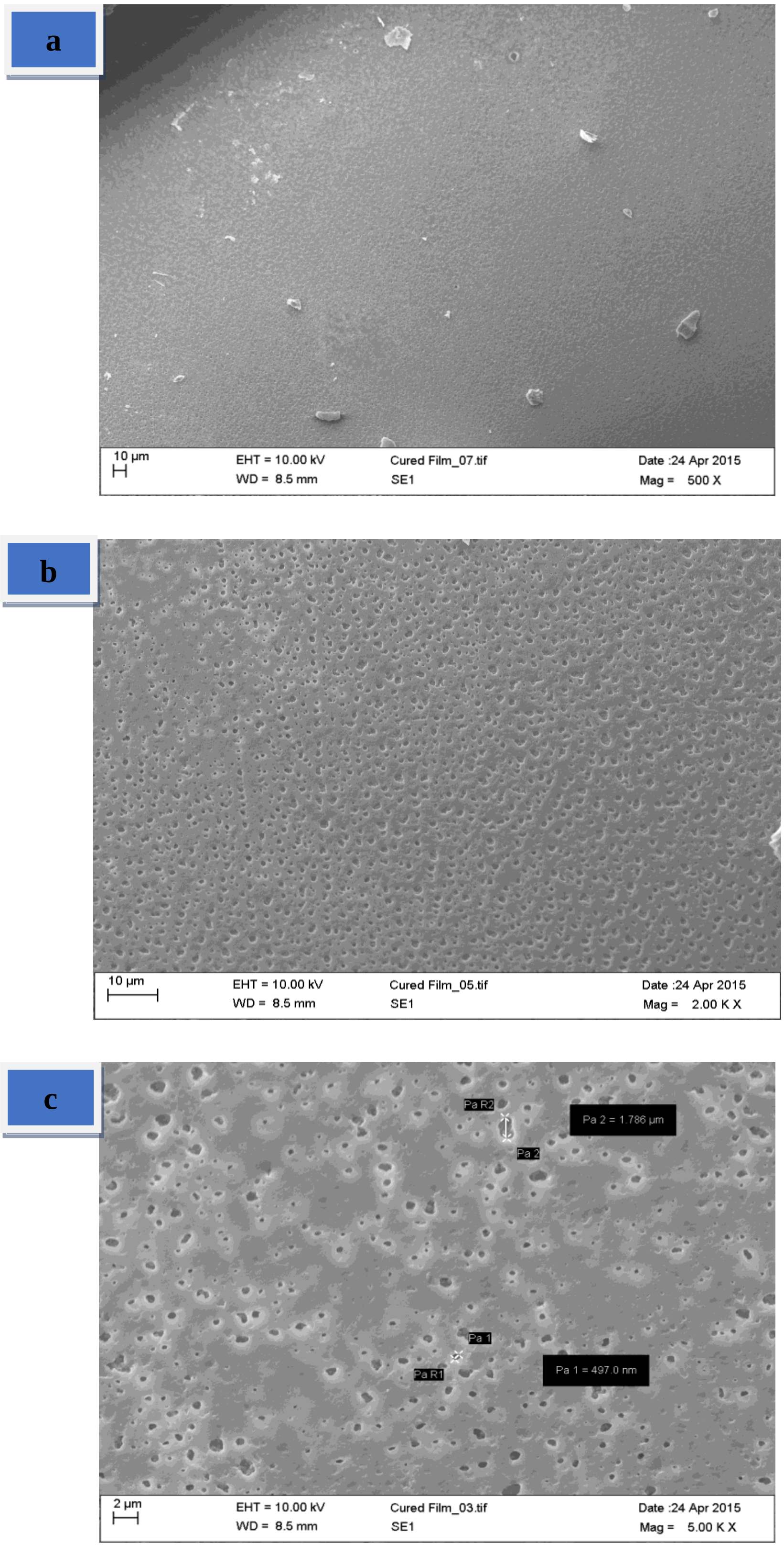


Figure 6.9 SEM images of dried + cured sol-gel film captured at 500x (a), 2000x (b) and 5,000x (c) magnification

6.4.2 SEM analysis of sol-gel treated knitted cotton

The influence of the fabric construction and structure were considered during the investigation of sol-gel coating that formed on the cotton fabric samples. Sol solutions were applied on different forms of cotton such as its fibre, yarn and knitted fabric. Sol synthesis, using the base formulation containing the silane composition of MTES: GLYMO: OTES: QUAT, was carried out as described in Section 3.3.3. For the sol application onto fibres and yarns, plastic frames (Figure 6.10) were used to secure the fibres and yarns during the 4 hour treatment, to prevent cross-linking, overlapping and clumping of fibres and yarns, respectively.

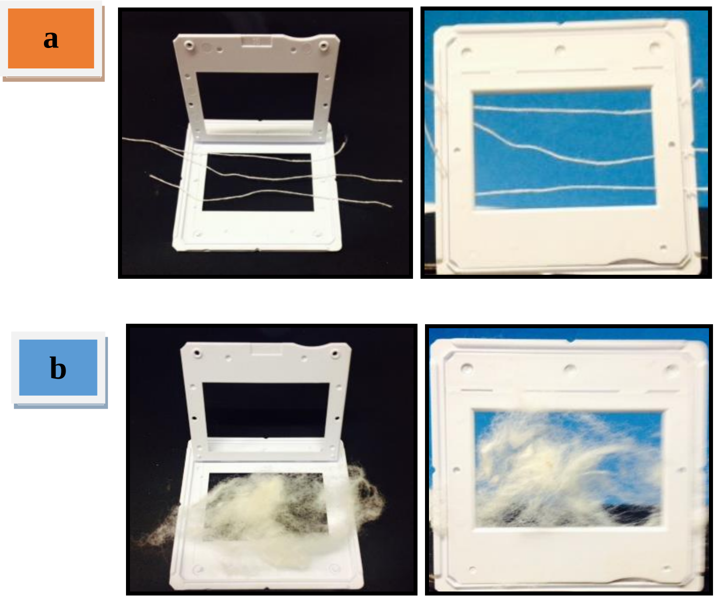


Figure 6.10 Illustration of how plastic frames secured and prevented clumping of yarns (a) and fibres (b)

SEM was carried out on fibres, yarns and knitted fabric samples as described in Section 6.3.2.2 and results shown in Figure 6.11. Results showed that the smooth surface of the untreated cotton fibres (a) were roughened by different sized particles as shown in samples (b) and (c). These images confirmed the presence of the sol-gel coating on the fibres and also illustrated that the same type of coating, with differently sized particles, was seen for the two levels of pad pressure.

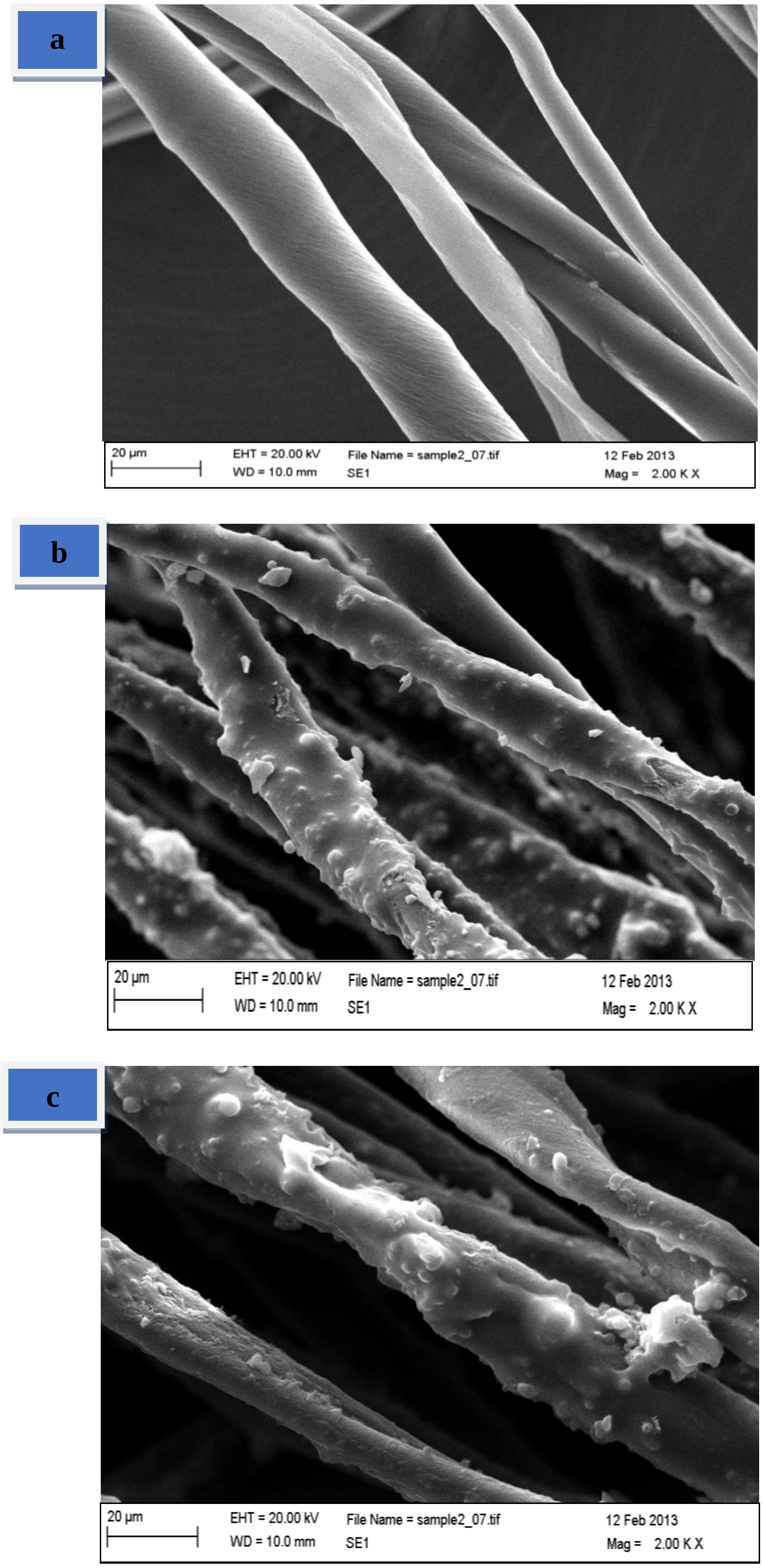


Figure 6.11 SEM imaging of control (bleached) cotton fibres (a) and cotton fibres treated in fibre form padded once at 15 kg/cm (b) and padded twice at 45 kg/cm (c)

The influence of pad pressures on the amount of coating was observed on the fibre samples. More coating was seen on fibres padded once at 15 kg/cm than treated fibres padded twice at 45 kg/cm. This was due to a higher dry weight gain of 53% w/w for fibre samples padded once at 15 kg/cm as opposed to the 45% w/w gained by fibre samples padded twice at 45 kg/cm. A higher weight gain was achieved for treated fibres, when compared to treated cotton fabric padded at the same pad pressure, due to the high affinity for sol because of fibres being in their free form. This high affinity would lead to higher liquor pick-up for fibres.

The coatings formed on the fibres consisted of particles and agglomerates of varying sizes. These particles formed as a result of extensive condensation reactions between neighbouring particles during the drying and curing processes. To determine whether twisted cotton yarns would influence the type of coating formed, sol-gel treatment was applied on cotton yarns using methods as described in Section 3.3.3 and SEM analysis carried out. A higher accelerating voltage was used to reduce charge up that produces the brightness of backscattered electrons that produces poor images.

Two magnifications were used to show the overview of sol treatment on yarns and a closer magnification to observe any intricate patterns. The sol-gel coatings formed on cotton yarns were shown in Figures 6.12a-c. It could be seen that the polymeric sol-gel network did not stick the yarn fibres together but reacted around the individual fibres.

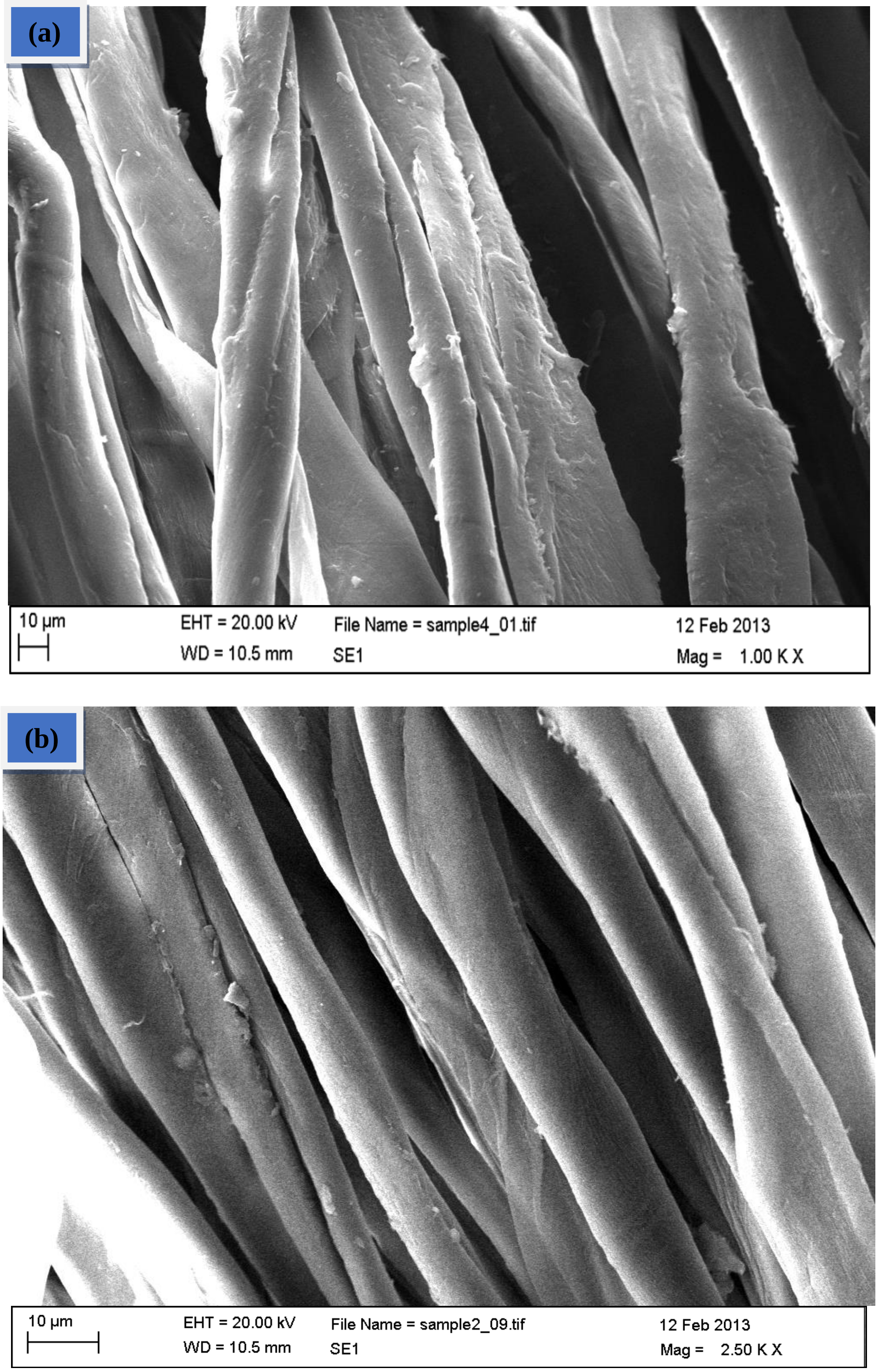


Figure 6.12a SEM imaging of control (bleached) cotton yarns at 1000x magnification (a) and 2500x magnification (b)

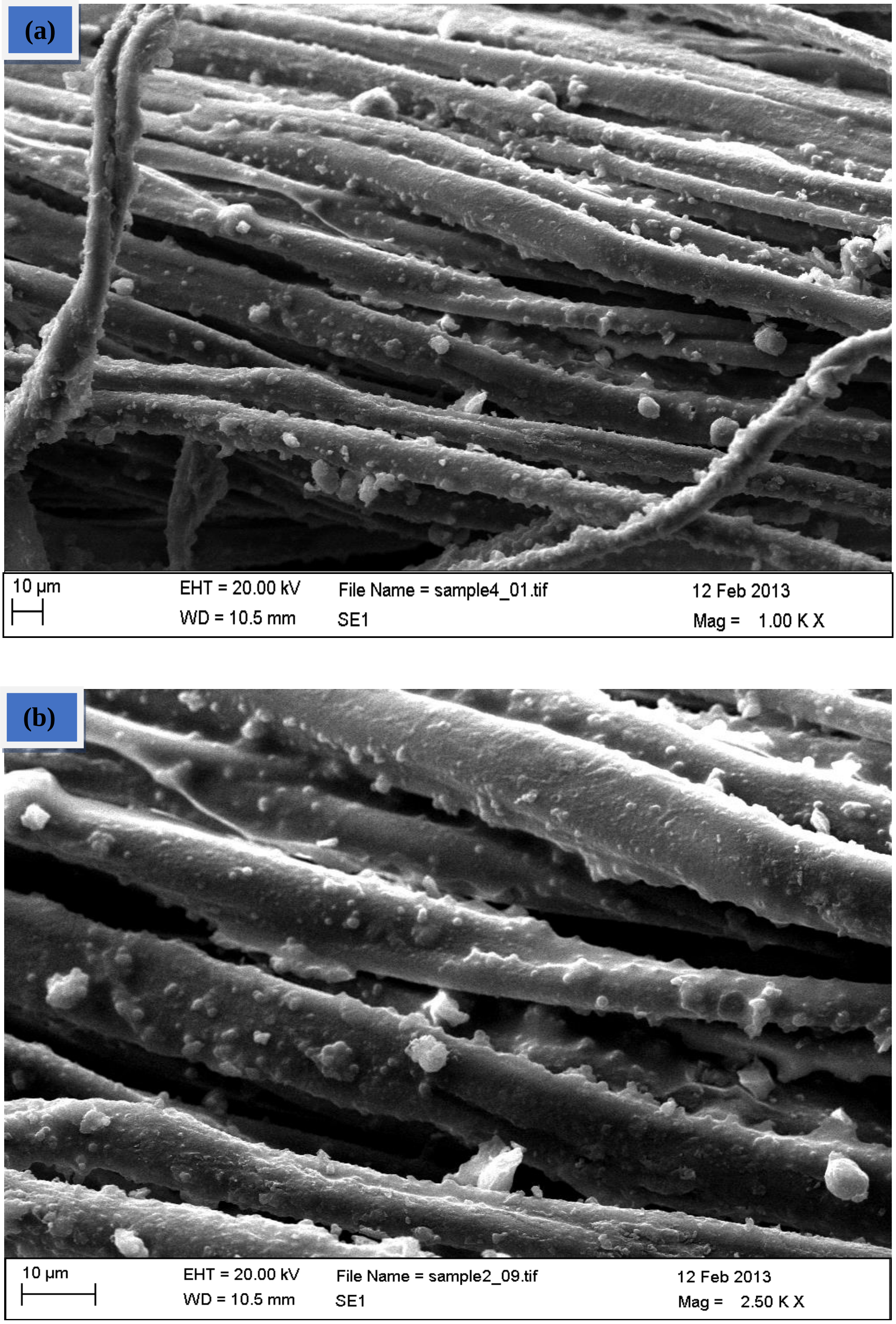


Figure 6.12b SEM imaging of sol-gel treated cotton yarns padded once at 15 kg/cm captured at 1000x magnification (a) and 2500x magnification (b)

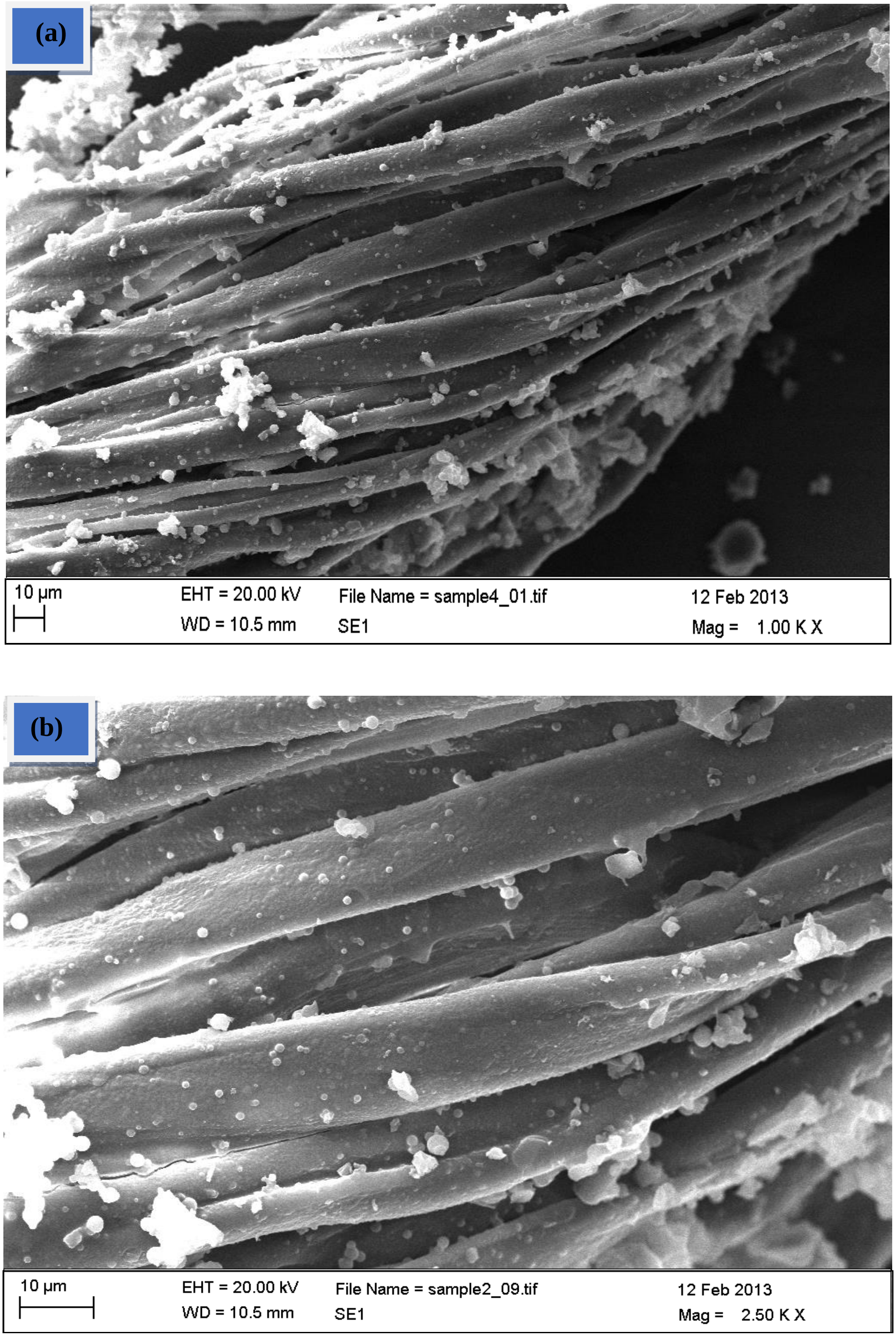


Figure 6.12c SEM imaging of sol-gel treated cotton yarns padded twice at 45 kg/cm captured at 1000x magnification (a) and 2500x magnification (b)

Sol-gel films formed on the watch glass consisted of a continuous film with embedded particles. When sol was applied onto cotton fabric, it was seen that the sol-gel coating reacted around the individual fibres in yarns, as most fibres were not stuck together. This was because of the hydroxyl groups on the cotton fibres that provided a high affinity for the sol solution because of their high absorption properties. The cotton's reactive surface, because of the functional hydroxyl groups, caused reactions to occur between these groups and the silanols present in the sol. The agglomerates observed may have formed due to continued reaction of proximal seed particles present in the sol as a result of initial sol synthesis (Sakka, 2005).

Where there is a high supply of silanol groups, upon evaporation, the silanol groups react and form linkages that lead to particle growth. Further condensation reactions between particles would result in particle size growth that would precipitate out of solution to form agglomerates. The irregularity of the sol-gel particle sizes formed as sol reacted on cotton fibres provided an uneven surface topography that influenced the degree of hydrophobicity achieved.

With results obtained for sol-gel coating interaction with fibres and yarns, SEM imaging was also carried out on the knitted cotton fabric samples, to observe the influence of the fabric construction and structure on the sol-gel coating formed on the cotton surface. From images in Figure 6.13, it was seen that more sol-gel coating was present on treated fabric samples padded once at of 15 kg/cm (c) than treated cotton samples padded twice at 45 kg/cm (b). This illustrated that, with low pad pressure, more solution, due to high liquor pick-up remained at the surface while higher pressures led to reduced liquor pick and less coating on the surface of the fabric sample.

