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Mechanical Properties of De-Colored Cotton

A Step Towards Textile Reuse

Master's Thesis in Materials Engineering

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CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2019

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Abstract

A successful de-coloration technique would enable reuse of a fabric and subsequently large savings of natural resources. This work presents a de-coloration method with a pH responsive polymer of the pigments Heliogen Blue 15:3 and Pigment Violet 23. The primary focus was to evaluate the method's impact on the textile properties. The method itself involved chemical and mechanical treatments (cationization, sonication and acidification) which ultimately changed the mechanical properties of the used cotton fabric. Through tensile tests and scanning electron microscopy, it was observed that cationization method causes the more damages on the fabric surface than the sonication and acid.

Colorimetric measurements were used to determine the color intensity after pigment removal. Fiber interactions with the pigment were also studied in detail. Methods of measurements for this study included dynamic light scattering, that determined the pigment size and zeta potential measurements, that characterized the pigment surface charge, at the interacting pH. Through these results, pigment surface charge, hydrophobicity and size were considered to be the key parameters that influenced the color removal.

Keywords: color removal, colorimetry, pigment printing, textile coloration technology, textile, pigment adsorption.

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1

Introduction

The lifespan of a textile can today be described as linear with a principle of "take-make-use-dispose" [1]. Designers choose the materials and the manufacturers create the product that the consumer later buys and uses. After consumer's use, it gets disposed. Today's imbalanced consumption and disposal of textiles could be, among many other reasons, caused by the fast transitions between fashion trends and the availability of low-cost-high-fashion garments. This consumption pattern causes stress on the environment throughout the whole textile value chain, from production of raw material and recycling to water pollution and consumption. This is especially true for cotton fibers, that for instance is one of the most water-intensive natural material [2].

Since 1996 the total volume of purchased clothing increased with 40% for the average European consumer. Additionally it has been estimated that low price garments might be discarded already after seven or eight wears, with reasons pending between the item being out of style or having poor appearance and durability. Issues with overproduction have lately also been highlighted, where around 40% of produced textile products will not be sold or fails to reach the retail stores. This further means that a lot of textiles are ending up on landfills long before its actual end-of-life [1].

Industries are gradually moving towards a so called circular economy instead, where material's will not face their end-of-life stage instantly after use. Instead materials are being upcycled, downcycled or recycled to eliminate waste. Upcycling is a term being used when a product's material can be used in another product with an equal or better value, for example a clothing made of recycled PET bottle. Downcycling refers correspondingly to a product being reused in a product with lower value, where for instance textiles can be shredded and used as housing insulation. Incineration is the most common way of recycling, where the material's stored energy is released and generates heat [3]. Donations of clothing to charity is one of the most available options from a consumer perspective. Many of these garments are sorted and shipped to lesser developed countries. In that matter, the problem with over consumption of textiles in a rich country is being passed over to less rich countries. The issue with this concept is that when the textile is reaching its actual end-of-life, the waste management might be poor and the textile will not be recycled but instead end up on landfills [4].

Researchers have agreed on that energy consumption, water and chemical consumption, direct CO_2 emissions and solid waste, are the most concerning environmental impacts of the textile industry [1]. Water is used in most production steps, with or without chemicals, to clean equipment, remove excess dye to assure color fastness or similar. This means that almost all dyes and chemicals need a water bath. Further it is explained that an average sized textile mill, with production of about 8000 kilogram of textiles, consumes around 1.6 million liters of water per day. From this amount it is estimated that 16% of the total is consumed in the dyeing step and 8% in printing step. Residues reaching water streams from these finishing treatments gives the water bad appearance and will prevent sunlight to reach the living organisms. This further impedes the photosynthesis and self purification of the water [5].

As it seems, the environmental impact of a textile product is complex and the intensity differentiate depending on where in the "take-make-use-dispose" value chain. Due to the low-cost and highly appreciated appearances of fabrics blended with synthetic and natural fibers, one can not expect consumers nor manufacturers to start consuming or producing more sustainable and fully biodegradable alternatives. Instead, ways of coming around the problem with reuse and recyclability of textiles opens up for new technologies and business ideas. This report is further presenting a so called "On-Off coloring method", a solution enabling the removal of printed pigment and reuse of a fabric.