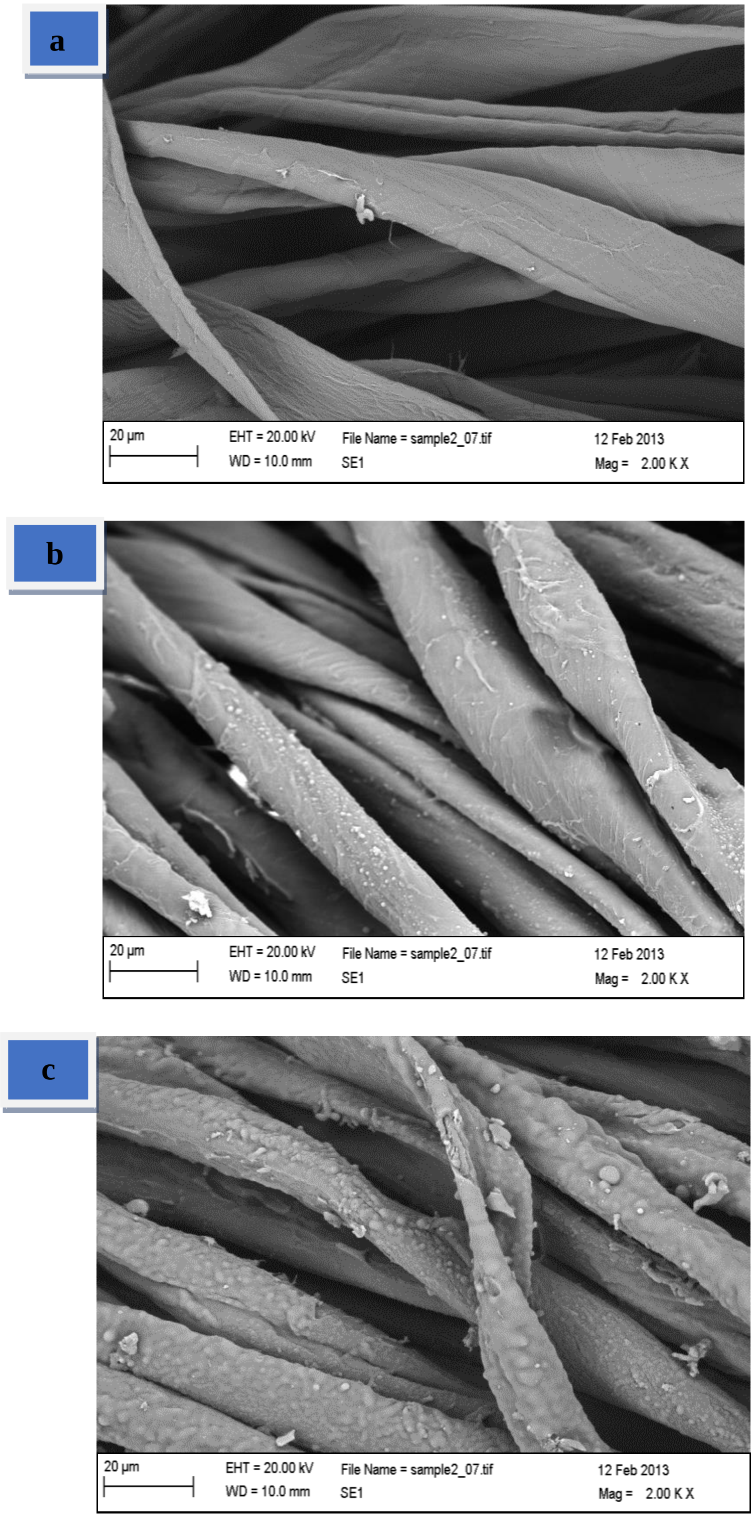


Figure 6.13 SEM images of knitted cotton fabric samples for control (bleached) cotton (a), treated cotton padded twice at 45 kg/cm (b) and treated cotton padded once at 15kg/cm (c) captured at 2000x magnification

Surface modification of the treated cotton fabrics could be seen, even when samples were viewed at lower magnifications (Figure 6.14). From the smooth appearance of the cotton fibres, a particulate sol-gel coating was formed on cotton fibres after sol-gel application, roughening its surface. The two pad pressures influenced the amount of coating on the treated cotton samples. The higher amount of coating seen for samples padded once at 15 kg/cm confirmed the discussions in Section 5.4 with regards to its influence on the abrasion properties. It was observed that samples padded at the lower pressure of 15 kg/cm achieved slightly better resistance to abrasion due to this coating. Further analysis on amount of coating and abrasion could be carried out to determine the relationship between the two factors.

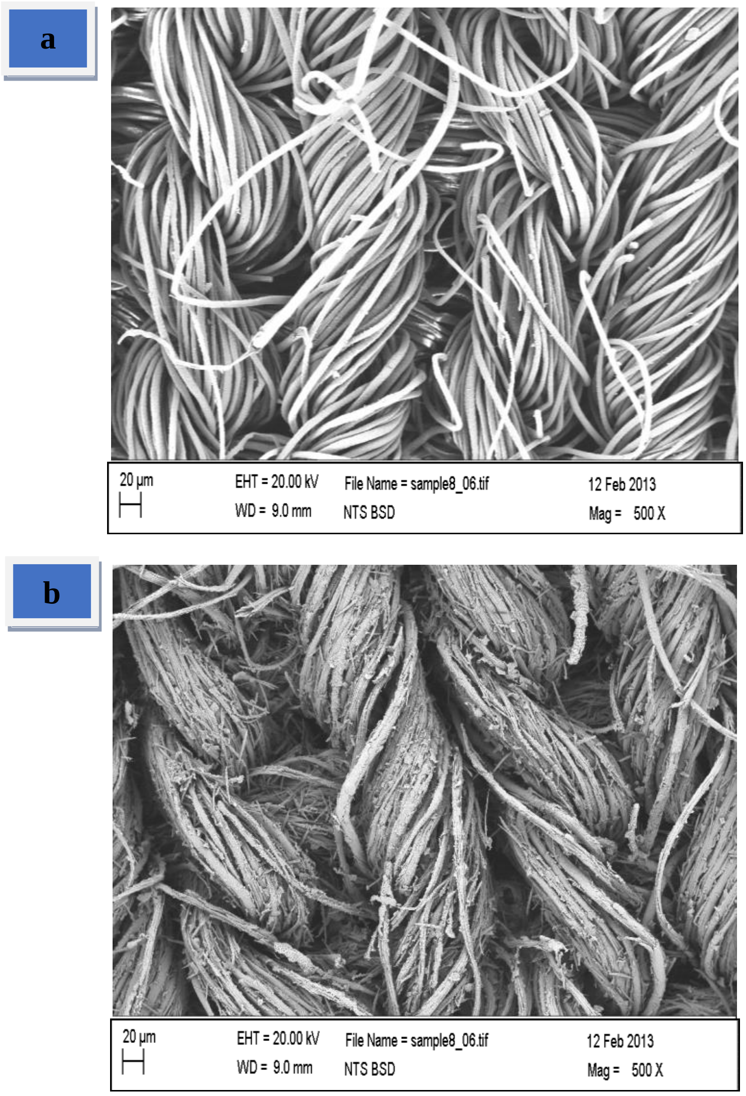
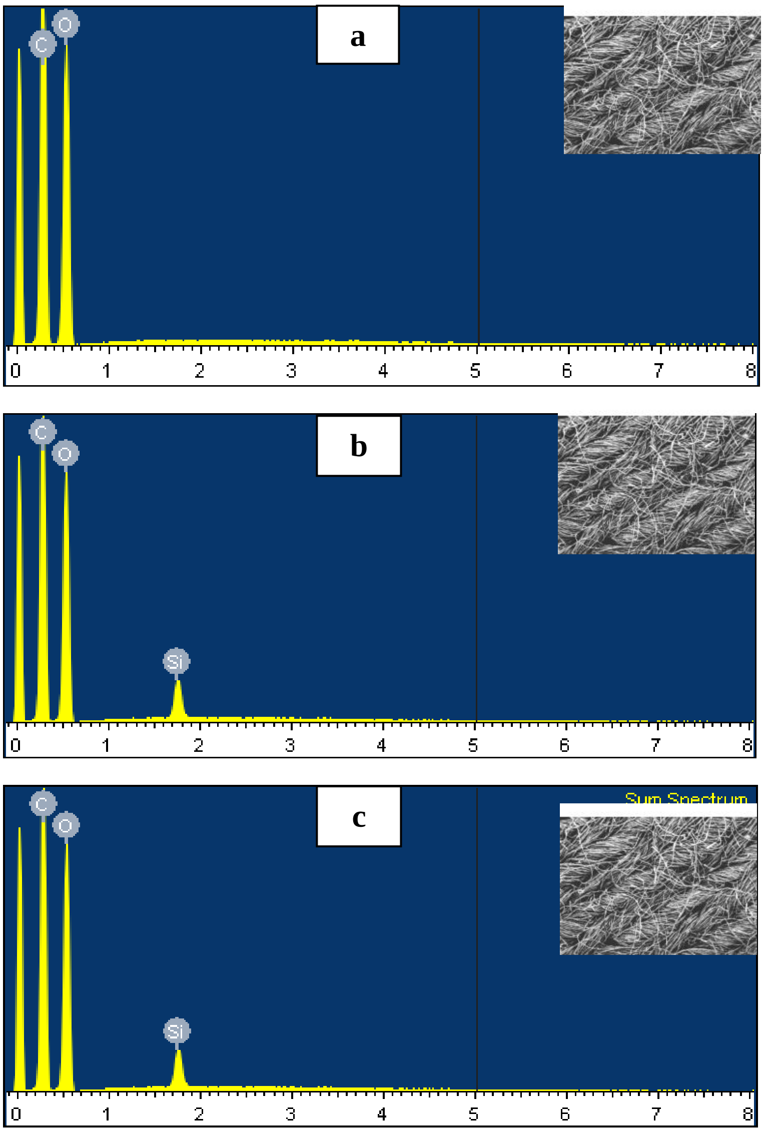


Figure 6.14 Overview of knitted cotton before (a) and after (b) sol-gel treatment (500x magnification) padded at 15 kg/cm

For the elemental analysis of the treated cotton surface, EDX analysis was carried out alongside SEM analysis. For comparative purposes, EDX analysis was also carried out on control cotton samples. Figure 6.15 (a) showed that the surface of the control cotton contained carbon (C) and oxygen (O) elements. To observe any changes in this elemental composition, EDX analysis was then carried out on treated cotton samples (Figure 6.15 (b) and (c)).



Element	Weight %	Atomic %
C K	47.81	54.96
O K	52.19	45.04
Totals	100.00	

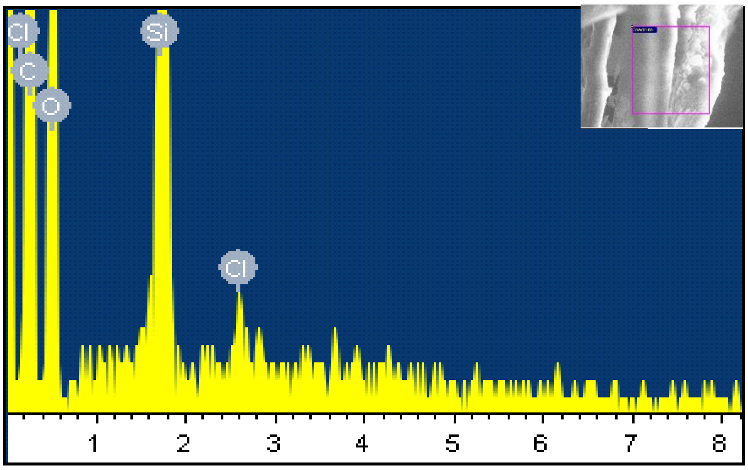
Element	Weight %	Atomic %
C K	47.60	55.05
O K	50.92	44.22
Si K	1.48	0.73
Totals	100.00	

Element	Weight %	Atomic %
C K	48.01	55.47
O K	50.48	43.78
Si K	1.52	0.75
Totals	100.00	

Figure 6.15 EDX analysis of control cotton (a), cotton treated with the synthesised sol using the base formulation and padded twice at 45 kg/cm (b) and padded once at 15 kg/cm (c)

The detection of the silicon (Si) element on the treated cotton samples confirmed the presence of the silicon-based alkoxides used in sol synthesis. Si content for treated cotton samples padded twice at 45 kg/cm and once at 15 kg/cm were 0.73 and 0.75, respectively, (Figure 6.15 (b) and (c)). These findings demonstrated that the Si content was comparable for treated cotton samples padded at different pressures.

EDX analysis on the treated cotton fabric was unable to detect other elements such as Cl (Chlorine) or N (Nitrogen) which would indicate the presence of QUAT on the surface. EDX analysis was therefore carried out on treated cotton fibres and results shown in Figure 6.16. This spectrum demonstrated that Cl could be detected using this method, however only on treated fibres are opposed to yarns (Figure 6.16). The detection of the Cl element could be due to the higher amount of coating on the fibre as a result of higher liquor pick-up because of higher affinity for sol in in their free form.



Element	Weight %	Atomic %
C K	58.60	67.14
O K	34.08	29.31
Si K	6.93	3.39
Cl K	0.40	0.16
Totals	100.00	

Figure 6.16 EDX analysis of treated cotton fibre treated with the sol synthesised using the base formulation and applied as defined in Section 3.3.3

These findings identified an area for further investigation to enable better detection of QUAT silane. Testing methods could be developed to detect the presence of the QUAT and its distribution on the surface through interaction with the positive charge on the nitrogen of QUAT silane. Stain acid dyes such as Coomassie Blue could be applied on the surface of the sol-gel treated cotton fabric, to determine QUAT distribution on the treated cotton fabric surface by ionic interactions with the positive charge on the QUAT. EDX analysis was able to detect the Si element, but no further distinction could be made between the different silanes of MTES, OTES and GLYMO. The exception was the QUAT, due to the presence of the chlorine element. From the results obtained, it was observed that EDX analysis was able to indicate the presence of the sol-gel on treated cotton surfaces (Vihodceva and Kukle, 2013).

6.4.3 ATR / FT-IR analysis of sol-gel treated knitted cotton yarns and sol-gel films

ATR / FT-IR analysis was used to investigate condensation reactions that would occur on the surface of the sol-gel treated cotton fabric and subsequently confirm the presence of the siloxane network. This tool had the capacity to achieve these detections due to different bond vibrations produced because of infra-red radiation on the sample. The theory behind this method of analysis states that as bonds constantly vibrate, the right amount of energy causes a shift to a higher state of vibration. In the case of FT-IR, this shift occurs when the atoms absorb the required amount of radiated light. Different energy levels are required for the shift to occur for different kinds of bonds. As a result, each bond absorbs a different frequency of the Infra-red radiation, which is then detected and interpreted as the FT-IR spectra (Clark, 2014). It is this principle that makes FT-IR a good tool for the analysis of chemical reactions and therefore a means to determine the type of bonds formed.

Beganskiene et al. (2004) analysed sol-gel colloidal SiO_2 nanoparticles using the FT-IR technique and was able to identify the absorption bands associated with absorption bands from asymmetric vibration of Si-O (1090 cm^{-1}), asymmetric vibration of Si-OH (950 cm^{-1}) and symmetric vibration of Si-O (795 cm^{-1}). It was observed that absorption bands between 800 and 1260 cm^{-1} appear to be superimpositions of various SiO_2 peaks while the peak around 1635 cm^{-1} was due to the “scissor bending vibration of molecular water” (Beganskiene et al., 2004; Patel et al., 2014; Lenza and Vasconcelos, 2000; Lin-Vien et al., 1991; Hegde and Rao, 2006). Further along the wavelength range, untreated TEOS was identified in the silica particles at absorption band of 2980 cm^{-1} (CH_3) and

2930 cm^{-1} (CH_2) (Beganskiene et al., 2004; Coates, 2000; Urlaub et al., 2000). These peaks were used as references for the identification of the peaks produced when the sol-gel treated cotton and control cotton samples were analysed. For the identification of long alkyl chains associated with the hydrophobic silanes, C-H bonds, singly bonded, are usually present within the range from 2853 - 2962 cm^{-1} (Clark, 2014; Horr and Reynolds, 1997). The O-H peaks of water has been detected at 1643 cm^{-1} and ethanol at 3318 cm^{-1} and Si-O-Si detected at 1085 cm^{-1} (Li, Xing and Dai, 2008).

For determination of bonds on the treated cotton fabric, ATR / FT-IR was carried out on treated cotton yarns and film, respectively. Cotton yarns were used for analysis as opposed to the knitted cotton fabrics to apply sufficient pressure for between yarn and the section on the ATR crystal to ensure contact with evanescent wave produced. With this observation, analysis was carried out on treated yarns obtained from the treated knitted cotton fabric samples. This was to ensure that the yarn used for analysis were representative of the treated fabric sample.

6.4.3.1 ATR / FT-IR analysis on sol solution

ATR / FT-IR analysis was initially carried out on the synthesised sol to determine the chemical reactions that occurred during the synthesis process as the reaction progressed over 4 hours. The sol solution was placed on the ATR crystal and programme run without the application of weight as per system design as shown in equipment in Figure 6.1. The spectra in Figure 6.17 showed the comparison of FT-IR spectra for sol at 0 hour reaction time and after 1 hour reaction. Further comparison after 1 hour reaction were not presented because there was no obvious change in spectra for the sol after the first hour to the fourth hour of synthesis.

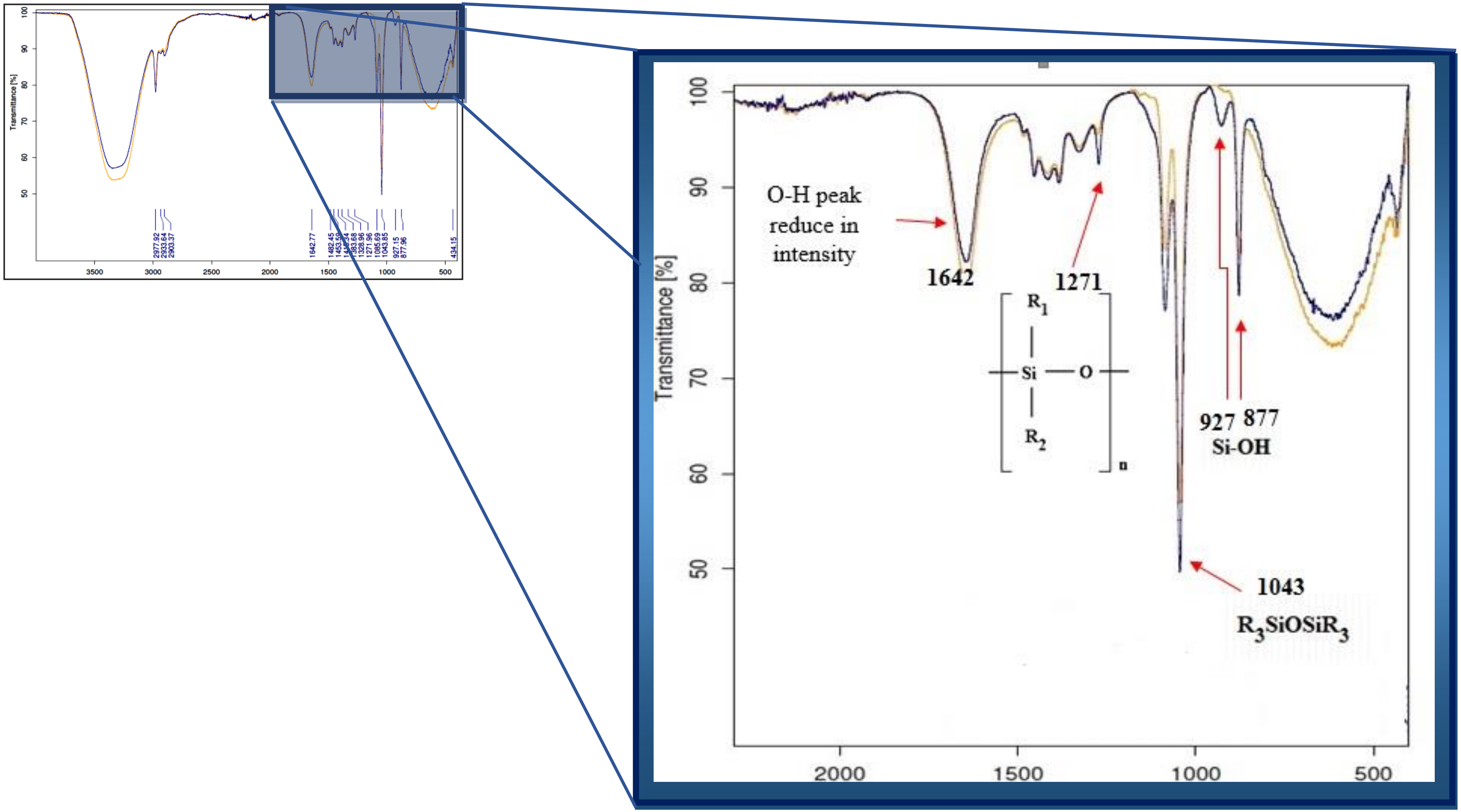


Figure 6.17 Comparison of sol spectra at 0 hour (orange) and after 1 hour reaction (blue)

Analysis as shown in Figure 6.17 demonstrated very distinct peaks for the silane mixture at 0 hour and after 1 hour reaction time. The very sharp peak at 877 cm^{-1} could be associated with Si-OH group and disiloxanes ($R_3SiOSiR_3$) were detected at 1043 cm^{-1}. Si-O-Si bonds that represent the siloxane bond were detected at 1271 cm^{-1}. The stand-alone peak at 1642 cm^{-1} is a characteristic peak of the O-H of water and the 3318 cm^{-1} associated with the O-H of ethanol in the solution.

After 1 hour reaction time, a new peak at 927 cm^{-1} appeared. This peak was responsible for Si-OH group associated with the silanol groups which were formed during hydrolysis reaction process and therefore demonstrated that hydrolysis was still taking place in the sol system within 1 hour of synthesis. The Si-OH peak at 877 cm^{-1} and disiloxanes ($R_3SiOSiR_3$) at 1271 cm^{-1} were more distinct after the 1 hour reaction which indicated that both hydrolysis and condensation reactions occurred simultaneously in the sol solution as the reaction progressed.

These results also suggested that rapid hydrolysis and condensation reactions occurred from the onset of silane mixing in the acidic ethanol solution and as a result, silanol and siloxane bonding could be detected even at the stage of mixing. This would be plausible as alkoxysilanes are expected to hydrolyse in the presence of water and ethanol, especially when a catalyst is present (Arkles et al., 1992); which, in this reaction system, was HCl catalytic component that initiated the hydrolysis reactions.

6.4.3.2 ATR / FT-IR analysis on formation of sol-gel film

To investigate the bonding that occurred as the sol solution dried and formed a sol-gel film, sol solutions were placed on ATR crystal and allowed to dry. This method of testing was ideal as it eliminated the use of substrates that could interfere with analysis and also allowed for the same film to be analysed for accurate results. Analysis was carried out on air drying sol at 5 minute intervals and results shown in Figures 6.18 and 6.19.

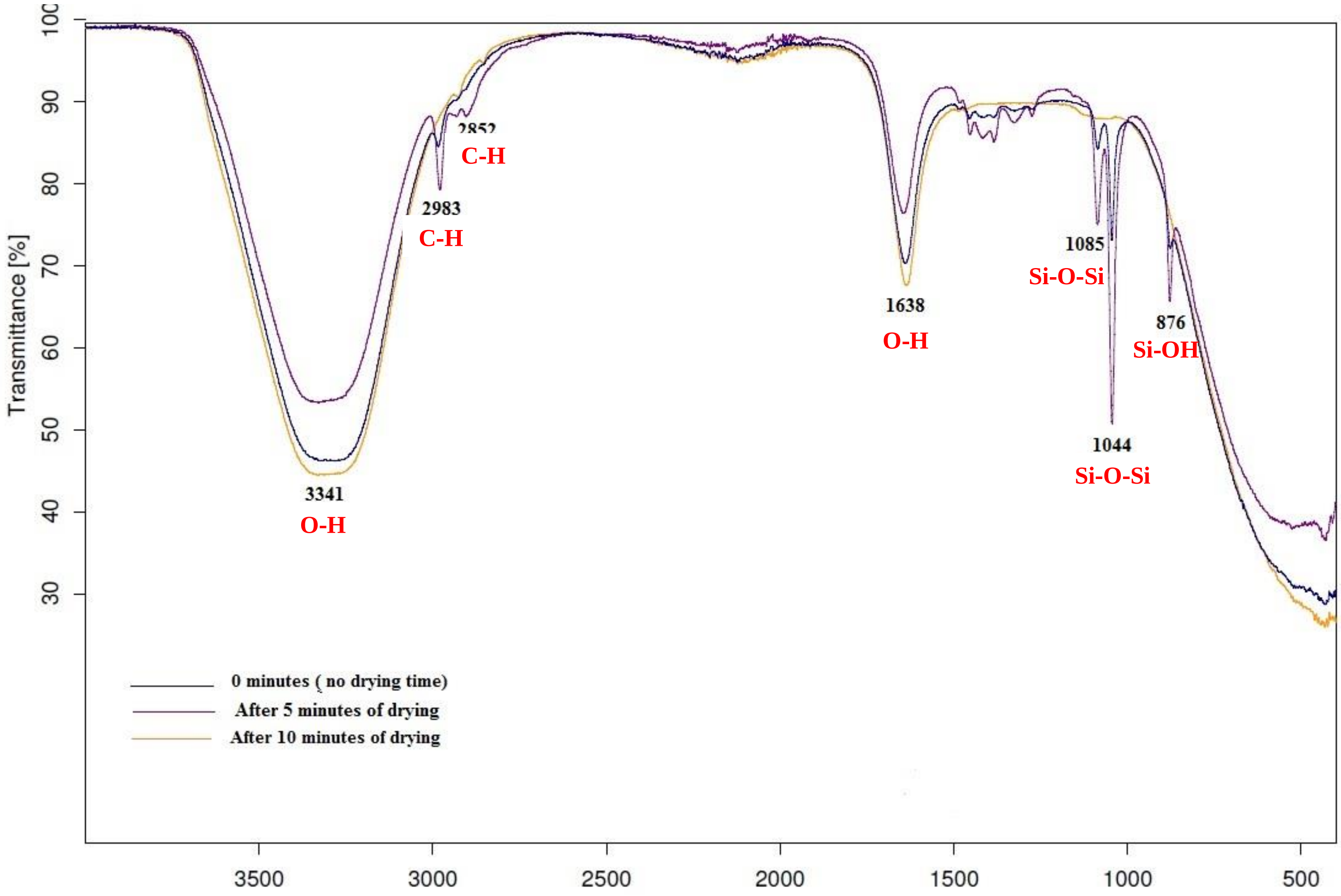


Figure 6.18 Comparison of spectra of sol after 0 minute, 5 minutes and 10 minutes of drying time

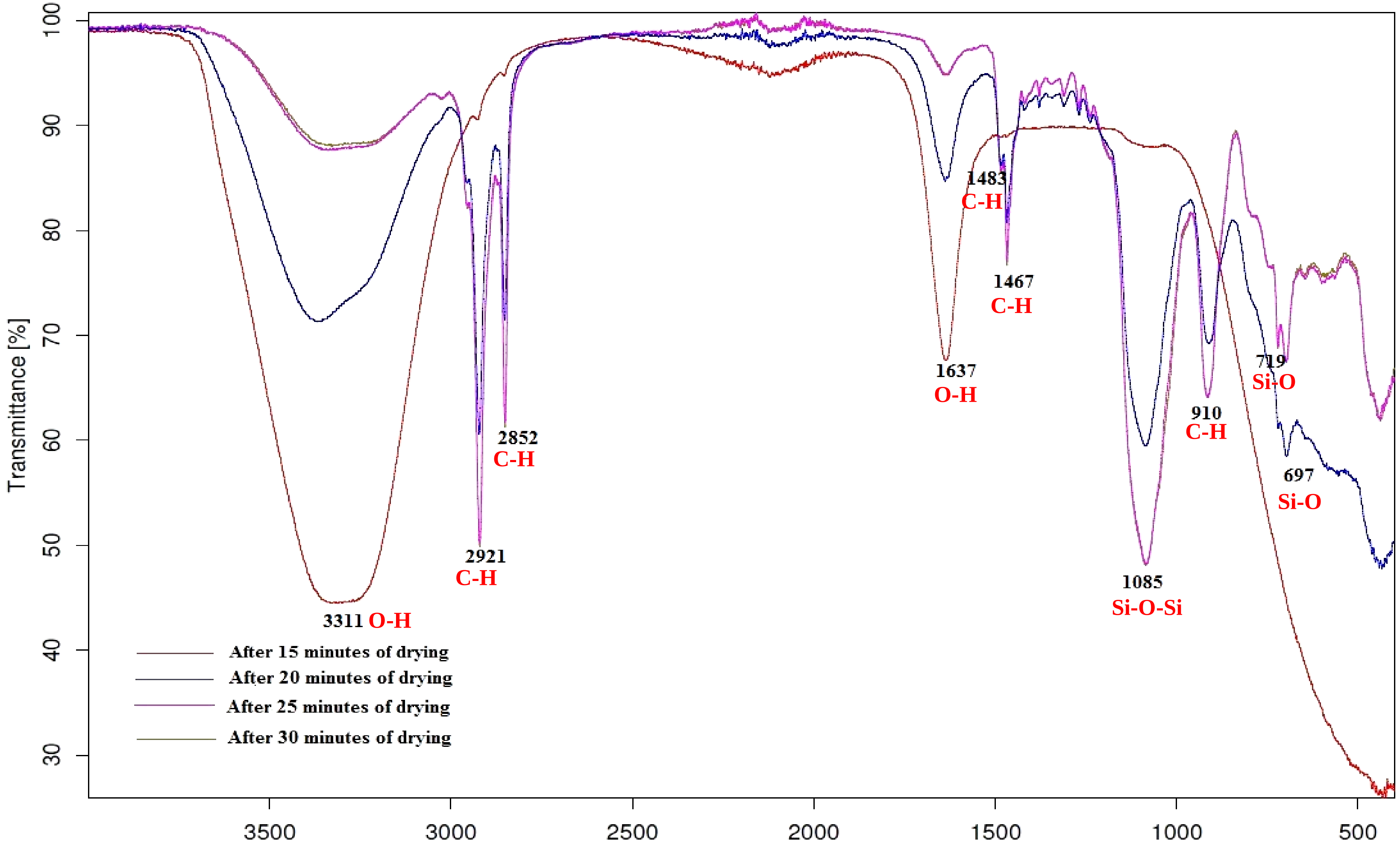


Figure 6.19 Comparison of spectra of sol after 15 minutes, 20 minutes, 25 minutes and 30 minutes of drying time

With reference to Figure 6.18, spectral peak changes were noticed as the sol solution dried over the first 10 minutes. The Si-OH and Si-O-Si bonds detected at 876 cm^{-1} and 1044 cm^{-1} and 1085 cm^{-1}, respectively, decreased; while the peaks for water (1638 cm^{-1}) and ethanol (3341 cm^{-1}) increased. This could be as a result of water and alcohol condensation reactions that would occur with rapid evaporation of solvent as sol-gel film formed. Results in Figure 6.19 illustrate spectra obtained as sol was allowed to dry further. It was observed that 30 minutes was sufficient for the sol-gel film to form from the drying sol. It was also seen that as drying continued, there was a decrease in the peak intensity of ethanol and water detected at 1637 cm^{-1} and 3311 cm^{-1} with increase in drying time. There was however an increase in Si-O-Si bonds as drying occurred as the peak intensity at 1085 cm^{-1} increased. This suggested that condensation reactions occurred as the sol dried. C-H species could be easily detected after 20 minutes as peaks appeared at the positions 1467 cm^{-1}, 1483 cm^{-1}, 2852 cm^{-1} and 2921 cm^{-1}. These peaks are associated with alkyl groups that were present on the hydrophobic silanes (Clark, 2014). These species were detected at later stages of drying due to loss of solvent (water and ethanol) through evaporation, which would concentrate their levels as the film was formed.

6.4.3.3 ATR / FT-IR analysis of treated cotton fabric yarns

To observe any changes in bonding of sol on cotton fabrics, ATR / FT-IR analysis was carried out on the treated cotton fabrics during their drying and curing stages. Analysis was carried out on the treated cotton fabric samples that were allowed to dry overnight and cured as described in Section 3.3.3. Comparison of spectra obtained for dried treated cotton and cured treated cotton are shown in Figure 6.20. This comparison showed that the distinct peaks that represented ethanol detected at approximately 3300 cm^{-1} and water at 1640 cm^{-1} reduced in intensity for the cured treated cotton yarn, compared to the dried treated cotton yarn. This demonstrated that at the heating stages of drying and curing (70°C for 5 minutes and cured at 120°C for 20 minutes), there was further removal of water and solvent as the coating was dried and cured. It was also seen that peaks representing the $-CH_2$ and $-CH_3$ groups became more distinct after curing. This was similar to what was observed for the sol-gel coating as discussed in

Section 6.4.3.2. This indicated that more of the silanes could be detected as the solvent and water were removed. Peak at 1240 cm^{-1}, associated with the epoxide, indicated that not all epoxy groups in the coating were involved in cross-linking between the sol-gel coating and the fibre at the drying stage. After curing, this peak reduced, indicating epoxy ring opening and cross-linking reactions between the sol-gel coating and the cotton fibre.

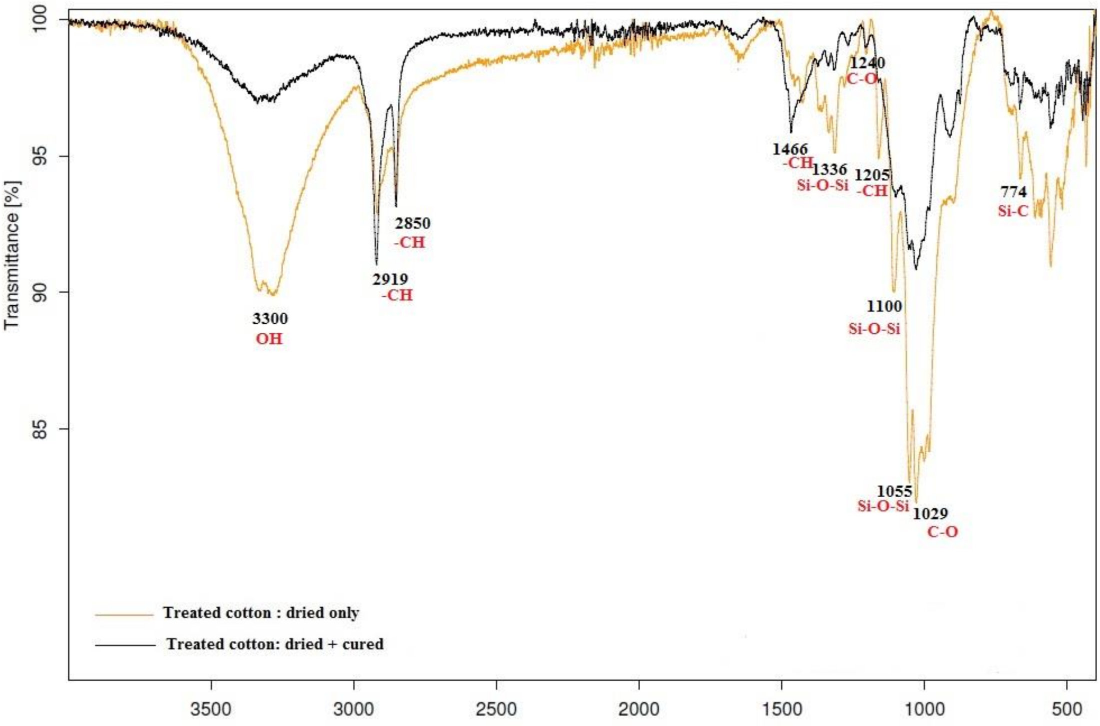


Figure 6.20 Comparisons of FT-IR spectra of sol-gel treated cotton yarns after dry and cure stages

This demonstrated that curing allowed further cross-linking through epoxide ring opening and associated reactions, which would have contributed to the durability of the sol-gel coating discussed in Chapter 7. Comparisons were made between untreated cotton and the treated cotton samples to demonstrated regions were overlay would occur if the cotton was not used as the background (Figure 6.21). it can be seen that peaks for Si-O-Si linkages fell within the regions were most peak were detected on untreated cotton.

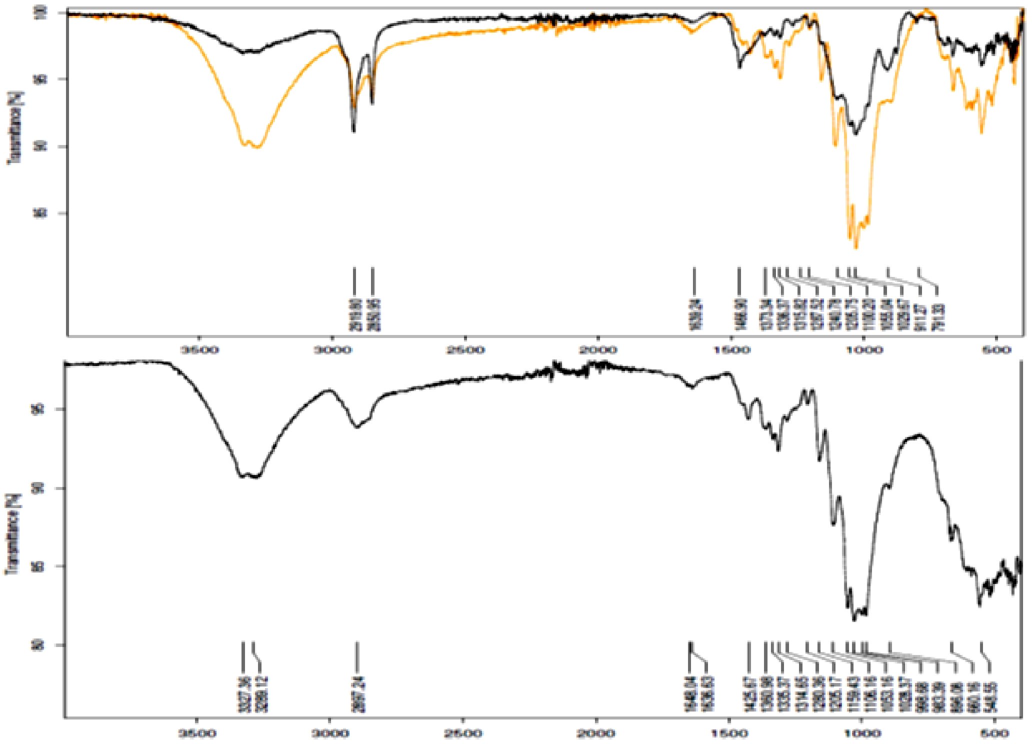


Figure 6.21 Comparison between spectra of dried and cured treated cotton yarns (top) and untreated cotton (bottom)

6.4.3.4 ATR / FT-IR analysis of treated cotton fabric yarns

Further comparisons were made between dried + cured sol-gel film and dried + cured treated cotton fabric yarn samples. Results obtained were illustrated in Figure 6.22. Results in Figure 6.22 demonstrated the increase in peak intensities for the sol-gel film, when compared to the spectra obtained for sol-gel treated cotton fabric. This was because less sol-gel coating was applied on the fabric sample (7% weight gain) while the sol-gel film, in comparison, was more concentrated at 100% coating. More Si-O-Si bonds were detected on the surface of treated cotton yarn samples than the sol-gel film. Although the sol-gel film was of a higher concentration that sol-gel on the treated cotton, these higher intensities were only on a few peak positions. When compared to spectra of the treated cotton fabric yarn, more Si-O-Si bond are detected. This suggested that these Si-O-Si bonds could be as a result of bonding between cotton fabric and sol-gel coating.

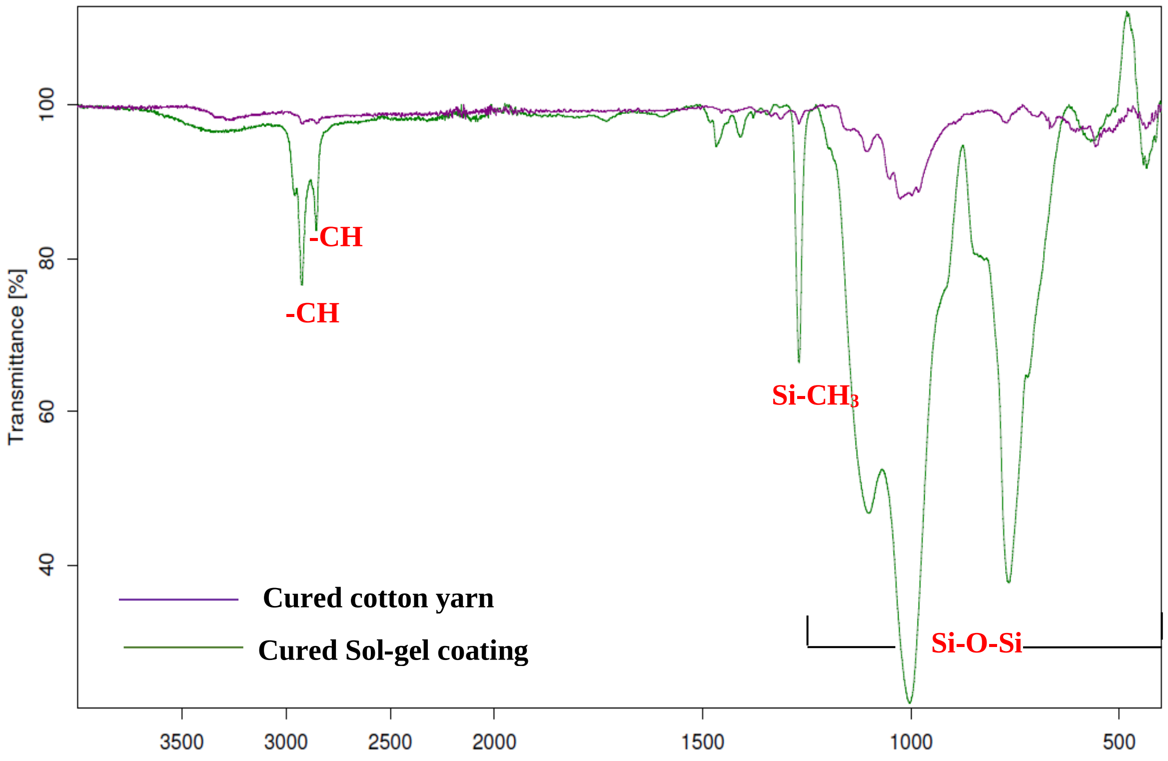


Figure 6.22 Comparison between cured treated cotton yarn and cured sol-gel film

6.4.4 Moisture management analysis of sol-gel treated knitted cotton

Moisture management can be defined as the controlled movement of water vapour and liquid from the skin surface to the atmosphere through the fabric. It involves the ability of clothing to maintain the state of comfort by creating a balance between the body's ability to evaporate perspiration and the tranfer of the moisture through the fabric (Chinta and Gujar, 2013). The measure of moisture management has become a key performance criteria for apparel clothing because it evaluates the comfort level of fabrics. "Consumers prefer the comfort and softness of cotton over synthetic fibres; however cotton's propensity to absorb moisture exceptionally well can often be a negative in performance apparel. Now with the development of moisture management technologies for cotton, consumers can enjoy the fast-drying and moisture-wicking performance of synthetic fabrics but in the comfort and softness of natural cotton." The development of Cotton Incorporated's TransDRY technology has allowed the treated cotton fabric to mimic lower absorbent capacities that would be likened to synthetic fabrics such as nylon and polyester (Cotton Incorporated, 2014). It is the fabric’s ability to manage the movement of moisture that improves its comfort.

The AATCC Moisture Management test method (AATCC 195-2011) works on the following principle; the fabric specimen is placed between upper and lower electrical sensors with seven concentric pins that measure the electrical conductivity changes, with the aid of a test solution. This solution is placed on the centre of the top surface and the transfer of this liquid observed. The test method highlighted that this “test solution is free to move in three directions: radial spreading on the top surface, movement through the specimen from top surface to the bottom surface, and radial spreading on the bottom surface of the specimen. During the test, changes in electrical resistance of specimen are measured and recorded. The electrical resistance readings are used to calculate fabric liquid moisture content changes that quantify dynamic liquid moisture transport behaviours in multiple directions of the specimen.

The summary of the measured results used to grade the liquid moisture management properties of a fabric by using predetermined indices.” The moisture management property of the treated cotton fabric was determined by the collaborative partners INOTEX. This investigation was beneficial as it provided the opportunity to discover any additional properties that may have been added as a result of sol-gel treatment. The measure of a textile’s moisture management considers several factors that use a grading system as shown in Table 6.1. The indices observed are the one-way transport and overall moisture management index. The One-way transport index is the difference between the cumulative moisture content of the top and bottom surfaces. The overall moisture management index sum of the bottom absorption rate, one-way transport index and drying speed of the bottom surface (Achour et al., 2015). Moisture management results for treated cotton samples are shown in Figures 6.23 - 6.25.

Table 6.1 Moisture management indices used to grade samples tested (table table as described in Journal by Baltusnikaite et al., 2014)

Index		**GRADING**					
		Definition	**1**	**2**	**3**	**4**	**5**
Wetting time	**Top**	The time (in seconds) when the top or bottom surfaces begin to wet after test has started.	≥120 no wetting	20-119 Slow	5-19 Medium	2-5 Fast	<2 Very fast
	Bottom		≥120 no wetting	20-119 Slow	5-19 Medium	2-5 Fast	<2 Very fast
Absorption rate	**Top**	The average speed of liquid moisture absorption during the initial change of water content during testing	0-10 Very slow	10-30 Slow	30-50 Medium	50-100 Fast	>100 Very fast
	Bottom		0-10 Very slow	10-30 Slow	30-50 Medium	50-100 Fast	>100 Very fast
Max. wetted radius	**Top**	The greatest ring radius of wetted area measured	0 -7 no wetting	7-12 Small	12-17 Medium	17-22 Large	>22 Very large
	Bottom		0 -7 no wetting	7-12 Small	12-17 Medium	17-22 Large	>22 Very large
Spreading speed	**Top**	The accumulated rate of surface wetting from centre to max. wetted radius	0-1 Very slow	1-2 Slow	2-3 Medium	3-4 Fast	>4 Very Fast
	Bottom		0-1 Very slow	1-2 Slow	2-3 Medium	3-4 Fast	>4 Very Fast
One- way transport index		Difference in liquid moisture content between top and bottom	<-50 Poor	-50-100 Fair	100-200 Good	200-400 Very good	>400 Excellent
Overall moisture management		Overall capability of test samples to manage transport of liquid moisture	0-0.2 Poor	0.2-0.4 Fair	0.4-0.6 Good	0.6-0.8 Very good	>0.8 Excellent

The control cotton fabric (Figure 6.23) had a good absorption rate and wetted time for both the top and the bottom surfaces of the tested sample. The tested sample also demonstrated good spreading speed and a large maximum wetted radius. These results showed that cotton was highly absorbent and had high liquid moisture retention. A very low one-way transport index and overall moisture management was recorded. When compared to the treated cotton samples, different behavioural patterns of the solution were seen. With reference to Figure 6.24, treated cotton, padded at pad pressure of 15 kg/cm, had good wetting time and very good absorption rate for the top surface but the bottom surface had slow wetting and achieved medium absorption rate. The spreading speed and maximum radius indices for both the top and bottom surfaces recorded as poor; leading to poor one-way transport and overall moisture management.

For treated cotton samples padded twice at 45 kg/cm (Figure 6.25), the top surface showed fairly poor wetting rate; however the absorption rate was good. The bottom surface had a better wetting time and even faster absorption rate. As seen for treated samples padded at 15 kg/cm, the spreading speed and the maximum radius were poor. The one-way transport was however good and moisture management considered fairly good. A better moisture management was achieved for the treated samples due to certain factors. Though the untreated cotton had high absorption, wetting rates and maximum radius, the very small difference in the water content between the top and the bottom surface demonstrated that the synthetic sweat (test solution) was not transported effectively.

The top surface represents the side of the fabric surface that would be in touch with the skin while the bottom signifies the fabric surface exposed to the environment. High wetting rates and radius of the top surface would lead to wet skin as much sweat would be present on the surface of the fabric in contact with the skin as that exposed to the environment. Though the larger wetted radius would promote high levels of evaporation, the ability of the top surface to retain water would cause sweat build up cause the fabric to become wet, which would cause fabric sticking to the skin, causing discomfort. With reference to the one–way transport index for treated samples in Figures 6.24 and 6.25, it was observed that there was a larger difference in the water content for the top and the bottom surfaces; when compared to the control sample. The top surface for treated samples padded at 15 kg/cm had higher water content than treated samples padded at 45 kg/cm. A higher water content on the top surface indicated water accumulation on the top surface before its transport through the fabric. This fabric was described as water repellent. Water repellence has been defined as the ability of a fabric material to withstand wetting or penetration by water under test conditions (Kissa, 2001). Water repellent fabric are however permeable to water vapour; which would explain the ability of the treated cotton fabric to allow some transport of liquid moisture through the fabric.

Moisture is generally transported through capillary action or wicking. In textiles, the spaces between the fibres effectively form tubes, which act as capillaries, and transport the liquid away from the skin surface (Nemcokova et al., 2015). The limited ability of the test solution to travel through the fabric as seen in the sample padded at 15 kg/cm, which would lead to the build-up of sweat between the skin and the fabric; causing some discomfort. Treated samples padded at 45 kg/cm had higher water content on the bottom surface. This demonstrated that the test solution accumulated at the bottom surface. This indicated efficient transport from source of sweat to outer surface in contact with air i.e. environment. This surface would allow evaporation of the transported liquid / sweat.

A good one-way transport indicates that sweat can transported quickly and easily from next to skin to the outer surface to keep the skin dry. It was therefore concluded that the treated samples padded at the higher pressure of 45 kg/cm demonstrated better moisture management properties as the test solution was transported better from top to bottom surface, where the sensors were placed, with minimal wetting. From the results obtained, the control cotton fabric had high levels of absorbency but also high water retention. High retention leads to heavier fabric that then affects the comfort of the fabric (Nemcokova et al., 2015). Better moisture management properties was measured for treated cotton fabric samples padded at the high pad pressure of 45 kg/cm due to wicking action with minimal water retention.