1.1 The De-coloring Process

Research have continuously created new and better colorants in order to meet consumer demands with high colorfastness on textiles. Consequently, the durability of the color is too good and nearly impossible to remove from a textile fiber with conventional methods. The most common conventional color removal process is peroxide bleach, which is used when removing impurities and off-white colors from a fabric prior coloring. These impurities are easily removed, meaning that the bleaching is not affecting the fibers much in terms of mechanical properties. However, removal of colorants would require harsher treatments, resulting in a decrease of the fiber's mechanical and physical properties [2]. A research group at Chalmers University of Technology has developed a method which is based on a "switchable" polymer system. The concept simply enables a pigment to change its surface charge by changing pH. In alkali conditions the pigment charges becomes negative (anionic) which will create electrostatic interactions with a positively charged (cationic) textile. When lowering the pH the surface charge will become cationic which causes repulsion and the surface of the cationic textile will repel the pigment. This theory lays the foundation for this report where pigment printing is the coloring technique being used.

1.1.1 Previous Research of De-Coloration Techniques

Attempts of color removal from cotton fabrics have been assessed in another study. Manufacturing of lyocell requires dissolution of cellulose fibers in swelling solvents and through different processes. This study claims that, at the end-of-life of cotton fabrics, they could become new regenerated lyocell fibers. However, it further explains that dyes and finishing agents are limiting the dissolution of cotton fibers and consequently need to be removed. With these motives, the study has tried to remove reactive dyes from cotton fabrics through sequential treatments with acid, alkali and hydro peroxide. Since the expressed purpose of the color removal was to reuse fibers, rather than fabrics, the treatments were considered harsh. Treatments were performed on C.I. Reactive Blue 19, C.I. Reactive Red 228 and C.I. Reactive Black 5. It was demonstrated that the red and black color was easier to remove whilst the blue color was more resistant to the chemical treatments [6]. However, this research area is very small and information has been limited.

1.2 Aim

In terms of energy and water consumption, printing textiles has shown to be more beneficial than dyeing. At the same time, to extend the lifetime of a clothing item would imply even more savings of natural resources. This report explores a new coloring system allowing de-coloration of printed goods, getting one step closer towards the reuse of textiles. The aim is to evaluate if the de-coloring method is reproducible on cotton fabrics without compromising its mechanical properties.

1.3 Objectives

- Discuss which charge ratios of the pigment in acid and alkali conditions are optimal.
- Discuss if pigment particle size influences the outcome of the pigment removal.
- Analyze if the outcome of de-coloring is the same when different pigments are used.
- Determine how the method damages the fibers through tensile test and microscopy.

1.4 Limitations

Along with the experiments of the coloring method, some limitations and set parameters were defined due to the complexity of fiber-pigment interactions. These are stated below.

- Analysis will only focus on two pigment types, Heliogen Blue 15:3 and Pigment Violet 23.
- Printing will be performed on one single fabric, a plain weave purchased from "Stoff och Stil", Gothenburg, Sweden.
- Cationization of the cotton fabric was carried through in a home made reactor and will not be optimized due to the lack of time and resources.

2

Theory

When creating a new textile coloring method it is important to not only focus on the colorant, but also on the properties of the textile fibers. This chapter will explain the most essential characteristics and properties of both pigments and cotton fibers to make sure the reader has enough prior knowledge to understand the analysis of the On-Off Coloring method.

2.1 Cotton Fibers

Examples of natural fibers based on cellulose are cotton, flax, viscose and lyocell among others. They all have in common that they origin from a plant which at a molecular level is composed of cellulose. However, the total amount of cellulose percentage may differ. The original cotton fiber consist of 94% cellulose compared to flax that contain around 71%. They are also classified depending on how they grow, where cotton is a seed fiber and flax a bast fiber. Viscose and lyocell on the other hand are produced from naturally occurring polymers and are not a fiber in its original state. Processing is needed to create the formation of a fiber [2].

The internal structure of a fiber results from polymer assembly. Depending on how they are connected, they can have different length and shape which will differentiate seed fibers from bast fibers. The size and polydispersity of the polymer chains can also be different depending on season, origin of growth and so on. This means that fibers can have the same natural origin but still have different internal structures and surface characteristics. These properties will essentially have an impact on fiber strength and ability to absorb water, among other features [7].

2.1.1 Chemical Composition

Cellulose fibers are composed of thousands of repeating glucose monomers, where each monomer contain carbon, hydrogen and oxygen. In figure 2.1 two repeating glucose monomers are shown and is called a cellobiose. The hydroxyl groups promote the uptake of moisture, colorant and finishing agents that the fiber is exposed to [2].