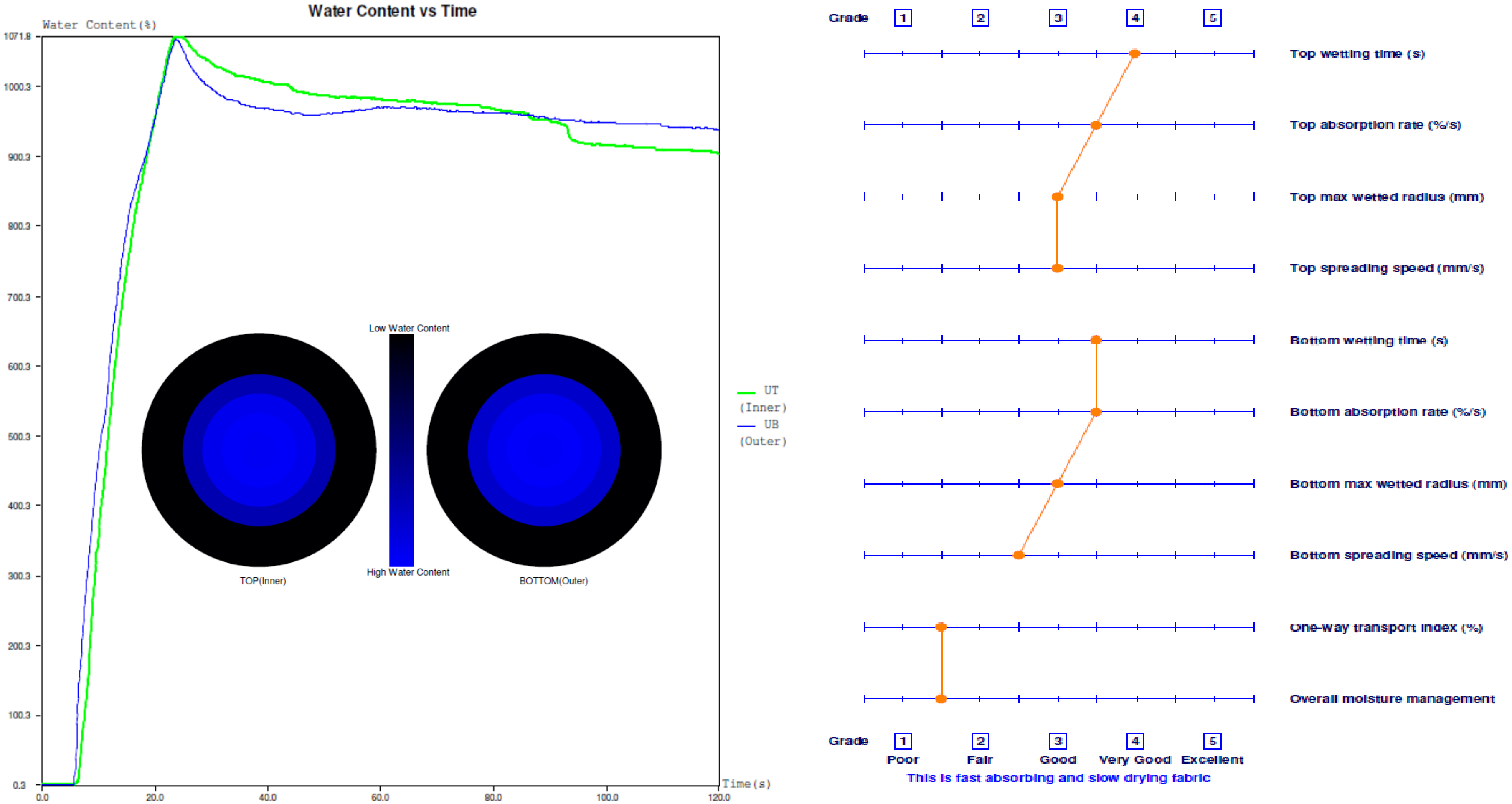


Figure 6.23 Moisture management measurements of control knitted cotton fabric

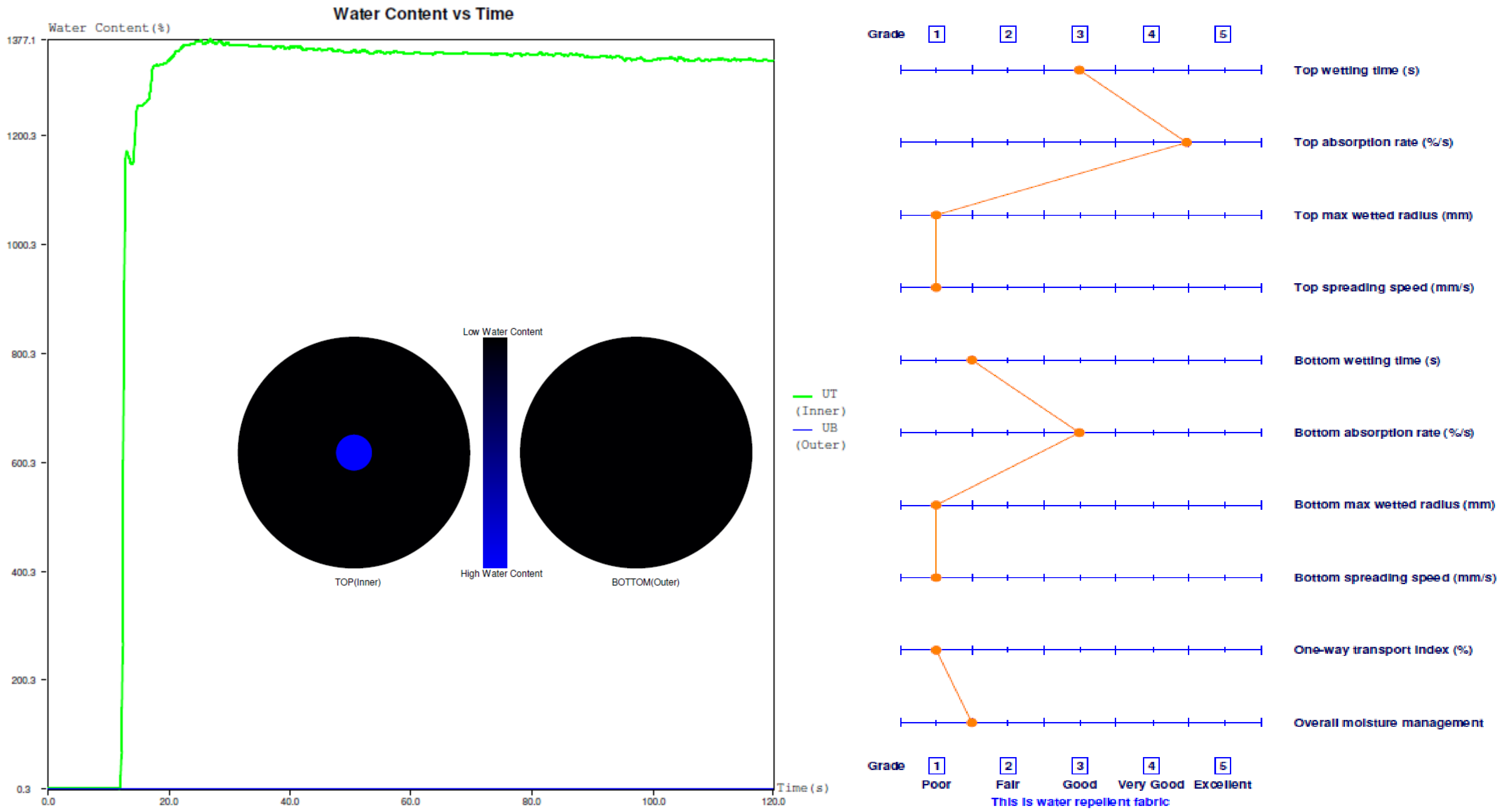


Figure 6.24 Moisture management measurements of treated knitted cotton fabric padded once at 15 kg/cm

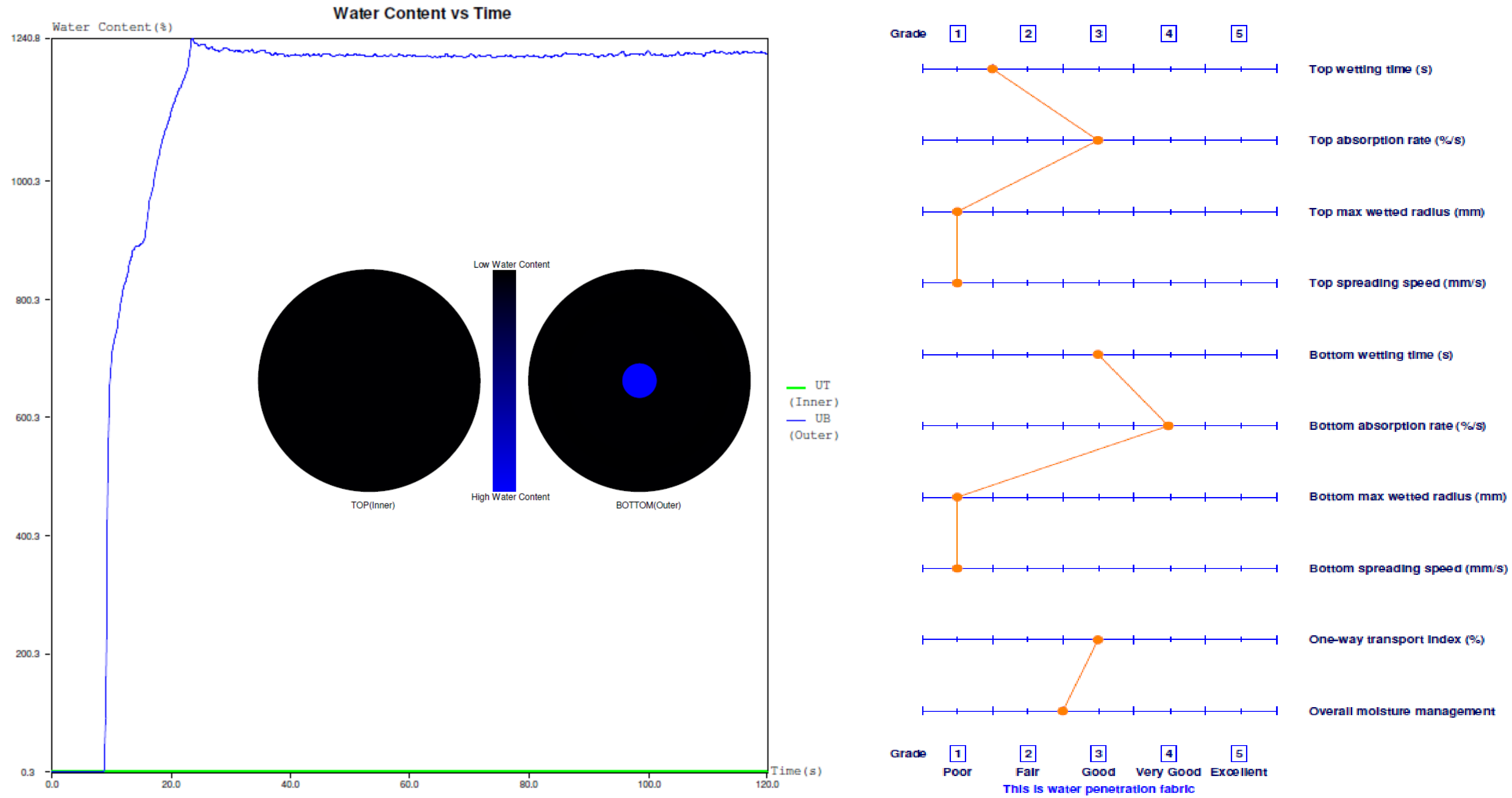


Figure 6.25 Moisture management measurements of treated knitted cotton fabric padded twice at 45 kg/cm

6.5 Conclusions

SEM analysis was able to demonstrate that through the application process developed, fibres in yarns were coated individually with sol-gel coating rather than cross-linked between neighbouring fibres; this was why the treated cotton fabrics maintained their soft handle. The sol-gel film developed also assumed a porous nature that would have contributed to the moisture management measured for the treated cotton fabric. The moisture management test demonstrated that cotton fabrics were highly absorbent and had high liquid and moisture retention, resulting in poor moisture management. The sol-gel treated cotton fabrics padded twice at the higher pressure of 45 kg/cm had a good one-way transport property for moisture or sweat passing through the gaps between the knitting structure of cotton fabric rather than retention of moisture. Therefore, the sol-gel treatment of knitted cotton fabrics improved the moisture management of the cotton fabric. If the treated fabric is used for apparel, the moisture will be easily and quickly transported from next to skin to the outer surface, resulting in comfort for the wearer by keeping the skin dry.

EDX analysis was able to identify the Si element belonging to the sol-gel coating. Analysis of the sol system using ATR / FT-IR technique demonstrated that hydrolysis and condensation reactions occurred simultaneously within 1 hour of synthesis as Si-OH and Si-O-Si bonds were detected. Further analysis of drying, dried and cured sol-gel films showed further condensation reactions within the film and analysis of dried and dried + cured treated cotton demonstrated the further condensation reactions of sol with fibres as well as epoxide reactions to demonstrate cross-linking with the fabric. Further methods to distinguish any changes during the different stages of sol-gel synthesis and application on the fabric could be used. Analytical methods such as Si NMR analysis could be used to determine the reaction kinetics during sol synthesis. This method of analysis would be able to show the chemical changes in the sol and provide further understand of the chemistry of sol synthesis and highlight the reaction kinetics of the hydrolysis and condensation reactions that occur on the sol solution and also kinetics during fabric treatment.

CHAPTER 7:

DURABILITY OF HYDROPHOBIC AND ANTIBACTERIAL PROPERTIES OF SOL-GEL TREATED COTTON FABRIC TO LAUNDERING

7.1 Introduction

The durability of a textile material determines the longevity of its intended end-use. The popularity of durable products has increased over the years due to positive impacts seen in textile industries and the environment. Textile materials with high production costs benefit from durable properties because this characteristic enables such materials to be cost effective due to offsetting of extra production costs by their longer life span. The efficiency of a product in its area of application contributes to the global objective of improving manufactured materials in order to reduce negative impacts on the environment.

One of the objectives for this research included the production of sol-gel treated cotton fabric samples that exhibited good durability of its functional properties. Laundering was one of the means of assessing durability because generally, laundering of textiles is required in most areas of their application. To demonstrate the effect of laundering on properties of the treated cotton fabric, the treated fabric samples were washed repeatedly and any changes observed and evaluated.

Measurements of water rating numbers (WRN) and water contact angles (WCA) to test the hydrophobic property and antibacterial testing to determine antibacterial activity were undertaken to demonstrate whether these properties remained on the washed treated cotton samples. For closer analysis, evaluations using SEM-EDX and ATR / FT-IR were used to determine whether sol-gel coatings applied on cotton fabric samples were present after laundering. The mechanical properties of laundered treated samples were evaluated using abrasion testing. This chapter will discuss these results and show whether durability to laundering was achieved through the application of sol-gel containing the cross-linking epoxy GLYMO, and using the 4 hour treatment time.

7.2 Materials and Equipment

7.2.1 Materials

Control cotton fabric

Knitted interlock fabric (scoured and bleached) consisting of 100% cotton, supplied by Vertical Garments Ltd (Leicester, UK). This sample was used as the control fabric and referred to as control (bleached) cotton.

Treated cotton fabric

Control (bleached) cotton was treated with sols synthesised as described in Section 3.3.2 using the base formulation containing silanes of MTES: GLYMO: OTES: QUAT in their ratio of 300: 5: 10: 5 mL. These silanes were added to 300 mL of 50% v/v ethanol solution adjusted to pH 3.2.

Sols were also synthesised using the base formulation with half the amount of GLYMO (2.5mL). Application of sols onto cotton fabric were as described in Section 3.3.3. Two different pad pressures of 15 kg/cm at 1 m^2/min (once) and 45 kg/cm at 1 m^2/min (twice), respectively, were used and their effect on the durability of the applied sol-gel coating on the cotton fabric were investigated.

Washing detergent

ECE non-phosphate reference detergent A (SDC) was used to carry out repeat washing of the control (bleached) cotton and the treated cotton samples.

7.3 Experimental

7.3.1 Washing procedure

For each wash cycle, 5 g/L of standard SDC ECE non-phosphate detergent A, in deionised water was prepared as washing liquor. A 50:1 liquor to goods ratio was used for washing the control and treated cotton fabric samples. Fabric samples were agitated in an Ahiba Nuance at 40 rpm for 30 minutes at a temperature of 40°C. On completion of a wash cycle, the fabric was rinsed thoroughly with hot and cold running tap water. The rinsed fabric samples were then hydroextracted and oven dried at 50°C for 4 hours. For repeat washing, cotton samples (control and treated) were washed using the procedure above. Water rating numbers (WRN) and water contact angles (WCA) were measured after each wash when the sample was dry. In order to investigate the effect of detergent, samples were also washed in deionised water without detergent at the 50:1 liquor to goods ratio for 30 minutes at 40°C.

7.3.2 Analytical and mechanical testing procedures

SEM-EDX and ATR / FT-IR analyses were carried out using methods as described in Section 6.3.2. Water Contact Angles (WCA) and Water Rating Numbers (WRN) were measured using methods as described in Section 3.3.4.1 and Section 3.3.4.2, respectively. Antibacterial properties were determined using the method as described in Section 4.3 and abrasion testing was carried out as described in Section 5.3.1.

7.4 Results and discussion

7.4.1 Durability to repeat washing

Cotton samples treated with sol synthesised using the base formulation were laundered up to 10 times, using the method described in Section 7.3.1. The water rating numbers (WRN) were measured after each wash to monitor and observe any changes in hydrophobic properties of the treated cotton fabric samples. Figure 7.1 showed the water rating numbers of the treated cotton fabric samples after each wash in ECE detergent solution.

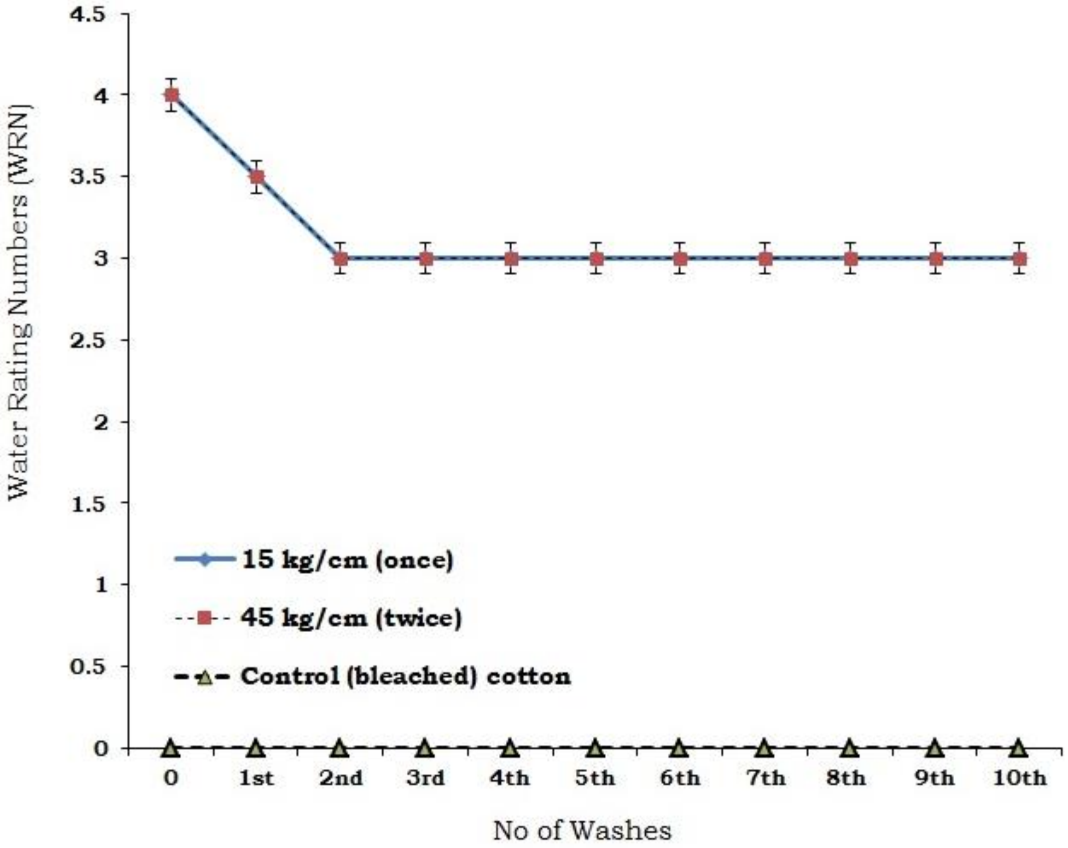
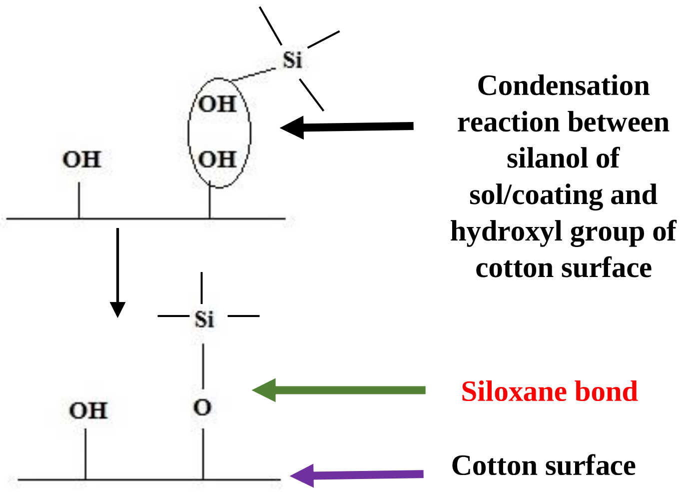


Figure 7.1 Effect of multiple washes with SDC ECE detergent A on the WRN values of treated and untreated cotton fabric samples

Cotton samples treated with sol synthesised using the base formulation and padded at the two levels of pad pressure showed a similar trend. After the 1st wash, the WRN value dropped from 4 to 3.5. After the second wash, the value dropped further to a WRN value of 3 which remained for further 8 washes. The initial drop in WRN value from 4 to 3 might be due to the removal of any loosely bound sol-gel particles and coating present on the surface of the treated cotton fabric. Once loosely bound particles were removed during the first two washes, the maintenance of a WRN value of 3 from the 2nd to the 10th wash demonstrated adhesion of sol-gel coating through covalent bonding. This type of bonding could have formed during the drying and curing stages of sol application (Scheme 7.1).



Scheme 7.1 Schematic demonstration of condensation reactions between silanols found in the sol-gel coating and the OH groups found of the cotton fabric to form covalent bonding of the siloxane bond

The incorporation of an alkoxysilane with an epoxy group such as GLYMO in the sol, could promote more effective bonding between the coating and the cotton fabric through epoxy ring opening and its associated reactions with the hydroxyl groups on the cotton surface (Torry et al., 2006). Further investigations were carried out to investigate whether the durable hydrophobic property was as a result of either the GLYMO in the sol solution, or the 4 hour treatment time or both the GLYMO and the 4 hour treatment time combined. Sols without the cross-linking silane GLYMO were synthesised and applied onto cotton fabric as described in Section 7.2.1 and illustrated in Figure 7.2. Samples were padded twice at 45 kg/cm as this pressure retained fabric handle and provided good moisture management.

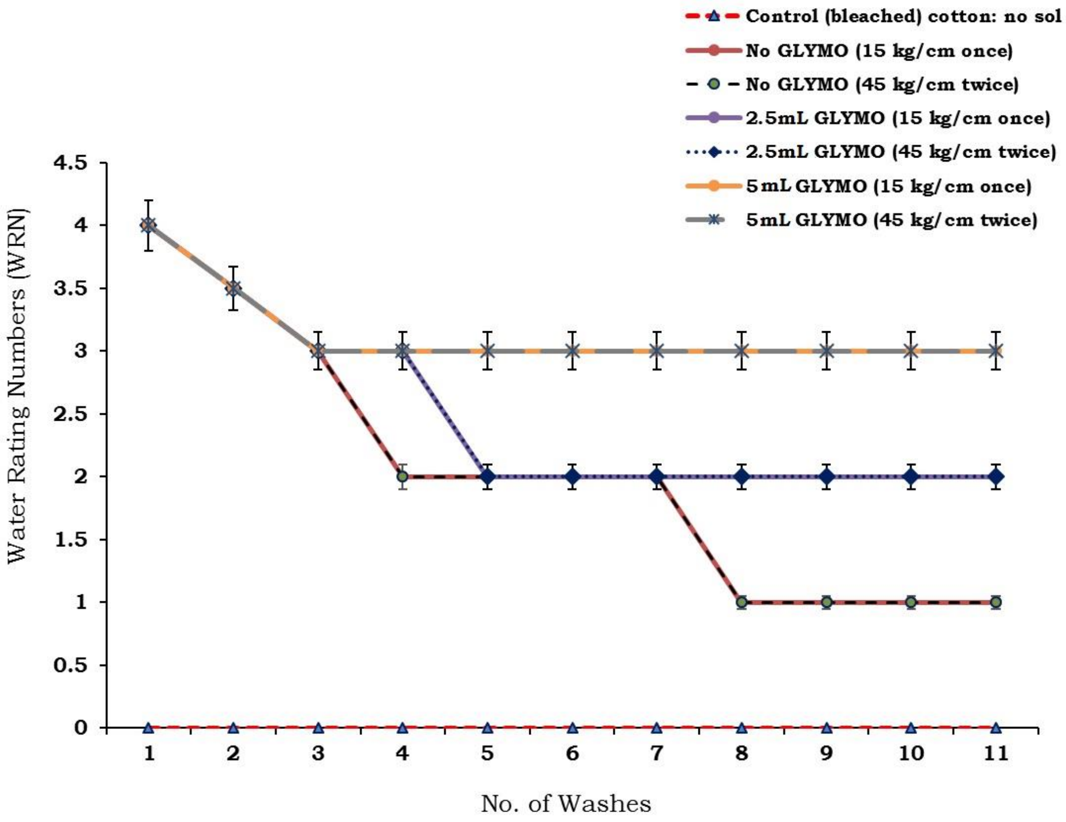


Figure 7.2 Effect of multiple washes with SDC ECE detergent A on the WRN values of treated cotton fabric samples with sols containing varying amounts of GLYMO

Cotton samples treated with sols containing 5 mL and 2.5 mL GLYMO achieved and maintained WRN values of 3 and 2, respectively, which were higher than the WRN value of 1 that remained after 10 washes for cotton samples treated with sols without GLYMO. This indicated the cross-linking ability of the epoxy group on GLYMO alkoxysilane and its association with the durable hydrophobic property. The epoxy group on the GLYMO silane (Figure 7.3) exhibits cross-linking properties due to adhesion promoting properties of the epoxy functional group (Gelest Inc., 2006; Kumar, 2015).

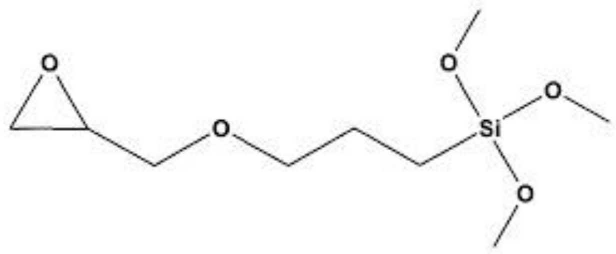


Figure 7.3 Schematic diagram of GLYMO silane used for cross-linking in the sol applied on cotton fabric

The epoxy group on the GLYMO silane enables cross-linking not just between the coating and substrate surfaces, but also within the sol-gel coating network. The GLYMO alkoxysilane has been reported to improve the strength of coatings between surfaces and coating networks due to this cross-linking nature. This feature has been confirmed through the study of changes in the glass transition temperatures (Tg) of films formed using the sol solution containing GLYMO and its effect on coating strength (Carey, 2001). This cross-linking ability of the GLYMO silane is achieved through the ring opening of the epoxy group. The rate of ring opening of the epoxy is initiated and influenced by the solution pH. At different pH values, especially lower than pH values of 4, higher rates of epoxy ring openings occur through the nucleophilic reactions. Once the ring is opened and hydroxyl groups are formed from the epoxy, polymerisation reactions occur between proximal hydroxyl groups.

Cross-linking between GLYMO silanes and the sol network occurs through reactions of the hydroxyl groups on opened epoxy groups with neighbouring silanol groups during sol synthesis. The presence of the reactive hydroxyl groups in the sol and also sol-gel coating allows further reactions with the hydroxyl groups of cellulose on the cotton fibres under the right conditions (Vengadaesvaran et al., 2014; UNEP PUBLICATIONS, 2004), which improve the durability properties of the sol-gel coating applied on the cotton fabric.

To investigate the influence of treatment time, different durations of treatment time were used to observe their influence on the durability of the sol-gel coating applied onto cotton fabric samples. Cotton fabric samples were either soaked for 30 seconds, treated for 30 minutes, 1 hour, 2 hours and 4 hours in a synthesised sol solution using the base formulation and results shown in Figure 7.4.

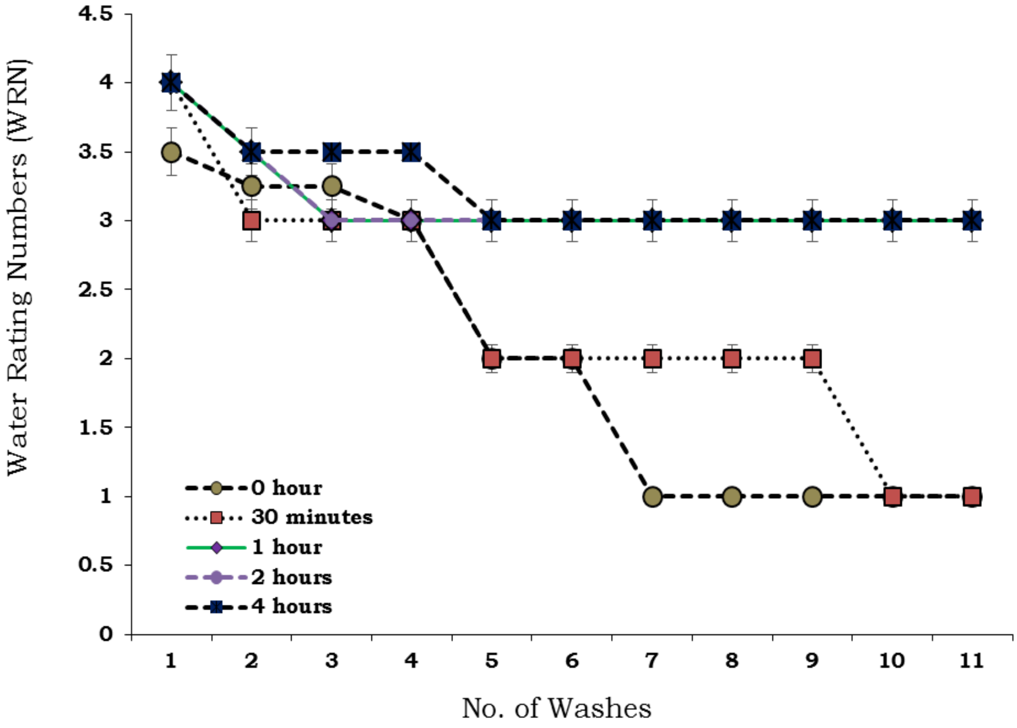


Figure 7.4 Wash fastness for cotton samples treated at different treatment times and padded twice at 45 kg/cm

Cotton samples soaked for 30 seconds achieved WRN values of 3 which were slightly lower than the WRN values of 4 measured for cotton samples that were treated over a longer period of time. With repeat washing, the WRN values decreased with an increase in wash cycles and different trends observed. Cotton samples treated for 1, 2 and 4 hours, respectively, maintained a higher WRN value of 3 while samples that were soaked and treated for 30 minutes demonstrated a reduction with WRN values eventually falling to 1, after maintaining at a WRN value of 2 for approximately 4 washes.

These results demonstrated that sufficient bonding could not be achieved through the 30 seconds soak in sol solution and thereby identified the benefit of continued treatment of cotton fabric in sol solution for a prolonged period of time. The treatment time and the addition of the cross-linker were therefore beneficial in producing durable hydrophobic properties for treated cotton samples as higher WRN values were achieved for samples treated over 1 hour as opposed to that of cotton samples soaked to simulate the dip-pad-dry method. Further testing could be carried out for optimisation of the sol-gel application process to provide efficient methods that compliment industrial production processes and associated lines by reducing treatment time. As the WRN values were indicative in their hydrophobicity, water contact angles (WCA) were measured to quantify the differences in hydrophobicity. Water contact angles (WCA) of sol-gel treated cotton samples before and after washing were measured, Figure 7.5 shows the WCA values of cotton fabric samples treated with sol formulation containing 5 mL and 2.5 mL of GLMYO, respectively, before and after 10 washes.

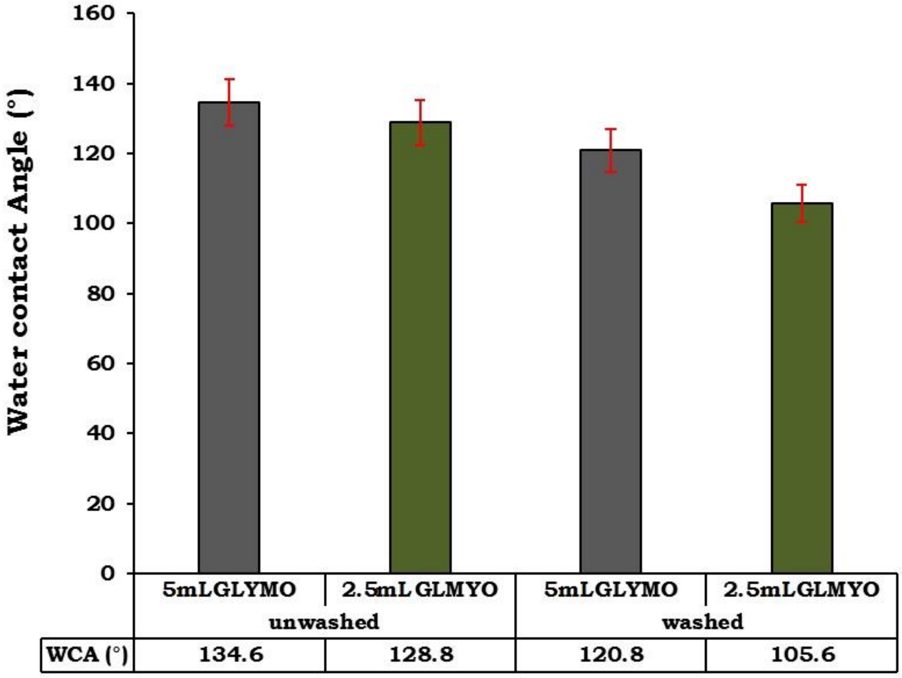


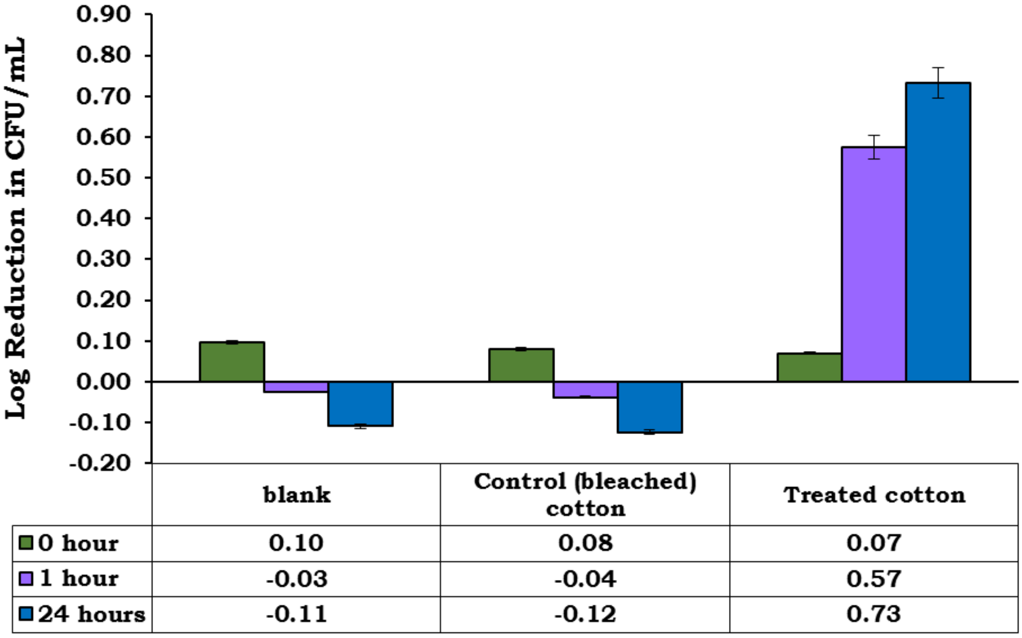
Figure 7.5 WCA values of cotton fabric samples treated with sol formulation containing 5 mL and 2.5 mL of GLMYO, respectively, before and after 10 washes

It was observed that WCA values reduced for the cotton samples treated with sol containing 5 mL and 2.5 mL amount of GLYMO from 134° to 120° and 128° to 105°, respectively, after 10 washes. The decrease in WCA values was an indication that the loosely bound sol-gel coating was removed with washing, however WCA values obtained after repeat washes were above 100° which indicated retained hydrophobic properties and demonstrated that the sol-gel coating still remained on the cotton surface even after 10 consecutive washes. These results also indicated that covalent bonding occurred between the sol and the cotton fabric that would promote adhesion of the sol-gel coating.

The amount of cross-linker used did contribute to the durability of the sol-gel coating applied on the cotton fabric samples. Further optimisation could be carried out to determine the optimal amount of GLYMO that would be needed for better durability of the applied sol-gel coating applied to maintain high WRN and WCA values even with repeated wash cycles.

7.4.2. Antibacterial property

One of the main objectives set for this research was to produce a durable dual-functional coating on knitted cotton fabric. To determine the durability of the antibacterial property of the treated cotton samples to wash, testing was carried out as described in Section 4.3. Because cotton fabric samples treated with sol synthesised using the base formulation and padded twice at 45 kg/cm maintained good fabric handle, hydrophobic property and burst strength, these samples were tested for their durability of antibacterial activity after 10 wash cycles and results shown in Figure 7.6.

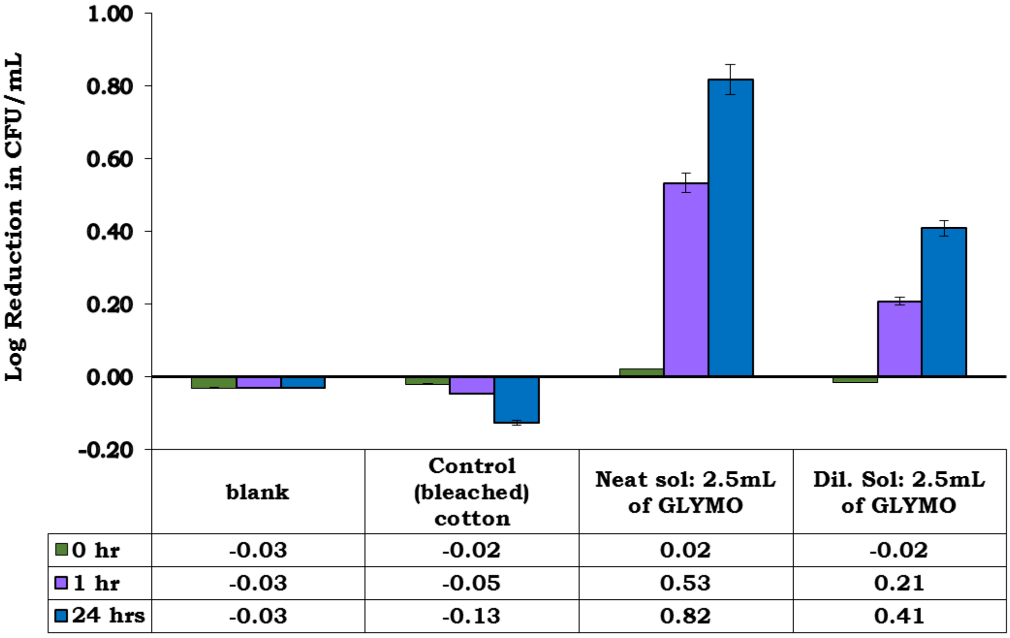


	blank	Control (bleached) cotton	Treated cotton
🟩 0 hour	0.10	0.08	0.07
🟪 1 hour	-0.03	-0.04	0.57
🟦 24 hours	-0.11	-0.12	0.73

Figure 7.6 Log reductions in CFU/mL of washed cotton fabric samples treated with sol synthesised using the base formulation with 5 mL of GLYMO against *S.aureus* bacterium. Samples after the 10th wash cycle

It was found that after 10 repeat wash cycles, the treated cotton fabric had antibacterial activity of a log reduction in CFU/mL of 0.57 and 0.73 after 1 hour and 24 hours incubation, respectively. These log reductions illustrated a decrease in activity when compared to the log reductions in CFU/mL of approximately 4 and 3 after 1 hour and 24 hours incubation for unwashed treated cotton samples. The higher log reduction in CFU/mL for the unwashed cotton fabric samples could be due to loosely bound coating that may have dislodged from the surface during continued agitation, which would provide increased exposure of the positive charge of the QUAT silane to the bacterium in the solution. Increased contact with the nitrogen charge atom on the QUAT would increase its antibacterial effect. The reduced activity observed suggested that though QUAT was present on the surface of the treated cotton, due to its inability to have sufficient contact with the inoculated solution, there may have been a reduction in its mode of action against the bacterium. This is because QUAT has been reported to require contact time of roughly 10 minutes for effective antibacterial properties and this may have contributed to its performance against the bacterium, especially with the continued movement of the inoculated solution, as this may have varied contact time and thereby reduced activity (Snow, 2012). With reference to the results in Figure 7.6, it would appear that the activity of the sol-gel coating was affected by washing. It should be stated that the sol-gel coating was still present on the surface as hydrophobic properties could still be detected even after laundering. Due to these conflicting observations, further investigations were carried out to determine the cause of reduced antibacterial activity and discussed in Section 7.4.3.1.

Antibacterial testing was also carried out on washed cotton fabrics treated with sol synthesised using base formulation containing 2.5 mL of GLYMO cross-linker. This was carried out to determine the antibacterial activity on cotton samples treated with sols containing reduced amount of GLYMO. Results obtained are shown in Figure 7.7.



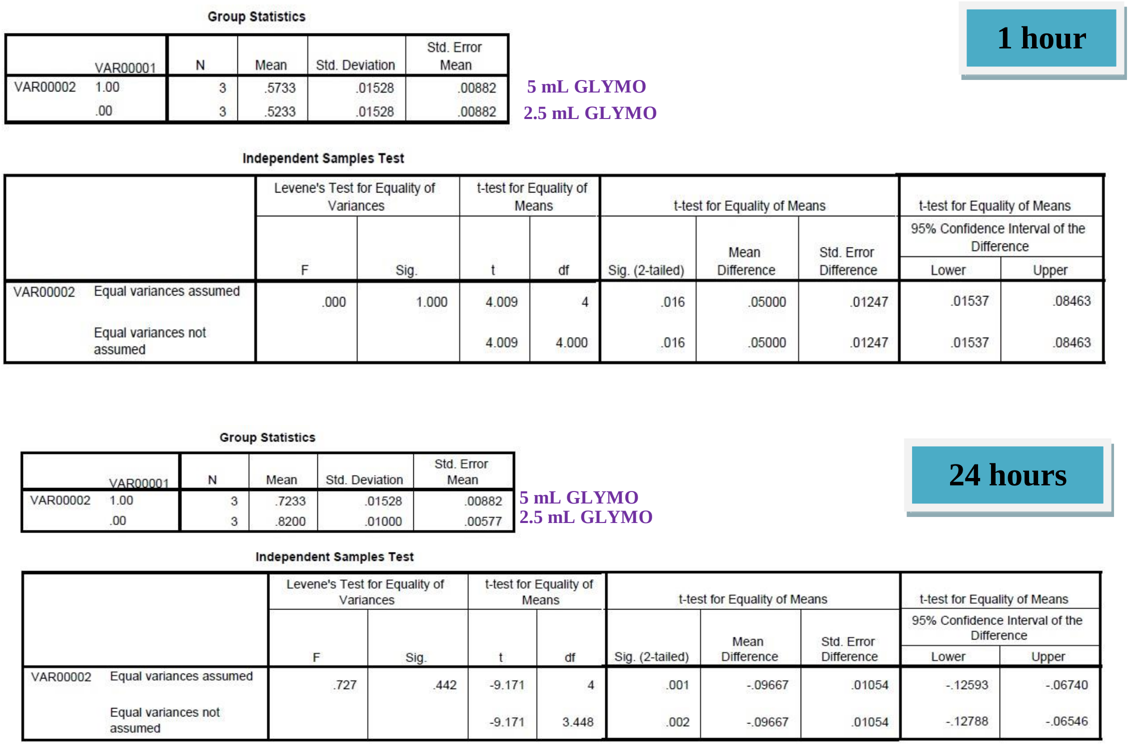
	blank	Control (bleached) cotton	Neat sol: 2.5mL of GLYMO	Dil. Sol: 2.5mL of GLYMO
🟩 0 hr	-0.03	-0.02	0.02	-0.02
🟪 1 hr	-0.03	-0.05	0.53	0.21
🟦 24 hrs	-0.03	-0.13	0.82	0.41

Figure 7.7 Log reduction of washed cotton samples treated with neat and dilute sol containing 2.5 mL of GLYMO against *S.aureus* bacterium after 10 washes

To compare log reduction values for cotton samples treated with sol containing 2.5 mL of GLYMO shown in Figure 7.7 (neat sol results) and log reduction values for cotton samples treated with sol containing 5 mL GLYMO shown in Figure 7.6, an independent *t* test were carried out using IBM SPSS statistics 21 licenced software provided by De Montfort University, to find any significant difference between these values. The independent *t* tests were carried on the values obtained after 1 hour and 24 hours incubation time.

The Levene's test used in SPSS software is similar to the *t* tests to determine the hypothesis that variances in the two groups are equal i.e. the difference between these two groups equals 0. If the Levene's test is significant at $p \leq 0.05$, this suggests that the assumption has been violated and there is some difference. If the Levene's test is non-significant, i.e. $p > 0.05$, it is assumed that variances are roughly equal and the assumption is tenable. This is labelled as *Sig* on a statistical data table. Once statistical analysis is carried out, this value is used to determine which data row to read on the statistical data table using p values stated above.

With reference to data tables in Figure 7.8, mean log reduction values after 1 hour incubation time achieved a *sig.* value of 1.000. This value was bigger than the p value of 0.05, which indicated that the Levene's test was not significant and variances equal. The same assessment was carried out for mean log reduction values obtained after 24 hours incubation. It was found that the *sig.* value was 0.442, which was also bigger than the p value of 0.05. This also indicated that for the two groups being compared, there was no significant differences in variances.



1 hour

Group Statistics

	VAR00001	N	Mean	Std. Deviation	Std. Error Mean	
VAR00002	1.00	3	.5733	.01528	.00882	5 mL GLYMO
	.00	3	.5233	.01528	.00882	2.5 mL GLYMO

Independent Samples Test

		Levene's Test for Equality of Variances		t-test for Equality of Means		t-test for Equality of Means			t-test for Equality of Means	
									95% Confidence Interval of the Difference	
		F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	Lower	Upper
VAR00002	Equal variances assumed	.000	1.000	4.009	4	.016	.05000	.01247	.01537	.08463
	Equal variances not assumed			4.009	4.000	.016	.05000	.01247	.01537	.08463

24 hours

Group Statistics

	VAR00001	N	Mean	Std. Deviation	Std. Error Mean	
VAR00002	1.00	3	.7233	.01528	.00882	5 mL GLYMO
	.00	3	.8200	.01000	.00577	2.5 mL GLYMO

Independent Samples Test

		Levene's Test for Equality of Variances		t-test for Equality of Means		t-test for Equality of Means			t-test for Equality of Means	
									95% Confidence Interval of the Difference	
		F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	Lower	Upper
VAR00002	Equal variances assumed	.727	.442	-9.171	4	.001	-.09667	.01054	-.12593	-.06740
	Equal variances not assumed			-9.171	3.448	.002	-.09667	.01054	-.12788	-.06546

Figure 7.8 Statistical data of independent *t* tests carried out to compare and determine any differences in log reductions values for cotton samples treated with sols containing 2.5mL and 5 mL GLYMO

With this established i.e. equal variances assumed, the column with *sig (2-tailed)* values was used to determine statistical differences as this value illustrated any differences in the mean, as calculated using the independent *t* test. The *Sig (2-tailed)* value indicates whether the dependent variable, which in this case was the amount of GLYMO in the sol, had a significant effect on the differences between the mean values of the two samples. Mean log reduction after 1 hour and 24 hours incubation were 0.016 and 0.001, respectively. These values were less that the p value of 0.05, which indicated that though at initial comparison, log reduction results for cotton samples treated with neat sols containing 2.5 mL and 5 mL of GLYMO appeared similar, statistically, there is a difference between these log reductions.

For washed cotton samples treated with diluted sol containing 2.5 mL of GLYMO, the activity reduced to 0.21 after 1 hour and 0.41 after 24 hours incubation time, demonstrating that with the reduction in cross-linker, there was a reduction in sol-gel coating adhesion to cotton surface that then influenced its ability to exhibit the antibacterial property. Due to this change in antibacterial activity for the washed treated cotton fabric, the surfaces of the washed cotton samples were analysed using SEM. This technique was used to observe changes on the surface of washed cotton samples and determine whether such changes influenced the hydrophobic and antibacterial properties. Any changes to surface roughness would affect hydrophobicity while the inactivation of the charged nitrogen on the QUAT would affect and render its mode of action as an antibacterial agent, ineffective.

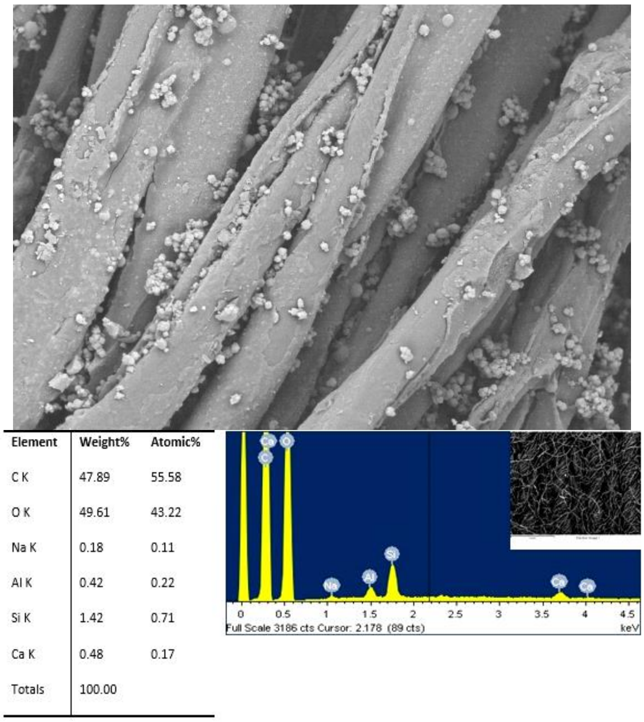
7.4.3 Analytical analysis

7.4.3.1 SEM imaging

SEM and EDX analysis were carried out on treated cotton samples after 10 washes to confirm the presence of the coating after repeat washing. The results are shown in Figure 7.9. It was seen that the sol-gel coating was still present on the surface of the washed treated cotton sample after 10 repeat washes. EDX analysis carried out alongside SEM imaging on the surface of the washed treated cotton fabric detected elements of calcium (Ca), sodium (Na), aluminium (Al), among the expected carbon (C), oxygen (O) and silicon (Si). The additional elements detected suggested that the larger particles that appeared on the surface of washed cotton fibres could be due to residual detergent aggregates. The SDC standard detergent was composed of the following: Alcohol Ethoxylate 5-15% , Antifoam 1-5% , Sodium Carbonate 5-15% , Sodium Dodecyl Benzene Sulphanate 5-15% (surfactant), Sodium Silicate 1-5%.

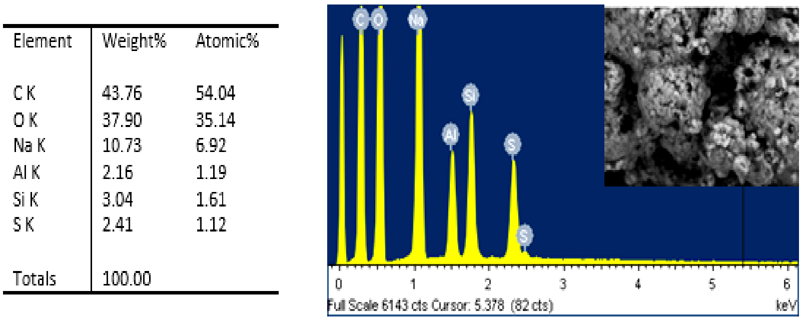
In order to determine whether these particles were aggregates of residual detergent, further EDX analysis was carried out on a detergent particle. It was found that the elemental composition obtained for the particles on the surface of the washed fabric sample were consistent with the EDX spectra of detergent particles as shown in Figure 7.11. The slight difference in EDX spectra between Figures 7.9 and 7.10 were the detected elements of sulphur for detergent and calcium for washed cotton samples.

Calcium would be found in the tap water that was used for the rinsing processes, while the sulphur element was confirmed to be one of the element in the detergent powder composition. The EDX analysis confirmed that detergent particles remained on the surface of the washed fabrics after hot and cold rinses.