There are many similarities between natural cellulose fibers. Their molecular arrangements are the same but vary in length and orientation, which gives them different physical structure. Cotton comprises up to 10,000 glucose monomers per molecule in a linear and spiral form within the fiber. The molecular length governs the fiber strength and is an important aspect in terms of quality [2].

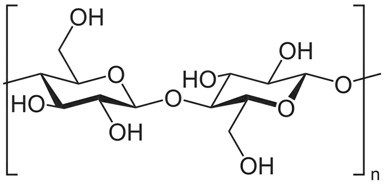

Figure 2.1: Cellulose consist of repeating glucose monomers. Two repeating units are called cellobiose.

2.1.2 Mechanical properties

Natural fibers from a cotton seed consists in average of 30-100 cellulose polymeric chains. Many features of the fibers are important for the overall mechanical properties of the fibers. Other than fiber diameter and length, the fiber orientation with respect to its axis will also affect its mechanical properties. A fiber is more ductile if the fiber has a spiral configuration, whilst if the fiber would be straight it would be more brittle and have higher tensile strength [8].

Crystallinity

As most materials, the cotton fibers contain crystalline and amorphous regions. Amorphous regions have randomly distributed molecular chains, whilst the crystalline regions consist of aligned molecular chains [7]. Through chemical treatments the crystallinity can be tuned, which is generally desired as a more crystalline structure would have higher stiffness and strength [8]. If the crystallinity decreases in a fiber, the strength would decrease accordingly. This is due to the fact that the amorphous regions are composed of molecules that are not aligned with the fiber axis, this means that shearing occurs when an axial force is applied. Cotton fibers are more amorphous than flax fibers, which is the reason of its apparent lower strength in comparison [7]. The elongation would on the other hand instead increase as the molecular chains in the amorphous regions would extend in the direction of the fiber [2][7]. As it is the amorphous regions that absorbs moisture, cotton and flax will be easier to dye than synthetic fibers as their crystallinity is much higher [2]. The higher degree of crystallinity, the more difficult for water to penetrate the closely packed molecules. This is affecting the dyeability of different fibers as water is carrying the dye molecule into the fiber [9]. This is, however, not valid for pigment dyeing.

Ultimate Strength and Elongation at Break

A fiber in tension will elongate and eventually break. In textile testing, this breaking point is known as the elongation at break (%), which is the ratio between the initial length and the length after breakage of a sample [8].

Polymer chains are aligned beside each other in a fiber and will have several contact points. These contact points play an important role in terms of strength as they ultimately prevent sliding. A higher amount of contact points will improve the overall performance of a fiber [7]. Initially when tension is applied to a fiber, these points will elongate first and break. This will weaken the fiber and eventually cause fiber fracture. Before fracturing the fiber will exhibit its maximum strength, the so-called Ultimate Strength (MPa) [8].

2.1.3 Physical Structure

The physical structure of cotton fibers influences the fabric performance and appearance in terms of its ability to be colored. Through different treatments or processes the end-fabric can be easier to color. Based on literature, some specific fiber characteristics are more discussed than others when it comes to coloring [9][2].

Cross-section
The cross-sectional shape of cotton is built up through the growth in its seed. Originally it has a distinct shape of a kidney bean but can become more or less round if subjected to an alkali treatment (mercerization) [2]. This will be explained further in section 2.2.1.

Length
Natural fiber lengths are dependent on type of plant, geographical origin and season. It is characterized by their naturally shorter length, where cotton fiber lengths can range between 1.2-3.8cm. Man-made fibers can be extruded into more complicated cross-sections and would be able to have long and continuous filament lengths. Yarn strength is strongly related to fiber length as the number of surface contact points between the fibers is higher at longer lengths. It creates greater frictional forces and in return a stronger fiber [9].

Yarn Twist
A yarn is constructed by combining several individual fibers through twisting. This twist has a constant and pre-determined direction, either a counterclockwise direction (S-twist) or clockwise direction (Z-twist). The level of twist can be measured by counting the number of twists per unit length. This information can be useful as it impacts density and strength of the yarn [9].

Yarns and fabric are considered porous structures and typically consist of 80% yarn and the rest is air voids. The fiber fineness, yarn twist and weave structure are influencing the level of porosity, that can range between 50-95%. With increasing yarn twist, the yarn compactness increases correspondingly which in return decreases the dyeability. This reduction is due to the smaller amount of air voids present which hinders the penetration of dye into the yarn [9].