Element	Weight%	Atomic%
C K	47.89	55.58
O K	49.61	43.22
Na K	0.18	0.11
Al K	0.42	0.22
Si K	1.42	0.71
Ca K	0.48	0.17
Totals	100.00	

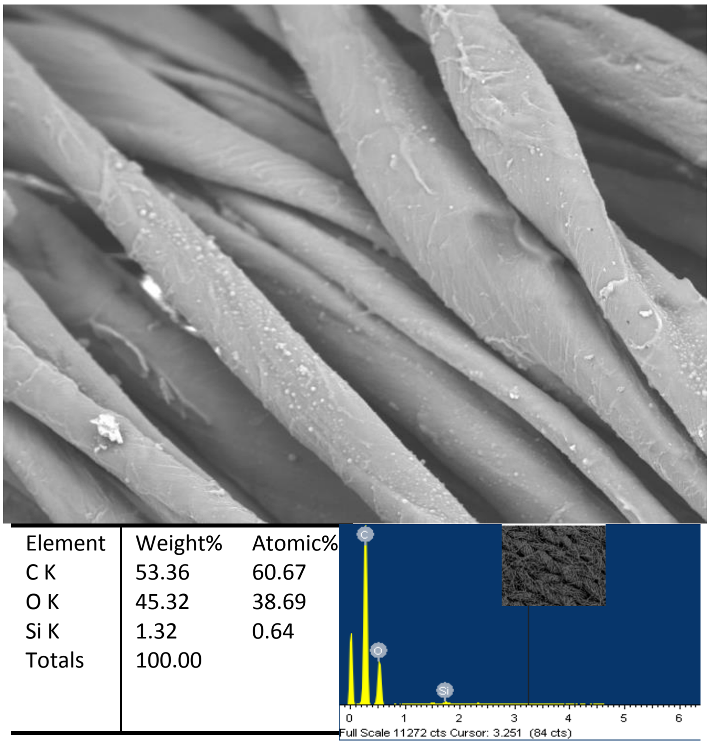
Figure 7.9 SEM image and EDX analysis of washed treated cotton samples showing residual detergent particles deposited on the surface of washed samples after 10 washes



Element	Weight%	Atomic%
C K	43.76	54.04
O K	37.90	35.14
Na K	10.73	6.92
Al K	2.16	1.19
Si K	3.04	1.61
S K	2.41	1.12
Totals	100.00	

Figure 7.10 EDX analysis of the SDC ECE standard detergent particle

The EDX analysis of the washed cotton fabric samples and the detergent particles both detected the silicon element (Figures 7.9 and 7.10). To confirm the presence of silicon on the washed treated samples, further rinses with acetic acid were carried out to remove the residual detergent particles on the washed samples. The acetic acid solution was prepared by adding 25 mL glacial acid into 500 mL deionised water. Liquor to goods ratio of 50:1 was used and samples washed at 70°C at 40 rpm for 30 minutes. The samples were then rinsed with deionised water to remove any residual acetic solution and then dried as per method described in Section 7.3.1. SEM and EDX analysis were carried out and results shown in Figure 7.11. It was found that a 5% v/v acetic acid solution at 70°C was effective in removing the detergent particles.



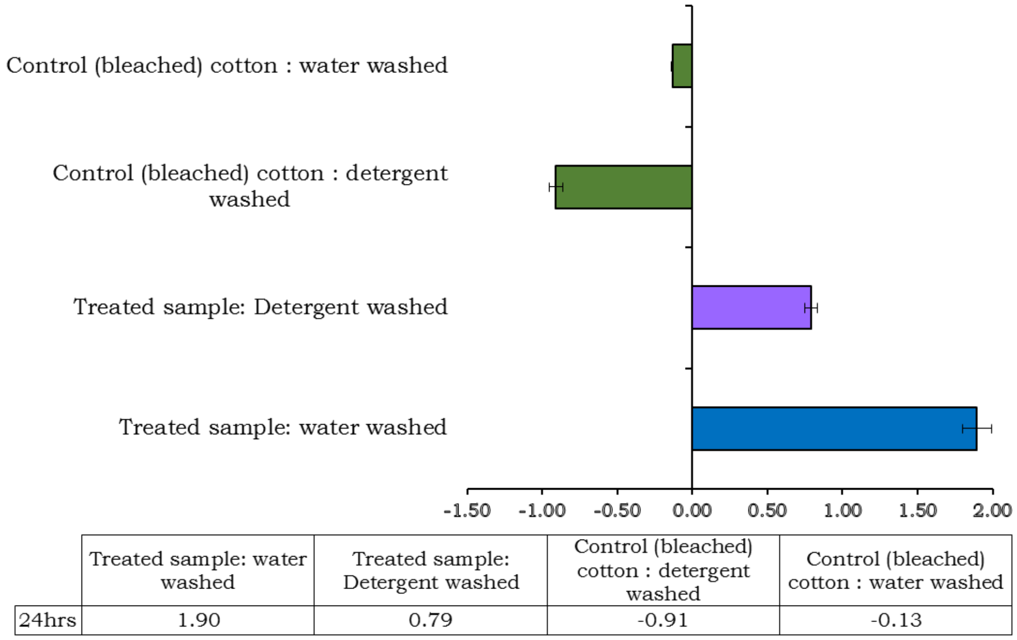
Element	Weight%	Atomic%
C K	53.36	60.67
O K	45.32	38.69
Si K	1.32	0.64
Totals	100.00	

Figure 7.11 SEM and EDX analyses of detergent washed samples after 1 rinse in 5% acetic acid solution at 70°C for 30 minutes at 40 rpm

SEM image showed that the larger aggregates initially seen on previous SEM images were not present on the washed treated samples after rinsing with acetic solution. EDX analysis of the rinsed cotton sample did not detected elements of Na, Al and S but elements of carbon, oxygen and silicon. The hydrophobic value was measured using the WRN measurement. The WRN values still remained at 3 after further rinsing with acetic solution. These results demonstrated that the residual detergent particles were not present after rinsing with acetic acid solution and the detection of silicon element confirmed that sol-gel coating was still present on the washed treated fabric.

A few studies have found that anionic detergents, elements such as calcium and hard water could neutralise the positive charged nitrogen on the QUAT compound; which inactivates and prevents its ability to attract the charged microorganisms (Kaya, 2010). The composition of the standard SDC ECE detergent showed that this standard detergent contained both anionic and non-ionic surfactants. The results discussed earlier demonstrated that residual detergent particles were present on the surface of the washed treated cotton samples. To determine the influence of these detergent particles on the QUAT's activity, treated cotton samples were washed up to 10 times with deionised water only and tested for their antibacterial activity.

For comparative purposes, the treated samples tested for their antibacterial activity included samples washed with either deionised water only or ECE detergent solution. Figure 7.12 showed the antibacterial activities of the samples washed with either deionised water or ECE detergent solution against *S.aureus* bacterium. It was found that a higher log reduction in CFU/mL of 1.90 was achieved for treated samples washed with deionised water when compared to the log reduction in CFU/mL of 0.79 achieved for treated cotton samples washed with the ECE detergent. These results demonstrated that QUAT activity was affected by the ECE detergent solution through repeat washes. This might explain the inactivation ability of QUAT by the detergent. Alternative washing processes or washing processes post detergent washing are required.



	Treated sample: water washed	Treated sample: Detergent washed	Control (bleached) cotton : detergent washed	Control (bleached) cotton : water washed
24hrs	1.90	0.79	-0.91	-0.13

Figure 7.12 Antibacterial results of samples washed with either deionised water or ECE detergent solution against *S.aureus* bacterium

Further testing could be carried out on samples washed with acetic acid to determine whether this rinse affected the activity of the QUAT. These processes could then be considered for effective removal of residual detergent particles that affected antibacterial properties. As cotton fabrics were treated with hydrophobic silanes to impart self-cleaning properties, the limitations that arise as a result of laundering could be avoided by ensuring that this self-cleaning property is maintained. Further improvements of self-cleaning properties would enable easier rolling off of water based stains, easily removed by water (Daoud, 2013), and reduce the need to laundering.

7.4.3.2 ATR/ FT-IR Analysis

ATR / FT- IR analysis of the treated cotton samples was carried out to determine the type of bonding present on the surface of washed cotton fabric after the 10th wash in ECE non-phosphate reference detergent A (SDC). The initial analysis was carried out on cotton samples treated with sols containing 5 mL and 2.5 mL of GLYMO, respectively, and their spectra shown in Figures 7.13 and 7.14.

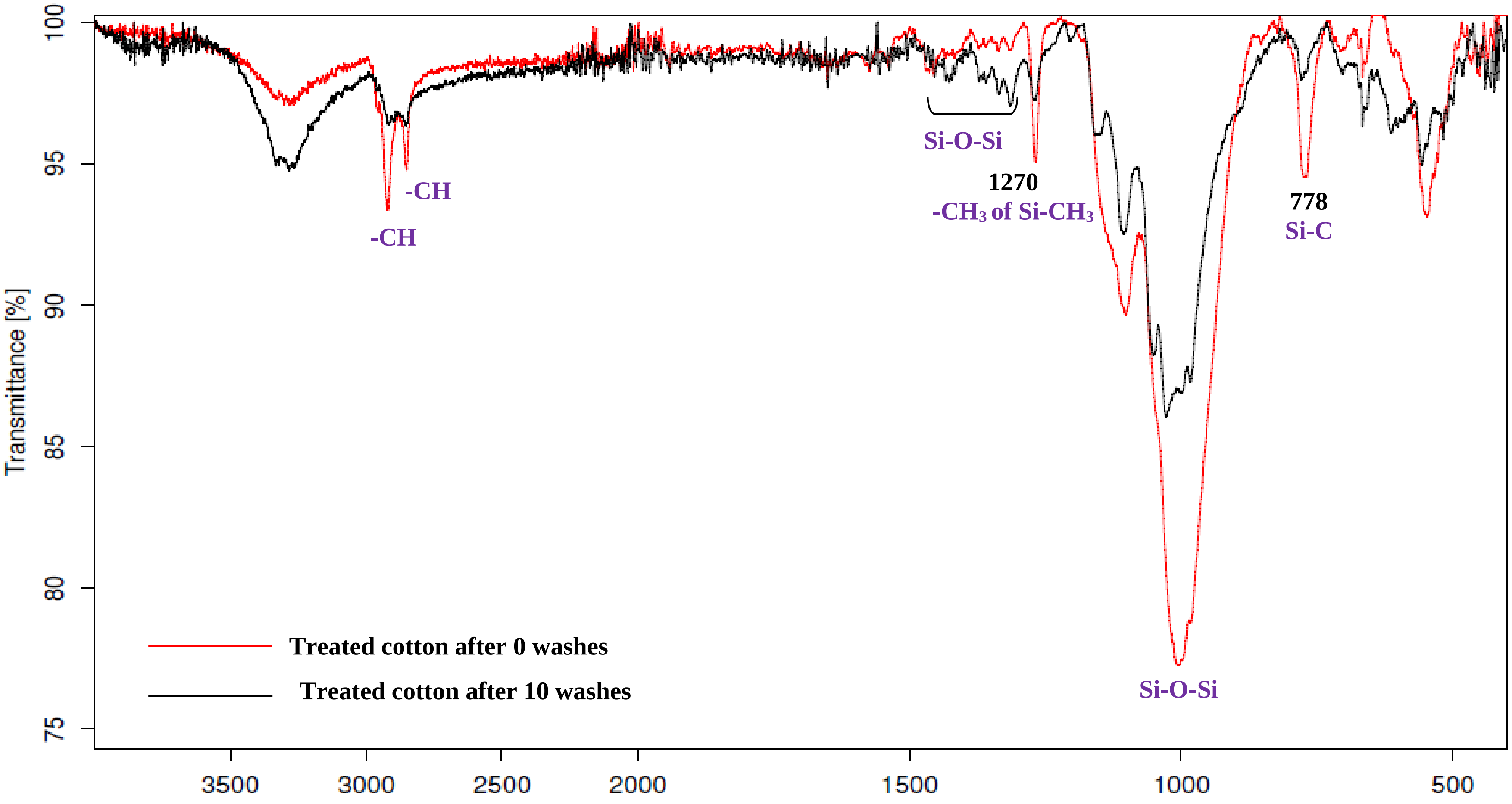


Figure 7.13 FT-IR spectra of cotton fabric treated with sol containing 2.5 mL of GLYMO before (red) and after (black) 10 repeat washes

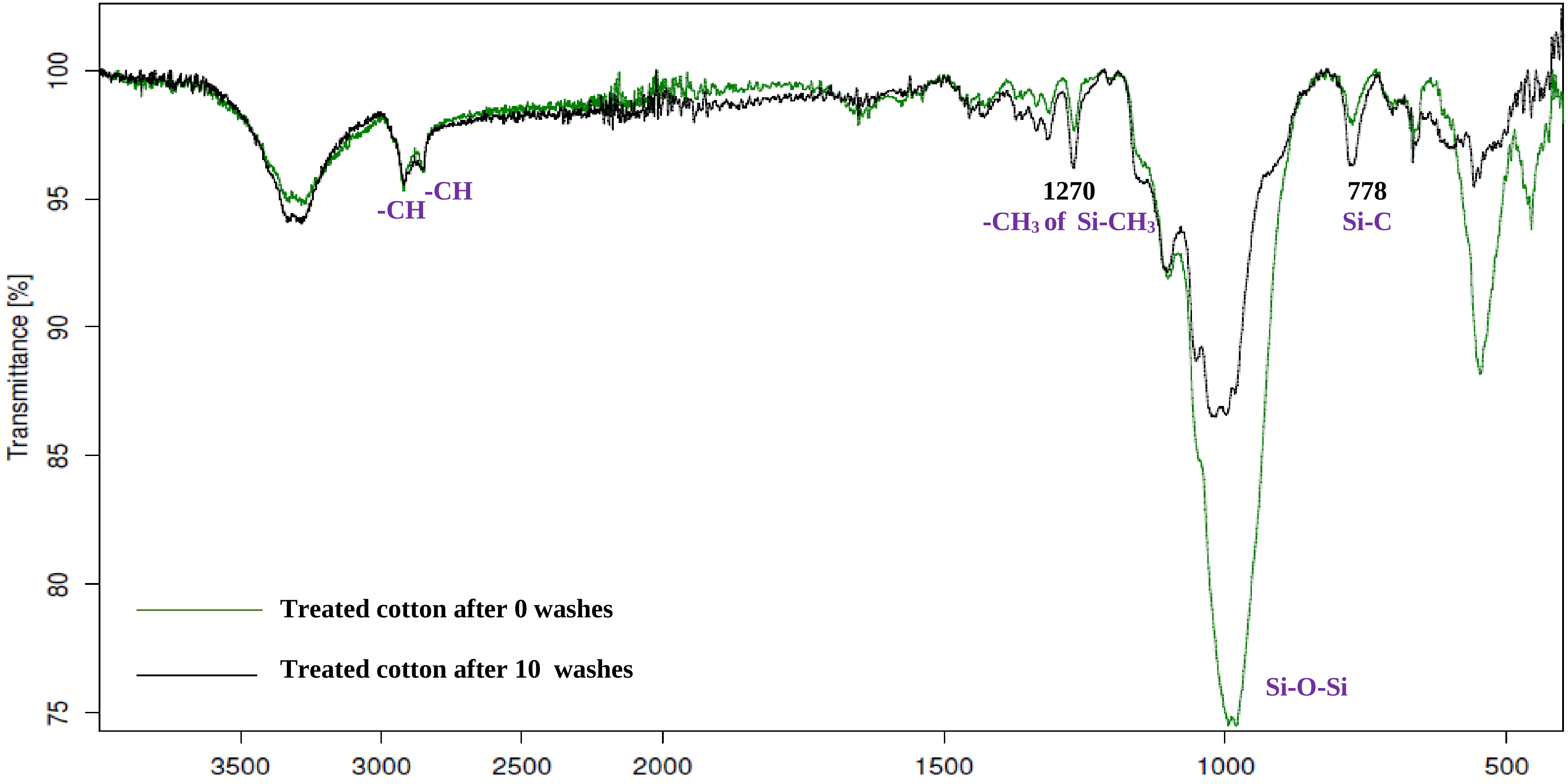


Figure 7.14 FT-IR spectra of cotton fabric treated with sol containing 5 mL of GLYMO before (green) and after (black) 10 repeat washes

From these results obtained, a change in the ATR / FT-IR spectra of the fibre surface was seen between the washed and unwashed treated cotton samples. From Figures 7.13 and 7.14, peak intensities at 778 cm^{-1} and 1270 cm^{-1} were reduced after repeat washing. These peak positions belonged to the Si-C bond associated with the modified hydrophobic silanes. The –CH peak intensity at approximately 2900 cm^{-1} reduced for cotton samples treated with sol containing 2.5 mL of GLYMO while there was no change in spectra of treated cotton treated with sol containing 5 mL GLYMO. When the spectra of two levels of GLYMO were compared, it was observed that higher intensities were observed for cotton samples treated with sols containing 5 mL of GLYMO, which suggested that more sol-gel coating could have been present on the surface than cotton samples treated with sols containing 2.5 mL of GLYMO. With repeat washing, the change in the intensity of peaks would indicate the removal of loosely bound sol-gel coating. For comparative purposes, the spectrum of untreated control cotton and treated cotton were overlaid to determine any similarities in peaks detected and shown in Figure 7.15.

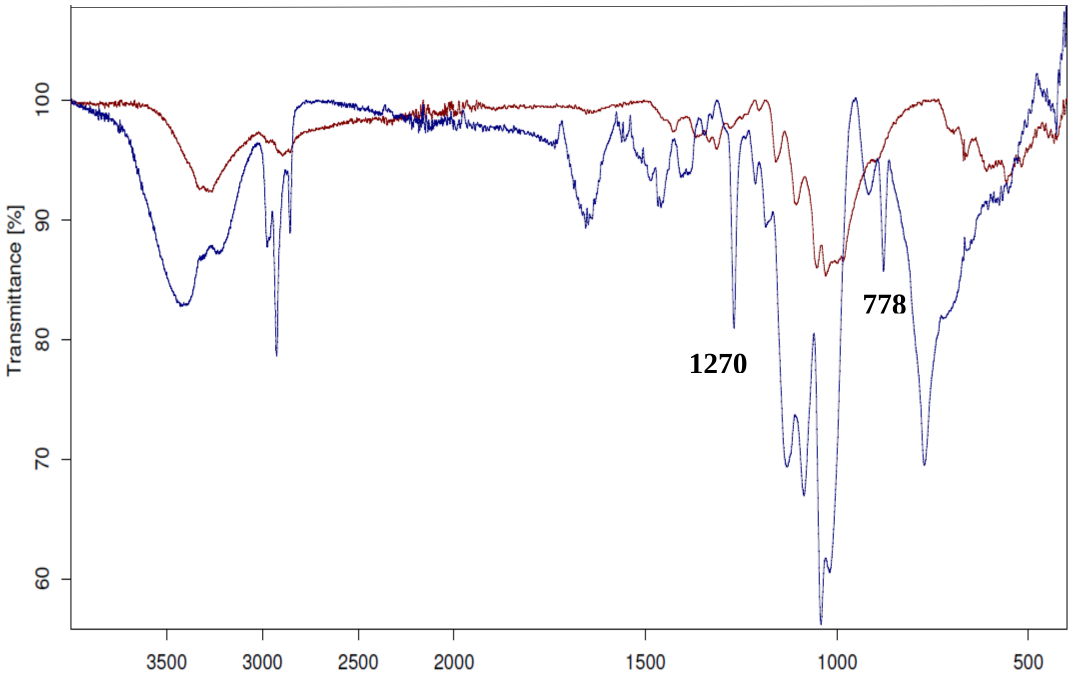


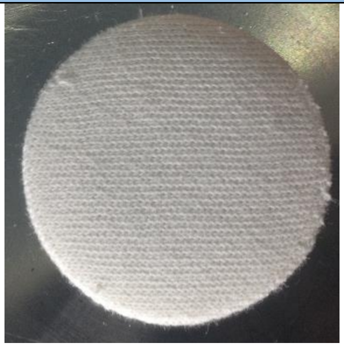
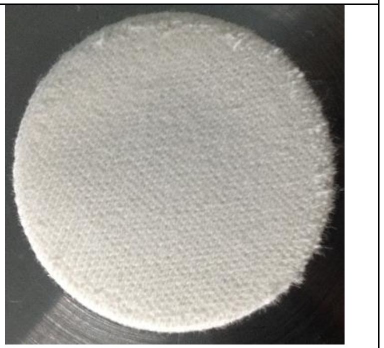
Figure 7.15 FT-IR spectra of untreated control (bleached) knitted cotton (blue) and cotton treated with sol synthesised using base formulation (red)

From the results, it was seen that certain peaks that belonged to the sol-gel coating and those that were for untreated cotton fabric overlapped. To avoid difficulties in analysis, the untreated control cotton was run as the background sample to ensure that the peaks detected were for sol-gel coating on the fabric surface. ATR / FT IR analysis was able to demonstrate the bonds on the surface of the laundered fabric did change as the complexity of Si-O-Si peaks detected before washing could not be observed for washed samples. These results confirmed that the sol-gel coating that was initially applied on the cotton fabric was removed from the surface by laundering however, the presence of the Si-O-Si bond did demonstrate that covalent bonding occurred, which enabled sol-gel coating to remain on the surface of washed treated cotton. This coating was able to demonstrate some hydrophobic and antibacterial properties.

7.4.4 Abrasion testing

The abrasion properties of the washed treated cotton samples were tested to determine the effect of repeat washing on this property. Testing was carried out on cotton samples treated with base sol formulation containing 2.5 mL or 5 mL of GLYMO silane, before and after 10 washes as described in Section 7.2.1. Abrasion testing was performed as described in Section 5.3.1.3 and results shown in Table 7.1. These results showed that the abrasion performance achieved for washed treated cotton fabric reduced to 12,000 revolutions from approximately 20,000 revolutions of unwashed cotton samples. Similar performance was seen for the both levels of 2.5 mL and 5 mL of GLYMO. As discussed in Section 5.4.3, the acidic ethanol solution used in sol application reduced cotton fibre’s abrasion resistance of 1,000 revolutions. The addition of silanes to this ethanol solution and application of the resultant sol to cotton fabric restored some abrasion resistance as values of 20,000 revolutions could be reached. Though there was a reduction in abrasion performance as a result of repeat washing, abrasion resistance and water repellence was still observed even after 10 repeat washes which indicated some durability properties of the sol-gel coating applied onto cotton fabric.

Table 7.1 Abrasion results of washed cotton samples treated with sol synthesised using formulation containing 5 mL and 2.5 mL of GLYMO cross-linker and padded at 45 kg/cm

Sample	**Number of Revolutions**		
	5,000	**10,000**	**12,000**
Treated cotton with sol containing 5 mL of GLYMO	 WRN value =3	 WRN value = 3	 WRN value = 3
Treated cotton with sol containing 2.5 mL of GLYMO	 WRN value = 2	 WRN value = 2	 WRN value = 2

7.4.5 Self-cleaning properties of treated cotton samples

As discussed in Section 7.4.1, to avoid limitations such as inactivation of QUAT silane that interferes with its ability to achieve antibacterial properties, the improvement of self-cleaning properties would eliminate the need for laundering. For demonstrative purposes, coloured water, cherry juice, tea and coffee were applied on the washed treated cotton and its self-cleaning ability measured as described in Section 3.4.3. Figure 7.16 shows the staining repellence and self-cleaning properties of the sol-gel treated cotton samples which were washed 10 times with ECE Detergent solution.

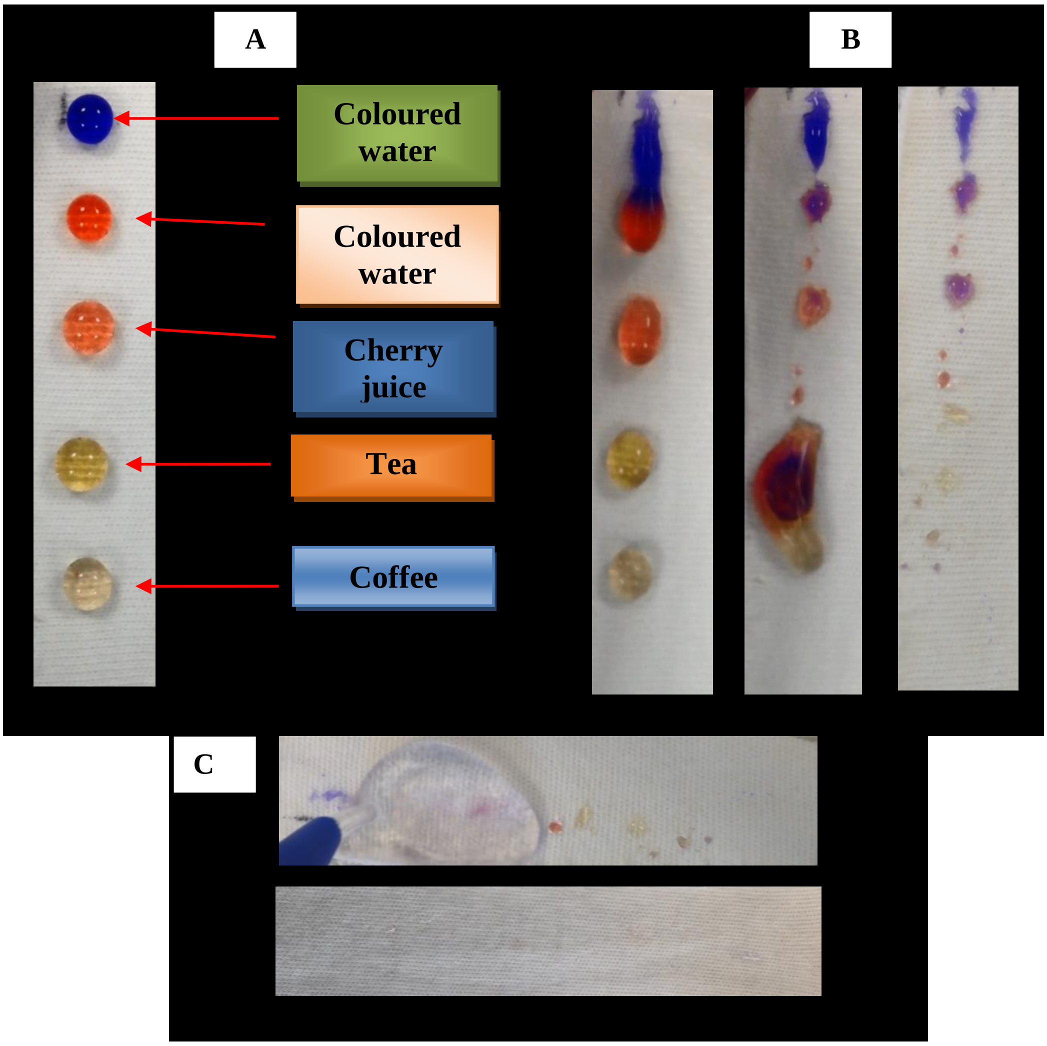


Figure 7.16 Droplet formation (A), rolling off of droplets (B) and rinsing of residual beads (C) of treated cotton samples after 10 washes with ECE Detergent solution

From the results shown in Figure 7.16, different droplet formation was observed for the different liquids and their ability to roll off the washed treated cotton sample. The washed treated cotton samples demonstrated reduced self-cleaning properties as more residual liquid droplets were present on the surface after tilting to enable rolling of the droplets. These residual droplets were rinsed easily with water and the fabric was not stained. This demonstrated that even after 10 repeat washes; self-cleaning properties were still present on the treated cotton surface. The improvement of self-cleaning properties would reduce the need for repeat laundering and reduce the effects that detergents would have on the hydrophobic and antibacterial properties of the treated cotton fabric.

7.5 Conclusions

The dual properties of self-cleaning and antibacterial activity of the treated cotton fabric were affected by the laundering process. The hydrophobicity property of the sol-gel treated cotton fabrics was slightly reduced from WRN values of 4 to 3 after 10 repeat wash cycles with detergent at 40°C for 30 minutes each time. This slight reduction demonstrated that the hydrophobicity property of sol-gel polymer coating was durable to washing. This hydrophobic property was also durable to abrasion as WRN values remained at the value of 3 even after 12,000 revolutions after fibre breakdown due to abrasion testing. However, there was a considerable decrease in the antibacterial activity from a log reduction in CFU/mL of 3 to just below 1 after 10 repeat washes of the treated cotton fabric. Further analysis using SEM imaging illustrated the deposition of residual detergent particles on washed treated cotton samples. Due to the presence of the anionic surfactants in the detergent, the QUAT was susceptible to inactivation; especially with the presence of detergent particles on the washed fabric samples. Preliminary investigations into further rinsing procedures were carried out. The rinse with a dilute acetic acid solution at the temperature of 70^{o}C could successfully remove the residual particles of detergent. Further investigations to develop an effective rinsing system for the removal of detergent particles could to carried out and other chemicals considered, avoiding adverse effects such as removal of the sol-gel coating from the cotton fabric.

The GLYMO epoxy cross-linker incorporated into the sol formulation did improve the durability of the sol-gel coating as higher WRN values were achieved for washed samples treated with sols containing this cross-linker, as opposed to those treated with sols without the cross-linker. Extensive optimisation, to develop a relationship between epoxy and sol-gel coating durability, could be carried out to further improve the durability of the coating and associated abrasion properties for the treated cotton fabric samples after washing.

SEM-EDX and ATR / FT-IR demonstrated that sol-gel coating was present on the treated cotton fabric even after the 10 detergent washes. This demonstrated that the sol-gel applied through the application process developed in this research was durable. With further optimisation of the sol and its application, these properties could be improved further. The degree to which this could be carried out would be determined by the area of application. As mentioned in the introduction, more durable products have become products of interest due to their cost-effective abilities and positive impact on environment through optimisation of industrial production processes.

CHAPTER 8:

CONCLUSIONS

8.1 General conclusions

The nanosol with the base formulation containing the silanes of MTES, GLYMO, OTES and QUAT at the ratio of 30: 5: 10: 5 mL was successfully synthesised and applied to 100% knitted cotton. The sol-gel polymers in the sol solution had good adsorption onto the cotton fibres resulting in subsequent chemical bonding on the surface of fibres during 4 hour treatment. Hydrophobic properties on cotton fabrics were achieved with WCA values of 142° and WRN values of 4. The treated cotton samples also achieved roll-off angle of 16°. This roll-off angle demonstrated that water droplets could easily roll off the surface of the treated cotton surface at a tilt of 16°. This feature was simulated to the lotus leaf effect associated with self-cleaning. The different water based liquids (coffee, tea, BlackBerry juice, milk and water itself) dropped on the treated cotton fabric could easily roll off the surface except milk which left very small residual traces on the fabric. However the residual milk traces could be rinsed off with water without staining. This demonstrated the extent of self-cleaning properties.

The antibacterial activity for treated cotton samples was determined using the ASTM E 2149-10 test method for immobilised antimicrobial agents. A log reduction in CFU/mL of 3 was achieved for treated cotton against *S.aureus*, showing the antibacterial activity of the coating containing the QUAT silane. The positive charge on the nitrogen of the QUAT was able to attract the Gram positive *S. aureus* to deactivate the cell membrane and perforate this membrane with the long hydrophobic chain. The addition of other hydrophobic silanes improved the antibacterial activity; demonstrating that hydrophobic chains assisted in the mode of action.

A reduction in abrasion resistance was noticed for cotton samples treated in the acidic sol solution. However, the introduction of silanes in the 50% v/v ethanol solution restored the abrasion performance at differerent extents, depending on the combination of silanes used. It was also observed that the sol-gel treatment improved pilling and burst strength properties of the cotton fabric, demonstrating that the sol-gel treatment method developed added these additional properties to the hydrophobic and anti-bacterial properties.

SEM analysis was able to show that through the application process developed, fibres in yarns were coated individually with sol-gel coating rather than cross-linked between neighbouring fibres. This feature and the porous sol-gel film enabled the treated cotton fabrics to maintain their soft handle. Sol-gel treated cotton fabrics padded twice at the higher pressure of 45 kg/cm demonstrated a good one-way transport property for moisture or sweat passing through the gaps between the knitting structure of cotton fabric rather than retention of moisture when tested for moisture management. These results demonstrated the sol-gel treatment improved the moisture management properties of treated knitted cotton fabrics. EDX analysis was able to identify the Si element belonging to the sol-gel coating while analysis of the sol system using ATR / FT-IR technique demonstrated that hydrolysis and condensation reactions occurred simultaneously within 1 hour of synthesis as Si-OH and Si-O-Si bonds were detected. Further analysis of dried and cured sol-gel films showed further condensation reactions within the sol-gel film. Analysis of drying, dried and cured treated cotton demonstrated the further condensation reactions of sol with fibres as well as epoxide reactions to demonstrate crosslinking with the fabric as several Si-OH and Si-O-Si bonds were detected.

The incorporation of the GLYMO cross-linker in the sol applied onto cotton fabric demonstrated its ability to produce durable sol-gel coatings as the hydrophobic properties (WRN value 3 and WCA of approximately 120°) as well as self-cleaning properties were achieved after 10 consecutive washes with ECE non-phosphate reference detergent A (SDC) at 40°C. Reduction in antibacterial properties was identified after repeat laundering. This may be because the detergent used for laundering may have affected the functionality of the QUAT through inactivation of its positive charge. However, the rinse with a dilute acetic acid solution could successfully remove the residual particles of detergent. This might be able to reactivate the antibacterial property of sol-gel treated fabrics. On the other hand, the improvement of self-cleaning properties would reduce the need for repeat laundering and reduce the effects of detergents on the antibacterial properties of the treated cotton fabric. Achieving a dual-functional textile using environmentally friendly synthesis process fits in current industry aim to improve industrial impacts on the environment, as a whole.

8.2 Further Work

Adequate self-cleaning and antibacterial properties were achieved using the application processes developed through this research. The treatment process incorporated in the sol-gel finishing process demonstrated improvement in durability of the sol-gel coating applied on cotton fabric. Through SEM and ATR / FT-IR analysis, siloxane bonding between cotton fabric and sol coating was established and EDX analysis illustrated the composition of the coating formed on the cotton surface. Feasibility tests could be carried out to determine the ideal duration of fabric treatment. These preliminary tests observed that 2 hours treatment time was able to achieve similar durability to washing with regards to Water Rating Numbers. Further testing of antibacterial and mechanical properties of cotton samples treated for 2 hours could be carried out to determine if this length of time would provide adequate chemical reaction time between sol and cotton fabrics and therefore bonding between sol and reactive groups on the cotton fabric. Identifying optimal treatment durations would allow further optimisation of the sol application process; subsequently improving overall finishing process.

The homogeneity of sols synthesised was important in the developmental stages of the sol synthesis process because it indicated sufficient alkoxysilane reaction within the medium and increased sol reproducibility. The consistency in producing clear sol solutions limited variables observed in the initial stages of method development where cloudy sols were synthesised. This homogeneity was achieved through adjustments of the pH of solvent used for sol synthesis. However, the low pH of the ethanol solution weakened the fibre strength of cotton as demonstrated by burst strength results. Weaken fibre strength of cotton fabrics reduces its ability to withstand stresses such as abrasion and applied pressures through stretching and therefore its reliability in applied fields.

Further optimisation of sol pH could be investigated to determine the pH required to ensure that the sol is homogenous. Other studies could investigate the use of surfactants to control particle size and therefore homogeneity.

To avoid limitations in the application of treated fabric samples, improvement of its self-cleaning properties would ensure that laundering is reduced and where possible eliminated. Self-cleaning properties are achieved through very low roll-off angles. Roll-off angles are in turn achieved by hydrophobic surfaces. Increasing the hydrophobicity of the treated cotton samples would reduce surface adhesion and thereby improve roll-off angles. Further investigations to improve the hydrophobicity of the coating could be carried out through the use of other long chain alkyl alkoxysilanes to observe their influence on the hydrophobic nature of the coating.

Sol-gel application onto textiles has been and currently carried out at higher temperatures, as widely reported in literature. Further studies in the drying and curing stages could be carried out to investigate the length of drying and curing, respectively. As temperatures lower than 200°C were used for curing, incorporating longer cure times and observing its influence on coating properties and durability could be studied. Factors such as yellowing of cotton fabric would be considered to ensure that the appearance of the cotton fabric is not altered as discoloured cotton fabrics remove from the aesthetic appearance of the white cotton fabric. The padding pressure of 45kg/cm at 1m^2/min was ideal as fabric handle was not affected. Variation in the amount of coating could be made depending on the identified area of application.

The ASTM E 2149-10 dynamic shake testing method was utilised because it was a test designed for the testing of the antibacterial properties for immobilised antibacterial agents. As the QUAT as incorporated in the sol-gel network that formed on the treated cotton fabric, such a test was suited. Further tests could be carried out by varying the amount of QUAT in the formulation. This would determine the minimum and maximum amounts of QUAT that would be needed to achieve the antibacterial property. This alkoxysilane is beneficial in the sol formulation as it not only introduced the antibacterial property but also contributed to the hydrophobic property. The limitations in the testing method included the inability to simulate real life instances by which bacterial solutions would come into contact with the fabric. Bacterial survival on the treated cotton fabric could then be investigated. As the treated cotton fabric possesses self-cleaning properties which caused water based liquids to roll off upon contact, tests to determine bacterial survival on such surfaces would indicate its antibacterial property and thus, its ability to inhibit bacterial growth.

Optimisation of processes and procedures ensures that techniques are developed to produce technical textiles that exhibit durability in the properties exhibited and ensures its reliability in fields of application. The sol-gel application method that has been developed enabled 100% knitted cotton to exhibit both self-cleaning and antibacterial properties, which with further optimisation, would ensure desired durability. Rinsing of the treated fabric could be carried out to ensure that any loosely bound coating is removed to minimise potential irritation to the wearer and alongside rinsing, testing of rinsing solution for island content could be carried out to quantify the loosely bound sol-gel.

REFERENCES

Abel, L-M., Joannic, R., Faips, M., Lafontaine, E., Shaw, J. S., Watts, F. J. (2006) Effect of solvent nature on the interaction of ɣ-glycidoxypropyl trimethoxy silane on oxidised aluminium surface: A study by solution chemistry and surface analysis. *International Journal of Adhesion & Adhesive*, 26, pp. 16-27.

Abel, T., Chen, I. J., Engel, R., Filshtinskaya, M., Melkonian, A., Melkonian, K.(2002) Preparation and investigation of antibacterial carbohydrate-based surface. *Carbohydrate Research*, 337, pp. 2495-2499.

Achour, S. N., Hamdaoui, M., Ben Nasrallah, S., Perwuelz, A. (2015) Investigation of Moisture Management Properties of Cotton and Blended Knitted Fabrics. *Journal ofChemical, Molecular, Nuclear, Materials and Metallurgical Engineering*, 9, pp. 879-883.

Ahiba Nuance Manual (2001). *User documentation Ahiba Nuance Top Speed II*. Lawrenceville: Datacolor.

Akaydin, M. and Can, Y. Pilling performance and abrasion characteristics of selected basic weft knitted fabric. *Fabric and Textiles*, 18, pp.51-54.

Anand, C. S, Kennedy, F. J., Miraftab. M, Rajendran, S. (2006). *Medical textiles and biomaterials for healthcare*. Cambridge: Woodhead Publishing Limited.

Anderson, J. R., Groundwater, W. P., Todd, A., Worsley, A. J. (2012). *Anitbacterial agents:chemistry,mode of action, mechanisms of resistance and clinical application.* Wiley online library: John Wiley & Sons Ltd.

Annis, P. A. (2012). *Understanding and improving the durability of textiles.* Cambridge: Woodhead Publishing.

Anthony, S. (2011). *Chinese invent self-cleaning cotton clothes.* [WWW] EXTREMETECH . Available from: http://www.extremetech.com/extreme/109215-chinese-invent-self-cleaning-cotton-clothes [Accessed 15/12/2011].

Arthur, T., Johnson, J., MacDonald, S. (2015). *Cotton Outlook.*Virginia: Agricultural Outlook Forum.

Arkles, B., Steinmetz, R. J., Zazyczny, J., Mehta, P. (1992) Factors contributing to the stability of alkoxysilanes in aqueous solutions. *Journal of Adhesion Science and Technology*, 6, pp. 91-104.

Arkles, B. (2006) *Hydrophobicity, Hydrophilicity and Silanes.* Marrisville: Gelest Inc.

ASTM E2149-13a (2013). International Standard Test Method for Determining the Antimicrobial Activity of Antimicrobial Agents Under Dynamic Contact Conditions. West Conshohocken, 2013.

ASTM International ASTM D3786 / D3786M – 13 (2013). Standard Test Method for Bursting Strength of Textile Fabrics—Diaphragm Bursting Strength Tester Method. Available from: http://www.astm.org/Standards/D3786 [Accessed 13/08/ 2013].

ASTM International ASTM D3885 - 07a (2011). *Standard Test Method for abrasion resistance of textile fabrics (Martindale abrasion test method).* Available from : http://www.astm.org/Standards/D3885.htm [Accessed 04/05/2012].

Bae, G. Y., Min,B. Y., Jeong, Y. G., Lee, S. C., Jang, J. H., Koo, G. H. (2009) .Superhydrophobicity of cotton fabric treated with silica nanoparticles and water-repellent agent. *Journal of Colloid and Interface Science*, 337, pp. 170-175.

Bajaj, P. (2002). Finishing of Textile Materials. J*ournal of Applied Polymer Science,* (1) , pp. 631-659.

Baltusnikaite, J., Abraitiene, A., Stygiene, L., Krauledas, S., Rubeziene, V., Varnaite-Zuravliova, S. (2014). Investigation of Moisture Transport properties of Knitted Materials intended for warm underwear. *Textile Institute, Center for Physical Sciences and Technology,* 4, pp. 93-100.

BBC News (2011) *Self-cleaning cotton nanoparticles coating invented.* London: BBC News.

Berendjchi, A., Khajavi, R., Yazdanshenas, E. M. (2011). Fabrication of superhydrophobic and antibacterial surface on cotton fabric by doped silica-based sols with nanoparticles of copper . *Nanoscale Research*, 6 , pp. 1-8.

Berendjchi, A., Khajavi, R., Yazdanshenaz, E. M. (2013). Application of Nanosols in Textile Industry. *International Journal of Green Nanotechnology*, 1, pp. 1-7.

Beganskiene, A., Sirutkaitis, V., Kurtinaitiene, M., Juskenas, R., Kareiva, A. (2004). FTIR, TEM and NMR Investigations of stober Nanoparticles. *Materials Science*, 10, pp. 287-290.

Bhusan, B., Jung, C. Y., Koch, K. (2009). Micro-, Nano- and hierarchial strcutures for superhydrophobicity, self-cleaning and low adhesion. *Philosophical Transactions of the Royal Society*, 367, pp. 1631-1672.

Brezezinski, S., Kowalczyk, D., Borak, B., Jasiorski, M., Tracz, A. (2011). Nanocoat Finishing of Polyester / Cotton Fabrics by the Sol-Gel Method tyo Improve their Wear Resistance. *FIBRES & TEXTILES*, vol 89, pp. 83-88.

Brinker, J. C. and G. W Scherer, W. G. (1990). *Sol gel science: The physics and Chemistry of sol-gel processing.* San Diego: Academic Press INC.

Bruker Corporation (2016) ATR / FT-IR Bruker equipment [Online image] Available from:https://www.google.co.uk/search?q=bruker+atr+ftir&rlz=1C1OPRB_enGB654GB654&espv=2&biw=1920&bih=979&source=lnms&tbm=isch&sa=X&ved=0ahUKEwi8obvCxvXLAhXIORQKHdNtDzQQ_AUIBigB#imgrc=zw8aKyKP-hkMsM%3A [Accessed 04/04/2016].

BS EN ISO 12945-1:2001 Textiles. Determination of fabric propensity to surface fuzzing and to pilling. Pilling box method

BS EN ISO 12947-1:1998 Textiles. Determination of the abrasion resistance of fabrics by the Martindale method. Martindale abrasion testing apparatus

Buyle, G. (2012). *Coatings and their application in textiles.* Belgium: Centexbel, 2012.

Carter, M. (1971). *Essential Fiber Chemistry*. New York: Marcel Dekker INC.

Carey, F. A. (2001). *Organic Chemistry.* New York: McGraw-Hill Companies.

Chattopadhyay, S., Heine, E., Keul, H., Moeller, M. (2014). Azetidinium Functionalized Polytetrahydrofurans:Antimicrobial Properties in Solution and Application to prepare Non-Leaching Antimicrobial Surfaces. *Polymers*, 6, pp. 1618-1630.

Chemspider (2015). *Dimethyloctadecyl[3-(trimethoxysilyl)propyl]ammonium chloride* [online image] available from : http://www.chemspider.com/Chemical-Structure.56561.html [Accessed 03/01/2015]

Chen, L., Zheng, L., Lu, Y., Liu, H.,Wang, G., Ren, N., Liu, D., Wang, J., Boughton, I. R. (2010). Chemical Assembly of silver nanoparticles on stainless steel for antimicrobial applications. S*urface & Coatings Technology*, 204, pp. 3871-3875.

Chinta, K. S, Gujar, D. P. (2013). Significance of Moisture Management for High performance textile fabrics. *International Journal of Innovative Research in Science, Engineering and Technology*, 2, pp. 814-819.

Choi, W., Tuteja, A., Mabry, M. J., Cohen, E. R., McKinley, H. G, (2009). A modified Cassie-Baxter relationship to explain conatcat angle hysteresis and anisotropy on non-wetting textured surfaces. *Journal of Colloid and Interface Science*, 339, pp. 208-216.

Choudhari, M and Menezes, E. (2011) *Pre-treatment of Textiles Prior to Dyeing* . Croatia : InTech.

Choudhury, A. K. R. (2006). *Textile Preparation and Dyeing.* Enfield: Science Publishers.

Clark, J. (2014) [WWW] CHEM GUIDE. Available from: http://www.chemguide.co.uk/analysis/ir/background.html#top [Accessed 31/08/ 2014].

Coates, J. (2000). *Interpretation of Infrared spectra, A Practical Approach.* Chichester: John Wiley & Sons Ltd.

Collop, C. and Deffenbaugh, M. (2008) Project Cotton: the university of Missouri [WWW]. Available from: http://cotton.missouri.edu/Classroom-Chemical%20Composition.html [Accessed: 05 /09/ 2011].

Cotton Australia (2016). *Public Galleries, Cotton bolls* [Online image] Available from: http://cottonaustralia.smugmug.com/Public-Galleries [Accessed 23/03/2016].

Cotton Incorporated (2014). *Cotton Brings Functional and Marketable Benefits to Nonwovens Products* [WWW]. Available from: http://www.cottoninc.com /product/NonWovens/Why-Cotton/ [Accessed: 01/12/2014].

Daoud, A.W (2013). *Self-Cleaning materials and surfaces :A Nanotechnology approach.* West Sussex: John Wiley & Sons.

Datacolor, Brochures [WWW]. Available from : http://marketing.datacolor.com/cd-textile/Brochures_E/NU%20II%20Product%20brochure.pdf [Accessed 30/06/2015].

Devan Chemicals (2013). *Antimicrobial Technology* [WWW]. Available from: http://www.devan.net/product.aspx?prodid=2 [Accessed 30/06/2015].

EFjeld Company (2003). *SEM sample carousel* [Online image] Available from: http://www.efjeld.com/images/fjeld/SampHold/3474.JPG [Accessed 10/03/2015].

Emresolutions (2014). *SEM sample stub* [Online image] Available from: http://emresolutions.com/sem-products/sem-stubs-and-mounts/mounting-adhesives/ [Accessed 15/03/ 2015].

Erdem, K. A., Sanli, Y. O. N. (2008). The evaluation of antibacterial activity of fabrics impregnated with Dimethyl tetradecyl (3-trimethoxysilyl)propyl ammonium chloride." *Journal of Biology*, 67, pp. 115-122.

Evans Analytical (2015). *Seal laboratories.* Available from:. http:// www. seallabs.com/how-sem-works.html [accessed 07/01/ 2015].

Fir, M., Vince, J., Vuk, A. S., Vilcnik, A., Jovanovski, V., Mali, G., Orel, B., Simoncic., B. (2007). Functionalisation of cotton with hydrophobic Urea/Polydimethylsiloxane Sol-Gel Hybrid. *Acta Chimica Slovenica*, 54, pp. 144-148.

Fischer, D., Pospiech, D., Scheler, U., Navarro, R., Messori, M., Fabbri, M. (2008) Monitoring of the Sol-Gel Synthesis of organic-inorganic hybrids by FTIR Transmission, FTIR / ATR, NIR and Raman Spectroscopy. *Macromolecular Symposia*, 265, pp. 134-143.

Forbes, P. (2008). Self-cleaning Materials: Lotus leaf-inspired nanotechnology. *Scientific American* (Scientific American), 299, pp. 88-95.

Gao, Y. and Cranston, R. (2008). Recent Advances in Antimicrobial Treatments of Textiles. *Textile Research Journal*, 78, pp. 60-72.

Gao, Q., Zhu, Q., Guo, Y. (2009). Formation of Highly Hydrophobic surfaces on Cotton and Polyester Fabrics Using Silica sol Nanoparticles and Non-fluorinated Alkylsilane. *Industrial and Engineering Chemistry Research*, 48, pp. 9797-9803.

Gashti, P, M., Alimohammadi, F., Song, G., Kiumarsi, A (2012). Characterisation of nanocomposite coatings on textiles: a brief review on microscopic technology. *FORMATEX*, pp. 1424-1437.

Gelest Inc. (2006). *Silane Coupling agents: Correcting across Boundaries.* Morrisville: Gelest Inc.

Gulrajani, L.M. (2006). “Nano Finishes.” *Indian Journal of Fibre & Textile Research*, 31, pp.187-201.

Gulrajani, M. L. (2013), *Advances in the Dyeing and Finishing of Technical Textiles*. Delhi: Woodhead Publishing, 2013.

Gohl , E. P. G. , Vilensky, L. D. (1981). Textile Science . Melbourne: Longman Cheshire Pty Limited.

Gouveia, C. I (2010). *Nanobiotechnology: A new strategy to develop non-toxic antibacterial textiles.* Portugal: Formatex.

Goy, C. R., De Britto, D., Assis. G. B. O. (2009). A Review of the Antimicrobial Activity of Chitosan. *Polimeros: Ciencia e Tecnologia*, 19, pp. 241-247.

Gupta, D. and Gulrajani, L. M. (2014). In: Paul, R. (ed) *Functional Finishes for Textiles: Improving Comfort, Performance and Protection*, 1st ed, Cambridge: Woodhead Publishing, pp. 257-277.

Hackbarth, T. (2012). *Cotton: in the "Wild"* [Online image]. Available from: http://www.taylortailor.com/2012/10/cotton-in-the-wild/ [Accessed 21/03/2016]

Harvey, A. R., Chample, C. P. and Fisher, D. B. (2007). *Microbiology*. Baltimore: Lippincott Williams & Wilkins.

Hegde, D. N., Rao, V. A. (2006). Organic modification of TEOS based silica aerogels using hexadecyltrimethoxysilane as a hydrophobic reagent. *Applied Surface Science*, 253, pp. 1566-1572.

Horr, J. T., Reynolds, D. G. (1997). The reactions of 3-glycidoxypropyltrimethoxysilane in acidic solutions on polymerization and in the presence of silica. *Journal of Adhesion Science and Technology*, 11, pp. 995-1009.

Hussain, S. (2010). *Quality control and textile testing* [WWW] Scribd. Available from: http://www.scribd.com/doc/44210612/Fabric-Bursting-Strength [Accessed 14/08/ 2013].

Interscience (2010). easySpiral Dilute® The world's first automatic diluter & plater [Online brochure]. Available from : file:///G:/interscience_easyspiral_dilute_brochure_en_web-2.pdf [Accessed 07/02/2015].

Interscience for microbiology (2014). Video. Directed by Interscience for microbiology. France. Interscience.

James Heal (2014). Abrasion testing equipment [Online image]. Available from: https://www.james-heal.co.uk/ [Accessed 02/02/ 2014].

James Heal (2014). *Truburst burst testing equipment* [Online image] Available from: https://www.james-heal.co.uk/en/truburst [Accessed 26/03/ 2015].

Jarrell, F. K. (2009). Pili and Flagella: *Current research and future trends*. Kingston: Caister Academic Press.

Jiang, X., Tian, X., Gu, J., Huang, D., Yang,Y. (2011). Cotton fabric coated with nano TiO_2-acrylate copolymer for photocatalytic self-cleaning by in-situ suspension polymerisation. *Applied Surface Science*, 257, pp. 8451-8456.

Jiang, S., Wang, L., Yu, H., Chen, Y. (2005). Preparation of crosslinked polystyrenes with quaternary ammonium and their antibacterial behaviour. *Reactive and Functional Polymers*, 62, pp. 209-213.

John, L. and Sobata, P. (2010). Alkoxide Molecular Precursors for Nanomaterials, A one Step strategy for oxide Ceramics.*Ceramic Materials*, pp. 70-84.