Fiber Fineness
In the textile industry, the diameter of a fiber is referred to as the fiber fineness. Natural fibers have in general a non-circular cross-sections, creating an irregular width along its length and a difficulty to measure. Instead there are standardized

systems that are used in order to measure fineness, usually by measuring the mass of a known length or the other way around. Various units are used to describe fineness, where tex and denier are most common. Studies have acknowledged that finer fibers create more lustrous and bright fibers. A greater dye uptake is in return needed to create the same visual depth of shade as a coarser fiber [9].

2.1.4 Surface Charge

By nature, all particles and dissolved substances carries electrical charges in water, where textile fibers in this condition are typically anionic. The charge density is affected by the fiber origin and its composition, where natural fibers in general shows more negative values of specific charge than synthetic fibers. Studies describe the importance of understanding the electro-kinetic properties. By quantifying the required interactions between a non-treated fabric and the applied surfactants, dyes or finishing agents, better quality can be obtained, as the level of charge are providing useful information for optimization of these so-called wet finishing treatments [10][11].

2.1.5 Resistance to Acid and Alkali

How cotton fibers react in alkali conditions is well known and used in mercerization. The fiber swelling, due to the exposure to alkali, is considered advantageous as it improves strength and durability properties in general. The acid resistance of cotton is much lower. Strong acids will degrade the fiber and cause severe fiber strength losses [2].

2.2 Wet Processing

After construction of a fabric it is common to treat it further to improve the appearance, this is usually referred to as wet processing. The processes are selected based on fiber origin and its type of construction (weave, knit), as all fibers may not withstand high temperature, certain chemicals or tension. Examples of wet processes are cleaning, bleaching, sizing, coloring, mercerizing and cationizing, where the latter three are considered in this report [12].

2.2.1 Mercerization

Mercerizing is a strong alkali treatment that is commonly used on cellulosic fiber like cotton, flax, rayon and lyocell [2]. This treatment causes the fiber to swell which aligns the cellulose molecules and changes the fiber shape and its lengthwise twist, known as convolutions. A non-modified cotton fiber has a somewhat flat, kidney bean cross section with several convolutions. Mercerized cotton fiber is shown to be rounder and have less convolutions [12]. The combination of a higher degree of molecular alignment and cross-section uniformity, the fiber breaking strength will increase. More details can be read in section 2.1.1.

The alkali will also rearrange the cellulose molecule and make more hydroxyl groups available to absorb water or water born substances, which is the reason of the increased absorbency. This is also the reason why dyeability is enhanced for mercerized fibers [2].

2.2.2 Cationization of Cotton

Cellulose fibers possess a negative charge when immersed in water. This charge can be reverted through reacting surface hydroxyl groups. These groups will react with the cationizaion agent and change the surface charge from negative to positive. This concept would enable the naturally negative colorant to attach to the cotton fiber through electrostatic forces. It is this principle that shortens the dyeing time and reduces resource usage and cost [13].

Cationic cotton will not require any addition of salts and will increase the dye efficiency to almost 100% on cotton fabrics. Cationization has further proven to reduce the water, energy and chemical consumption. These large savings of resources are related to the increased dye efficiency and the reduced need of wash-off to remove excess dye. Less cleaning of effluents and equipment are also directly related to the increased dye efficiency [13][14].

There are limitations with cationization in terms of waste management and chemical recycling. In order to increase the chemical re-usability the process can be divided into two baths to separate the cationizing agent and the alkali. The function of alkali is to activate the cotton prior cationization [14].

Review: Cationic Process Impact on Fiber Properties

Ideally the cationization should not change the physical structure of the fiber as it could decrease its durability. Fiber property changes can in turn affect fabric appearance and comfort, for instance if the fabric became stiffer. A specific study [14], has investigated the change in physical structure of cationized cotton. In this study a so called two-bath pad-bake process with sodium hydroxide and the cationic agent (3-chloor-2-hydroxypropyl)trimethylammoniumchloride (CHPTAC) was used. Through scanning electron microscopy and x-ray diffraction it was observed that no severe fiber damage or changes in crystallinity were present at the fiber after the treatment. However the tensile strength in both lengthwise and crosswise direction showed a reduction, but was still considered acceptable [14].

Another similar study [15], determined the fabric properties of bleached fabrics that was either mercerized, cationized in a bath containing 50g/l 2,3- Epoxypropyltrimet -hylammonium chloride (EPTAC) or both. The report explained the importance of bench marking the yarn count, mass per unit area and fabric thickness prior chemical treatments, as the treatments promote fiber swelling and fabric shrinkage [15].

Factors Determining Cationic Level

The same study as the one presented above [14], had also optimized its cationization process by observing the effects of not only cationic agent and sodium hydroxide concentrations but also reaction temperature and time. A successful result was characterized by enhanced color strength and fastness but also showed a low effect on fiber properties, compared to conventional methods. Surprisingly, the effect of cationic agent and sodium hydroxide decreased with increasing concentration. A reaction temperature higher than 60°C and a reaction time over 6 minutes was also not necessary as the apparent color strength did not increase [14].

2.2.3 Printing

Colored patterns can be added to fabrics through printing with pigment or dyes that have the consistency of paste or by applying it with special machines, such as screen printing machines. Distinct features of a printed fabric is that the fabric front has a pattern with precise edges, whilst the backside pattern is less sharp and irregular. In contrast, a dyed fabric is dipped in a color bath and consequently receives the same color of both front and back [2].

Digital printing was used in this study. Microdrops of pigment ink are transferred through nozzles of a printer head onto the fabric. A printer with many available colors will provide a great design flexibility. However, providing ink for printing is complex due to the limitations of the nozzle size and each color needs to be evaluated separately [2].

A limitation of using printing is the slow production speed and difficulty with color reproduction, among others. However, it is the only process by which many colorways can be applied at the same time [2].

2.3 Fabric Characteristics

There are many ways of producing a fabric and each method is contributing to the fabric appearance, cost, performance and texture. In an unknown fabric it is easier to primarily determine the starting material. It could be a yarn, film, only fibers or a combination of the three. The main focus in this report is fabrics made of yarns in interlacing patterns, referred to as weave. A weave consists of two components that are interlacing at right angles; warp and weft, with lengthwise and crosswise interlacing directions, respectively. If a yarn crosses more than one yarn, it creates a float. Floats generate an interlacing pattern and different textures [2]. Plain weave was the fabric being used in this study. It has an interlacing pattern of weft threads having an one-up-one-down pattern on the warp threads.

2.3.1 Warp and Weft Count of Woven Fabrics

The warp and weft count may increase after dyeing and finishing, due to shrinkage. The number of warp and weft yarns per square centimeter is an indication of the fabric quality, the higher the count the better fabric quality which in return gives less shrinkage. This is due to a higher cover of the fabric that prevents the fibers from moving and shrinking [2].

2.3.2 Shrinkage

Throughout the manufacturing and finishing of a fabric it will most likely be subjected to tension. Meaning that at the final step of production the fabric's fibers will be set in a unfavorable position. When the fabric is subjected to a higher temperature and wetting, for instance laundry, there is a risk that the fabric will shrink as the fibers will try to return to its natural state. This phenomena is referred to as relaxation shrinkage [7].

Shrinkage can also occur due to fiber swelling which relates to the fiber's ability to absorb water and the amount of yarn twist. A greater amount of yarn twist results in less absorbency, causing the fiber to swell less [7].

In contrast to this, the fibrils and fibers can also be stretched when a fabric is being subjected to tension. Now the fibers will become more aligned, were the convolution will become straighten out. On a micro-level the amorphous regions of the fibrils will elongate and become more aligned, creating a stronger structure [7].

2.4 Coloration of Textile

When coloring textiles, there are two types of colorants that can be used; dyes and pigments. There are distinct differences between the two regarding solubility, chemical and physical structure and color fastness, which this section will explain [16].

2.4.1 Dyes

The main characteristics of a dye relates to its size and solubility. In comparison to pigments, dyes are molecular and soluble in aqueous media whilst pigments are insoluble and of particulate structure. There are many different types of dyes that are all widely being used; acid, basic, direct and reactive dyes. The dyes' individual ions or molecules will have some sort of affinity to the fiber and diffuse into its internal structure. For reactive dyes there will additionally be a reaction with formations of covalent bonds between fiber and dye [16][17].

The color properties are determined by the dyes individual chemical structures. Dyes consists of a molecule with one end being a chromophore and the other the auxochrome. The former is the color carrier. Due to the auxochrome's small size and affinity it is soluble in water and can further penetrate the fiber and bond covalently. Any excess dye will remain unattached to the fiber surface and could cause bleeding onto adjacent materials if not rinsed and removed. Dyes are considered to have greater color strength compared to pigments [2].