Karmakar, R. S. (1999). *Chemical technology in the pre-treatment processes of textiles*. Amsterdam: Elsevier Science.

Kathirvelu, S., D'Souza, L., Dhurai, B. (2008). Multi-functional finishing of cotton and blended fabrics treated with titantium dioxide nano-particles. *Indian Journal of Science and Technology*, 1, pp. 1-9.

Kaya, D. (2010). *Quaternary Ammonium Compounds* [SlideShare]. Available from: http://www.slideshare.net/dengbej/quaternary-ammonium-compounds [Accessed 21/01/2010].

Kickelbick, G. (2007). *Introduction to Hybrid Materials*. Weinham: Wiley.

Kim, J. H., Jung, H. D., Cifuentes, I. J., Rhee, Y. K., Hui, D. (2012). Enhancement of mechanical properties of aluminium/epoxy composites with silane functionalization of aluminium powder. *Composites: Part B*, 43, pp. 1743-1748.

Kiron, M. L. (2014). Bursting Strength Test.Available from: http://textilelearner.blogspot.co.uk/2012/02/bursting-strength-test-diaphragm-of.html [accessed 26/03/ 2015].

Kim, W. H., Kim, R. B., Rhee, Y. H. (2010). Imparting durable antimicrobial properties to cotton fabrics using alginate-quaternary ammonium complex nanoparticles. *Carbohydrate Polymers,* 79, pp. 1057-1062.

Kissa, E. (2001). *Fluorinated surfactants and repellents.* Basel: Marcel Dekker.

Kumar, D., Wu, X., Fu, Q., Chye Ho, W. J., Kanhere, D. P., Li, L., Chena, Z. (2015). Development of durable self-cleaning coatings using organic–inorganic hybrid sol–gel method. *Applied Surface Science*, 344, pp. 205-212.

Kumar, R. G., Krishnaveni, V. (2011). An Eco-Friendly Herbal Antimicrobial Finish on Cotton fabric using Aloe Barbadensis Milter (Aloe Vera). *Fibre2Fashion*, pp. 1-6.

Lacasse, K and Baumann, W. (2004). *Textile Chemicals: Environmental Data and Facts*. New York: Springer.

Latella, A. B., Swain, V. M, Ignat, M. (2012.) Indentation and Fracture of Hybrid Sol-Gel Silica Films. In: Nemecek, J. *Nanoindentation in materials science*. Intech open access publisher.

Lenza, S. F. R., Vasconcelos, L. W. (2000). Structural Evolution of silica sols modified with formamide. *Materials Research*, 4, pp. 1439-1516.

Li, Z., Xing, Y., Dai, J. (2008). Superhydrophobic surfaces prepared from water glass and non-fluorinated alkylsilane on cotton substrates. *Applied Surface Science*, 254, pp. 2131-2135.

Li, Z. R. (2005). *Industrial Application of Electron Microscopy.* New York: Marcel Dekkar Inc.

Li, S-Y., Ba, A. (2008). spectroscopic studies of triethoxysilane sol-gel and coating process. *Spectrochemico Acta Part A*, 70, pp. 1013-1019.

Lin-Vien, D., Colthup, B. N., Fateley, G. W., Grasselli. G. J. (1991). *The handbook of Infrared and Raman characteristic frequencies of organic molecules.* California: Academic Press.

Lu, Y., Han, L., Brinker, J. C., Niemczyk, T. M., Lopez, P. G. (1996). Chemical sensors on hydrophobic poprous sol-gel films and ATR-FTIR spectroscopy. *Sensors and Actuators,* 36, pp. 517-521.

Mahltig, B. (2011). Hydrophobic sol-gel based coating agent for textiles: improvement by solvothermal treatment. *Journal of the Textile Institute*, 102, pp. 455-459.

Mahltig, B., Bottcher, H. (2003). Modified silica sol coatings for water-repellent textiles. *Journal of Sol-Gel Science and Technology*, 27, pp. 43-52.

Mahltig, B., Fiedler, D., Bottcher, H. (2004) Antimicrobial sol-gel coatings. *Journal of Sol-Gel Science and Technology,* 32, pp. 219-222.

Mahtig, B., Haufe, H. and Bottcher, H. (2005). Functionalisation of textiles by inorganic sol-gel coatings, *Journal of Material Chemistry*,15, pp. 4385-4398.

Mahltig, B., Haufe, H., Muschter, K., Fischer, A., Kim, H. Y., Gutmann, E., Resbold, M., Meyer, C. D., Textor, T., Kim, W. C., Kahg, S. Y. (2010). Silver nanoparticle in SiO_2 Microsphere-perparation by spray drying and use as antimicrobial agent. *Slovenian Chemical Society,* 57, pp. 451-457.

Mahltig, B., Textor, T. (2008). *Nanosols and Textiles.* Singapore: World Scientific.

Mammeri, F., Le Bourhis, E., Rozes, L., Sanchez. C. (2005). Sol Gel Background: Chapter II. *Journal of Materials*, 15, pp. 35-36.

Materne, T., De-Buyl, F. and Witucki, L. G. (2012). Organosilane Technology in Coating Applications: Review and Perspectives. *Dow Cowing Corporation*, pp. 1-15.

Menno, W. L. and Koole, H. L. (2011). New Strategies in the Development of Antimicrobial Coatings: The Example of Increasing Usage of Silver and Silver Nanoparticles. *Polymers,* 3, pp. 340-366.

Messaoud, M., Houmard, M., Briche, S., Roussel, F., Langlet, M. (2010). Hydrophobic functionalisation of cotton-based textile fabrics through a non-fluorinated sol-gel route. *Journal of Sol-Gel Science Technology*, 55, pp. 243-254.

Mishra, S. P. (2005). *A Textbook of fibre Science andf Technology.* New Dehli: New Age International Ltd.

Mittal, K. L. (2009). *Silanes and Other Coupling Agents.* Leiden: IDC Publishers.

Montazer, M., Golshani, P., Moghadam, B. M. P. (2013). Hydrophobic cross-linked and photoactive cotton fabric using nano TiO_2 and BTCA-Statistically optimised by RSM. *Indian Journal of Fibre & Textile Research*, 21, pp. 35-43.

Monticello, R. A. (2010). *Smart FabRx Germ Resistant Fabric* [WWW]. Smart FabRx. Available from: http://smartfabrx.com/docs/The-use-of-reactive-silane-chemistries.pdf [Accessed 04/07/ 2015].

Murphy, T. (2004). Physical and chemical Control of microorganisms.[WWW]. Available from: http://faulty.ivytech.edu/~twmurphy/txt_202/disinfect.html [Accessed 27/09/ 2011].

Myers, R. (2003). *The Basics of Chemistry.* Westport: Greenwood Press.

Nazari, A., Montazer, M., Moghadam, B. M., Anary-Abbasinejad, M. (2011). Self-cleaning properties of bleached and cationised cotton using nano TiO_2:A statistical approach. *Carbohydrate Polymers,* 83, pp. 1119-1127.

Nemcokova, R., Glombikova, V., Komarkova, P. (2015). Study on liquid moisture transport of knitted fabrics by means of MMT, Thermography and microtomography systems. *AUTEX Research Journal*,15, pp. 233-242.

New York University, *Carl Zeiss SEM equipment.* [Online image]. Available From: http://chemistry.fas.nyu.edu/object/chem.emlf [Accessed 10 /02/ 2015].

Niederberger, M. and Pinna, N. (2009). *Metal Oxide Nanoparticles in organic solvents: Synthesis, Formation, Assembly and Application.* London: Springer.

Nischala, K., Rao, N. T., Hebalkar, N. (2010). Silica Silver Core sell particles for antibacterial textile application. *Colloids and Surfaces B: Biointerfaces*, 82, pp. 203-208.

O'Byrne, K. (2015). *Why cotton* [WWW] CottonIinc. Available from: http://www.cottoninc.com/product/NonWovens/Why-Cotton/. [Accessed 03/07/2014].

Onar, N., Aksit, C. A., Sen, Y., Muthe, M. (2011). Antimicrobial UV-Protective and Self-Cleaning properties of cotton fabrics coating by dip-coating and solvothermal coating methods. *Fibers and Polymers*, 12, pp. 461-470.

Ornes, S. (2012). *Self-cleaning clothes.* Science News for Kids. Available from: https://mrsbushnell.wikispaces.com/file/view/sciencenewsforkids.org-Selfcleaning_clothes__Science_News_for_Kids.pdf [Accessed 10/01/2012].

Osterholtz, D. F., Pohl, R. E. (1992). Kinetics of the hydrolysis and condensation of organofunctional alkoxysilanes, a review. *Journal Adhesion Science and Technology*, 6, pp. 127-149.

Ozcelik, G., Supren, G., Gulumser, T., Tarakcioglu, I. (2008). A study on sugjective and objective evaluation of the handle properties of shirt fabrics. *Fibres &extiles* (Fibres & Textiles), 3, pp. 56-62.

Pakdel, E. and Daoud, A.W. (2013). Self-cleaning cotton functionalised with TiO_2/SiO_2: Focus on the role of silica. *Journal of Colliod and Interface Science*, 401, pp. 1-7.

Paldiya, B. (2014) Different Parts of Modern Cotton Ginning Machine. [Online image] Available from: http://textilelearner.blogspot.co.uk/2014/08/different-parts-of-modern-cotton.html [Accessed 15/03/2016].

Pan, N. and Sun, G. (2011). *Functional Textiles for Improved Performance.* Cambridge: Woodhead Publishing.

Parsons, L. (2006). *What is a martindale rub test?* [WWW] Available from: http://blog.kothea.com/2009/06/11/what-is-the-martindale-rub-test/ [Accessed 06/07/ 2014].

Patel, H. B., Chaudhari, B. S., Patel, N. P. (2014). Nano silica loaded cotton fabric; characterization and mechanical testing. *Research Journal of Engineeering Sciences*, 4, pp. 19-24.

Paul, R. (2015). *Functional Finishes for Textiles: Improving comfort, performance and protection.* Kidlington: Woodhead Publishing.

Perkin Elmer (2005). *FT-IR Spectroscopy Attenuated Total reflectance.* Shelton: Perkin Elmer.

PIKE Technologies (2015). *ATR Theory and Applications* [WWW] PIKE Technologies. Available from: http://www.piketech.com/files/pdfs/ATRAN611.pdf [Accessed 10/01/2015].

Plueddemann, E.P. (1991). *Silane Coupling Agents.* New York: Plenum Press.

Pompe, W., Rodel, G., Weiss, H-J., Mertig, M. (2013). *Bio-nanomaterials: Designing materials inspired by nature*. Weinheim :Wiley-VCH.

Poole, B. (2007). How Nature holds the key to self-cleaning clothes and windows, molecular velcro and superior sticky tape. Weblog [Online] 13th July. Available from:http://www.google.co.uk/imgres?imgurl=http://www.thenakedscientists.com/HTML/uploads/tx_naksciimages/lotus_leaf_jpg.jpg&imgrefurl=http://www.thenakedscientists.com/HTML/articles/article/biomimeticsborrowingfrombiology/&h=275&w=869&tbnid=F13tJEvhB_q3YM:&zo [accessed 14/03/ 2015].

Radeshkumar, C. and Munstedt, H. (2006). Antimicrobial polymers from polypropylene/silver compositities-Ag release measured by anode stripping voltammetry. *Reactive and Functional Polymers,* 66, pp. 780-788.

Raghavendra, R. H., Dahiya, A., Kamath, G. M. April (2004). University of Tennesse. Available from: http://www.engr.utk.edu/mse/pages/Textiles/Cotton%20fibers.htm [accessed August 2, 2014].

Rajendran, R., Karthik Sundaram, S., Radhai , R., Rajapriya, P.(2011). Bioscouring of Cotton Fabrics using Pectinase Enzyme its Optimization and Comparison with Conventional Scouring Process. *Pakistan Journal of Biological Sciences*, 14, pp. 519-525.

Ramachandran, T., Rajendrakumar, K., Rajendran, R. (2004). Antimicrobial textiles-An overview. *Internet Explorer(India) Journal -Textile*, pp. 42-47.

Rao, A. S. (1997). *Introduction to Microbiology.* New Delhi: Prentice-Hall Limited.

Reigel, B., Blittersdorf, S., Keifer, W., Hofacker, S., Muller, M., Schottner, G. (1998). Kinetic investigations of hydrolysis and condensation of the glycidoxypropyltrimethoxysilaneraminopropyltriethoxy-silane system by means of FT-Raman spectroscopy, I. *Journal of Non-Crystalline Solids*, 226, pp 76-84.

Russell, A. D. (2002). Mechanisms of Antimicrobial action of antiseptics and disinfectants: an increasingly important area of investigation. *Journal of Antimicrobial Chemotherapy*, 49, pp. 597-599.

Sakka, S. (2005). *Handbook of sol gel science and technology: processing, characterisation, and application.* Massachusetts: Kluwer Academic Publishers.

Saleemi, S., Ejaz, A., Almasi, R., Tanwari, U. A. (2013). Sol-gel Treatment of driect dyed cotton fabric with aerosil 200 to enhance water repellency and fastness properties. *Science Inernational (Lahore)*, 25, pp. 823-827.

Samiey, B., Cheng, C-H., Wu, J. (2014). Organic-Inorganic hydrid polymers as adsorbents for removal of Heavy Metals ions from solutions: A Review. *Materials*, 7, pp. 673-726.

Sarmadi, M. (2013). Advantages and Disadvantages of Plasma Treatment of Textile Materials. *International Symposium on Plasma Chemistry* . Queensland: International Symposium on Plasma Chemistry .

Schindler,W. D., Hauser, J. P. (2004). *Chemical Finishing of Textiles*. New York: Woodhead Publishing.

Schmidt, H. (1984). Principles of hydrolysis and condensation reaction of alkoxysilanes. *Journal of non-crystalline solids*, 63, pp. 1-11.

Sen, A. K. (2001). Coated Textiles:Principles and Applications. Lancaster: Technomic Publishing CompanyInc.

Sestak, J. and Balogova, L. (2013). *Multifunctional fabric with camouflage print,hydrophobic self-cleaning and antimicrobial nanofinish.* Czech Republic: Nanacon.

Shateri-Khalilabad, M. and Yazdanshenas. E. M. (2012). Fabrication of superhydrophobic, antibacterial, and ultraviolet-blocking cotton fabric. *The Journal of The Textile Institute*, 104, pp. 861-869.

Shateri-Khalil-Abad, M. S., Yazdanshenas, M. E. (2010). Superhydrophobic antibacterial cotton textiles. *Journal of Colloid and Interface Science,* 351, pp. 293-298.

Shanmuggsundaram, O. L. (2007). *Antimicrobial Finish in Textiles.* Tiruchengode: The Indian Textile Journal.

Shen, J., Smith E. (2010) TEAM Research Report.

Siepmann, J., Siegel, A. R., Rathbone, J. M. (2012). *Fundamentals and Applications of Controlled Release Drug Delivery* London: Springer.

Sigma Aldrich (2015). [Online Image]. Available from: https://www.sigmaaldrich.com/united-kingdom.html [accessed March 08, 2015].

Simoncic, B., Tomsic, B., Orel, B., Jerman, I.(2010). *Sol-Gel Technology for Chemical Modification of Textiles*. [WWW] University of Ljubljana. Available from: http://www.utwente.nl/ctw/efsm/advanbiotex/excellenceteam/btomsic/proceedings3.pdf [Accessed 01/07/2013].

Simoncic, B., Tomsic, B., Orel, B., Jerman, I. (2010). Sol-gel Technology for Chemical Modification. In: university of Twente *Surface Modification Systems for Creating Stimuli-responsiveness of Textiles: Workshop Proceedings : [6th Framework Programe ADVANBIOTEX of the EU]*. Twente: University Twente (CTW), pp. 17-34.

Singh and Tomar (2008). *Cell Biology*. Meerut: Rastogi Publications.

Slater, K. (2003). *Environmental impact of textiles: production, processes and protection.* Cornwall: Woodhead Publishing.

Smith, B. C. (2011). *Transform Infrared Spectroscopy.* Boca Raton: Taylor and Francis Group LLC.

Snow, S. S. (2012). *Understanding the Chemistry of healthcare approved cleaner disinfectants.* [WWW] Canadian Association of Environmental Management. Availablefrom:http://caenvironmentalmanagement.com/Sarah%20Snow%20CAEM%202012%209%2010%2012.pdf [09/09/2013].

Song, J., Kong, H., Jang, J. (2011). Bacterial adhesion inhibition of the quaternary ammonium functionalised silica nanoparticles. *colloids and Surfaces B: Biointerfaces*, 82, pp. 651-656.

Srivastava, S. and Srivastava, S. P (2003). *Understanding Bacteria*. India: Springer-Science + Business Media, B.V

Taiz, L., Zeiger, E., Moller, M. I., Murphy, A. (2014). *Plant Physiology and Development* Canada: Sinauer Associates,Inc.

Tang, W-Y., Sussman, M., Liu, D., Poxton, I., Schwartzman. J. (2002). *Molecular Medical Microbiology*. San Diego: Elsevier Ltd.

Tarimala, S., Kothari, N., Abidi, N., Hequet, E., Fralick, J., Dai, L. L. (2006). New Approach to Antibacterial Treatment of Cotton Fabric with Silver nanoparticle-Doped Silica Using Sol-Gel Process. *Journal of Applied Polymer Science*,101, pp. 2938-2943.

Textile Fashon (2012). *Textile Fashion Study* [WWW] Available from: http://textilefashionstudy.com/cotton-fiber-physical-and-chemical-properties-of-cotton/. [Accessed 06/09/ 2013].

Textile Intelligence (2007). *Moisture Management Fabrics for Performance*, Performance Apparel Markets. Available from: http://www.Textilesintelligence.com/tispam/index.cfm?pageid=3&repid=TISPAM&issueid=20&artid=1307 [Accessed 01/09/2014].

Textile World (2000). *Natural Resources: Animal and vegetable fibers for the 21st century*[WWW]Available from: http://www.Textileworld.com/Issues/2000/June/Knitting-Apparel/Natural_Resources [Accessed 12/06/2014].

Textor, T., Mahltig, B. (2010). A sol-gel based surface treatment for preparation of water repellent antistatic textiles. *Applied Surface Science*, 256, pp. 1668-1674.

Tomsic, B., Simoncic, B., Orel, B., Zerjav, M., Schroers, H. (2009). Antimicrobial activity of AgCl embedded in a silica matrix on cotton fabric. *Carbohydrate Polymers*, 75, pp. 618-626.

Topac Inc. (2002). *easySpiral Dilute spiral plater* [Online image]. Available from: http://www.topac.com/spiraldilute.html [Accessed 14/02/2015].

Torry, A. S., Campbell, A., Cunliffe, V. A., Tod A. D. (2006). Kinetic analysis of organosilane hydrolysis and condensation. *International Journal of Adhesion and Adhesives*, 26, pp. 40-49.

Turova, Y. N., Turevskava, P. E., Kessler, G. V., Yanovskaya, I. M. (2002). *The Chemistry of Metal Alkoxide*. Kluvier Academic: Massachusetts.

Ullrich, M. (2009). Bacterial Polysaccharides: *Current Innovations and Future Trends*. Norfolk: Caister Academic Press.

University of OSLO (2006). *Sol-gel Methods* [WWW] University of Oslo. Available from:http://www.uio.no/studier/emner/matnat/kjemi/KJM5100/h06/undervisningsmateriale/10KJM5100_2006_sol_gel_d.pdf [Accessed 09/08/ 2014].

UNEP PUBLICATIONS (2004). *SIDS Initial Assessment Report :[TRIMETHOXY [3-(OXIRANYLMETHOXY)PROPYL]-SILANE]*. [WWW] INCHEM.ORG. Available from: http://www.inchem.org/documents/sids/sids/2530838.pdf [Accessed 16/10/2014].

Urlaub, B., Posset, U., Thull, R. (2000). FT-IR spectroscopic investigations on sol-gel derived coatings from acid-mofified titanium alkoxides. *Journal of Non-Crystalline solids*, 265, pp. 276-284.

Varesano, A., Vineis, C., Aluigi, A., Rombaldoni, F. (2011). Anitmicrobial polymers for textile products. *Formatex*, pp. 99-110.

Vilcnik, A., Jerman, I., Surca Vuk, A., Koselj, M., Orel, B., Tomsic, B., Simoncic, B., Kovac, J. (2009). Structural Properties and Antibacterial Effcets of Hydrophobic and Oleophobic Sol-Gel Coatings fro Cotton Fabrics. *Langmuir*, 25, pp. 5869-5880.

Vihodceva, S., Kukle, S. (2013). Cotton Textile Surface Investigation Before and After Deposition of the ZnO coating by sol-gel method. *Journal of Nano- and Electronic Physics*, 5, pp. 01006-1 - 01006-5.

Vengadaesvaran, B., Arun, N., Chanthiriga, R., Bushroa, R. A., Ramis Rau, S., Ramesh, K., Alshabeeb, E. H. G., Ramesh, S. (2014). Effect of Silver Nano Particles on the Mechanical and Physical. *Journal of Nano Research*, 26, pp. 153-158.

Wang, H., Ding, J., Xue, Y., Wang, X., Lin T. (2010). Superhydrophobic fabrics from hybrid silica and sol-gel coatings:structural effect of precursors on wettability and washing durability. *Journal of Material Research*, 25, pp. 1336-1343.

Wang, X., Yin, Y., Wang, C. (2010). New approach to impart antibacterial effect and improve ink jet printing properties with modified SiO_2 sols containing cationic biocides. *Colloids and Surfaces A:Physicochemical and Enginneering Aspects*, 361, pp. 51-55.

Wakelyn, J. P., Bertoniere, R. N., French, D. A., Thibodeaux, P. D., Triplett, A. B., Rousselle, A-M., Goynes, R. W. Jr., Edwards, V. J., Hunter, L., McAlister, D. D., Gamble, R. G. (2007). *Cotton Fiber Chemistry and Technology.* Florida: CRC Press.

Wei, Q. (2009). *Modification of Textile Surfaces using the Sol-Gel Technique.* Cambridge: Woodlead Publishing CRC Press LLC.

Wienhold, U., Westerwelle. U. (2006). New Routes to Sol-gel systems. *European Coatings Journal*, pp. 40-51.

White, C. W., Monticello, A. R., Clarke, R. D. (2007). *An Organofunctional Silane Microbe Shield Technology: A Broad Spectrum, Non-Leaching Antimicrobial for Protection of Medical Goods and Facilities.* Case Study, Midland: Aegis Environments.

Williams, M. R. (2006). *Triclosan-A controversial antibacterial.* Townsend Letter for Doctors and Patients [WWW] Available from: http://www.beyondpesticides.org/antibacterial/triclosan-williams.pdf:[Accessed 01/06/2014].

Williams, E. W. (2011). *Gold ion coating*. [Online image] Available from: http://link.springer.com/article/10.1007%2FBF03215445 [Accessed 03/08/2014].

Wittke, J. H. (2008). *Scanning Electron Microscope overview* [Online image] Available from:http://nau.edu/CEFNS/Labs/Electron-Microprobe/GLG-510-Class-Notes/Instrumentation/#SEM [Accessed 06/01/2015].

Xin, W. A., Daoud, J. H. (2004). Low temperature sol-gel processed photo-catalytic titania coating. *Journal of Sol-Gel Science and Technology*, 29, pp. 25-29.

Xing, Y., Yang, X., Dai, J. (2007). Antimicrobial finishing of cotton textile based on water glass by sol-gel method. *Journal of Sol-Gel Science and Technology*, 43, pp. 187-192.

Xiu, Y. (2009). *Fabrication of surface micro- and nanostructures for superhydrophobic surfaces in electric and electronic applications.* Ann Harbor: ProQuest LLC.

Xu, J. Z., Tian, L. Y., Liu, L. H., Du, Q. Z. (2014). Cotton fabric finishing with TiO2/SiO2 composite hydrosol based on ionic cross-linking method. *Applied Surface Science*, 324, pp. 68-75.

Xu, L., Zhuang, W., Xu, B., Cai, Z. (2012). Superhydrophobic cotton fabrics prepared by one-step water -based sol-gel coating. *Journal of the Textile Institute*, pp. 311-319.

Xue, L., Li, J., Fu, J., Han, Y. (2009). Super-hydrophobicity of silica nanoparticles modified with vinyl groups. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 338, pp. 15-19.

Xue, C-H., Jia, S-T., Zhang, J., Tian, L-Q. Chen, H-Z, Wang, M. (2008). Preparation of superhydrophobic surfaces on cotton textiles *Science and Technology of advanced Materials*, 9, pp. 1-7.

Yeast Culturing (2009). *Petri dish preparation* [Online image]. Available from: http://liddil.com/beer/culture/method1.html [Accessed 14/02/2015].

Yin, Y., Wang, C., Wang, Y. (2012). Fabrication and characterisation of self-assembled multifunctional coatings deposition on a cellulose substrate. *Colloids and Surfaces*, 399, pp. 92-99.

Yuan, Y. and Lee, R. T. (2013). Contact Angle and Wetting Properties. In: Bracco,G. and Holst, B. *Surface Science Techniques*. Berlin: Springer, pp. 4-33.

Yu, M., Gu, G., Meng, W., Qing, F. (2007). Superhydrophobic cotton fabric coating based on a complex layer of silica nanoparticles and perfluorooctylated quaternary ammonium silane coupling agent. *Applied Surface Science*, 253, pp. 3669-3673.

Young, S. K. (2006). *Overview of sol gel science and technology*. [WWW] Weapons and Materials Research Directorate. Available from: http://www.arl.army.mil/arlreports/2002/ARL-TR-2650.pdf [Accessed 19/08/2011].

Zanoaga, M., Tanasa, F. (2014). Antimicrobial reagents as functional finishing for textiles intended for biomedical application.in synthetic organic compounds. *Chemistry Journal of Moldova. General, Industrial and Ecological Chemistry*, pp. 14-32.

Zheng, Y., Gao, X., Jiang, L. (2007). Directional adhesion of superhydrophobic butterfly wing. *Soft Matter*, 3, pp. 178-182.