Most used dyes are synthetic and each color will be composed of different elements, in some cases even heavy metals. They all have in common their adverse effect on living organisms in the areas of textile coloration. Various treatments exist and will to some extent remove color and its including elements from effluents. These can be classified into physical, chemical and biological treatments. However, combinations of effluent treatments will only remove 85% of the unwanted residues from the coloration. Harmful chemicals as well as presence of sulphur, nitrites and heavy metals like copper, arsenic, nickel, mercury and cobalt in the dyes, make the treated effluent water toxic. In total the colors, oily scum and presence of other by-products, gives bad appearance to the water in terms of smell and transparency. The latter one is mostly concerning as the color prevents sunlight to reach the marine living organisms that are necessary for the photosynthesis and self-purification mechanisms [5].

In the coloration process with reactive dyes, large portions of salt are required. By nature, the anionic charge of cellulose repels the anionic dye. As a consequence, the dye auxochrome tends to remain in the aqueous solution rather than attaching to the cellulose hydroxyl group. The salt temporarily screens the charges and reduces the repulsion allowing the dye to react. The amount of salt needed is strongly dependent on the desired color shade. The salt concentrations can be up to 100 g/L for dark shades and is considered as one of the most toxic chemicals released in nature in the textile production [17].

As explained previously, all dye molecules will not attach to the fiber structure and need to be removed. The additional steps of washing fabric and effluent are very costly and are considered a huge limitation in the dyeing process. This is mainly due to the dye's high degree of water solubility. Chemical processes are in return needed to de-colorize and could also create harmful byproducts for wildlife close to the water streams [17].

2.4.2 Pigment

Pigments are defined as colored, black, white or fluorescent solid particles that are either inorganic or organic, where the former is more commonly used. Both are insoluble in any aqueous media, which means that its crystalline structure will be retained and the particles will instead be finely dispersed in the application media. Due to its larger particle size and insolubility, it will not diffuse into the fiber but instead adsorb on the fiber surface [16]. The pigments may carry charges due to attraction of hydrophobic tails from an anionic dispersant, the hydrophilic anionic heads being positioned so that they face the water [17]. This will more carefully be described in section 2.5. In conventional pigment application methods, a binder is necessary to permanently bond the pigment to the fiber. The reason is that the pigment particles will have no affinity to the textile fibers itself naturally [2].

The most distinct differences between organic and inorganic pigments are related to particle size, cost and toxicity. Organic pigments are smaller than inorganic pigments and they are synthetic. In general, they are also harder to disperse and have a higher cost. Some inorganic pigments are banished due to their toxicity from heavy metals, which makes organic pigments more favorable [18].

Advantages of pigments include fewer sustainability issues compared to dyes. As per example, no wash-off or rinsing is required to remove excess pigment from fabric or water effluents, due to its binder in the conventional application methods. Pigments larger size also makes it easier to remove as it can be flocculated and separated. It is also considered to be quick, simple and economical. Some downsides are also present. It has lower color strength compared to dyes, deep shades are possible to obtain but requires higher amounts of pigment. [2]

2.5 Surface Chemistry of Coloration Process

In this report, the interface between fiber and pigment is mainly studied. But in order to understand the phenomena causing attraction and repulsion between the two at different pH, the pigment formulation built-up is essential to understand as well. This section will describe the interface of liquid-pigment and fiber-dye. To clarify, most literature within the subject of textile coloring is based on dyes, but can generally be applied to pigments as well. To not bias any information from literature, the subsection describing the latter interface will be named "fiber-dye interactions" accordingly.

2.5.1 Surfactant

The used pigment in this study is hydrophobic by nature. This means that addition of wetting agents are needed in order to create a fine pigment dispersion, which is generally desired in coloring. Surfactants are used as wetting agents and as previously explained, they have a hydrophobic tail and an hydrophilic head. These will adsorb at the pigment surface and thereby changing the surface chemistry, resulting in increased solubility and dispersability [19].

Surfactant molecules consists of a hydrophobic tail and a polar hydrophilic head that could be ionic or non-ionic. Depending on the polar charge it can further be divided into anionic, cationic, nonionic or zwitterionic surfactant. Before the surfactant enters the liquid-pigment interface it will be positioned at the air-water interface and create a so called monolayer at the surface. When the surface is covered, the excess surfactant will strive to be placed in a energetically favourable position, which in this case is in the liquid-solid interface. The polar head will be pointing into the water, whilst the tail points towards the surface of the particle, when a hydrophobic surface is desired. The obtained structure is called a micelle, which will be created at a certain surfactant concentration called the critical micelle concentration (CMC). This value is specific for every surfactant and when continuing to increase the amount of surfactant after CMC, the number of micelles will increase accordingly [19][20].

2.5.2 Electrosteric Stabilization

If pigment particles would be added to an aqueous solution they would naturally adhere to each other and coagulate, resulting in large aggregations. Preventing agglomeration of the particles is important in order to create a stable dispersion. A system based on solid particles in a liquid media is called a suspension [19]. There are three ways of stabilizing a suspension, called electrostatic, steric and electrosteric stabilization, illustrated in figure 2.2 a)-c) respectively.

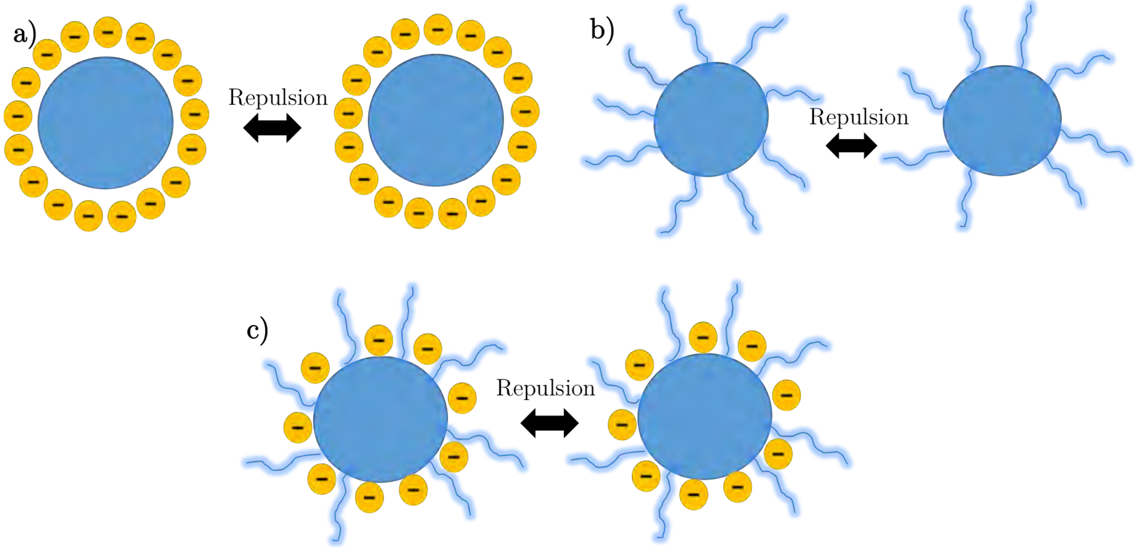

Figure 2.2: Variations of stabilization mechanisms in a suspension. a) Electrostatic stabilization. b) Steric stabilization. c) Electrosteric stabilization.

An electrostatic stabilization is created by adding a surfactant with a charged polar headgroups. The tail is hydrophobic and will attach to the particle surface whilst the head, carrying the charge, points out into the water. The charge will generate repulsive forces between the particles and prevent agglomeration. The steric stabilization on the other hand, is based on non-charged, hydrophilic surfactants that prevents the particle's surfaces to come too close. Commonly the mentioned principles are combined and leading to the so called electrosteric stabilization, see figure 2.2 c) [19].

2.5.3 Fiber-Dye Interactions

It is difficult to explain the exact intermolecular forces acting between the atoms, ions or molecules of a textile fiber and dye and it is an area that has been researched widely. The basic reason behind this is the large variety of available functional groups in different dye and fiber molecules (i.e. hydroxyl-groups on fibers). When evaluating a certain dye and fiber interaction, complex computational models are used that only can feature some of the fiber or dye characteristics, making the results approximate [9].

This means that it is not only the fiber-dye interactions that need to be studied in order to understand it, but also the dye and fiber properties separately. In cotton, or any other cellulose fiber, there are hydroxyl groups available in every polymer chain. This configuration of the fiber molecules enables hydrogen bonds to be created between hydroxyl groups, not only within the same molecular chain, but also with adjacent chains. The hydrogen bond will occur in one plane which naturally develops van der Waals forces. These bonds will alter the durability properties of the fiber, but also affect the chemical properties in terms of water absorption and in return the dyeability. The more tightly connected polymer chains are, the harder it is for a water molecule to penetrate the fiber [9].

This available information points out that there will more or less always be more than one type of force interacting between fiber and dye. Hydrogen bonds and Van der Waals interactions have been mentioned but covalent bonds can also be present, depending on colorant. A few of these interactions will be described briefly [9].

Ionic Interactions

These bonds appears between charged ions, molecules or particles and can be either attractive or repulsive. An ion-ion interaction is strong and the more available charges, the stronger the ionic bond is. From Coulomb's law, the resulting force (F) created by two different surfaces ($Q_{Pigment}, Q_{Fiber}$) can be calculated, see equation 2.1. Additionally, electrostatic interactions are in general considered long range and operate at longer distances than for example van der Waals. According to Coulombs law, the interactive force is inversely proportional to the square of the distance between the charges (r). The remaining variables, ϵ_0 and ϵ_r, are the permittivity constants of vacuum and the medium, respectively [9].

$$F = \frac{Q_1 Q_2}{4\pi\epsilon_0\epsilon_r r^2} \tag{2.1}$$

van der Waals Interactions

Van der Waals forces are considered the weakest of all intermolecular forces. In larger amounts it plays a significant role in the total attraction force between two elements, however. These forces appears in non-polar molecules when a temporary electron "cloud" will be induced in one part of the molecule/atom creating, for example, a positive charge. On the corresponding side of the molecule/atom there will be the opposite charge. Generally, van der Waals interactions can be related to the hydrophobic character of molecules. Pigments that are hydrophobic will have a strong tendency to stay with the fiber, through van der Waals interactions [9].

Covalent Bonds

Pigments and dyes are two different things, which was stated previously, this means that no covalent bonds will be present in the bonding between fabric and pigment this study's coloring process. These bonds are typically considered as strong. Covalent bonds are formed when dyeing or printing with reactive dyes, creating permanent interaction between fiber and dye [9].

2.6 Characterization Methods

When characterizing the mechanical, physical and chemical properties of fabric in this On-Off coloring concept, different methods will be used. This section will give information about these methods and justify why they are used.

2.6.1 Tensile Testing

A tensile test is a method that measures strength and extension of either a fabric of a single fiber, commonly referred to as stress and strain respectively. All fibers have their differences in terms of strength and extension as it is dependent on chemical composition and internal structure of the fiber. For instance, if a fiber is composed of less oriented molecules (more amorphous) it will stretch in tension as the polymer chains will extend in the direction of the tension. The more stretched the polymer chains are, the more crystalline fiber resulting in a higher strength but lower extension [7].

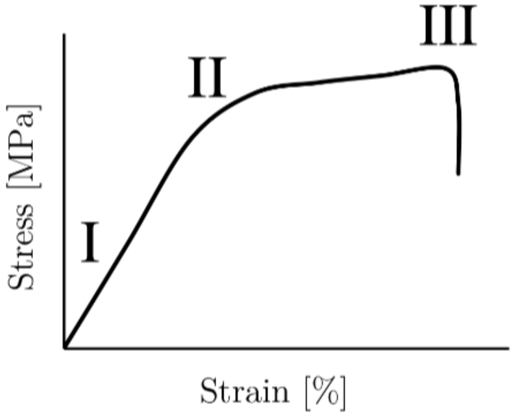

Figure 2.3: Stress-strain curve illustrating the different key stages. I) Elastic region. II) Yield point. III) Breaking point.

In a stress-strain curve, different stages of the extension can be observed, see figure 2.3. Region (I) is referred to as the elastic region, meaning that the extension is linearly dependent of the stress and is completely reversible when the load is removed. In this region Hooke's Law is applied and the textile's Young's Modulus (E) can be calculated, see equation 2.2. At the so called yield point (σ_y) (II) the fibers becomes completely stretched and contact points between the fiber molecules begin to break simultaneously. With less contact points more extension is allowed. This state is not reversible and the fiber has now permanent damages, also resulting in a declining strength. At the end of the curve (III) there will be a great strength reduction, this is at the point where all fibers are broken and is referred to the extension at break and breaking strength [7]. The area underneath the stress-strain curve is the energy required to break the fibers and is an indication of the fracture toughness.

$$E = \frac{\sigma}{\epsilon} \tag{2.2}$$

When discussing stress-strain curves, one can refer to materials as brittle or ductile. A brittle structure has in general high breaking strength, steep elastic region and short elongation to break. Ductile structures on the other hand, will have a longer elongation to break, lower breaking strength and more flat elastic region.

2.6.2 Particle Charge Density

Electro-kinetic properties of the textile will in this report be characterized by its specific amount of charge (eq/g). This property is primarily dependent on material surface, amount of impurities, finishing and/or dyeing [10][11]. It can also depend on chemical fiber composition, microstructure, porosity and fiber swelling capacity [10]. This means that fiber charges vary from fiber to fiber, depending on its surface properties. The electro-kinetic properties will indicate the fibers tendency to adsorb surfactants, dyes or other finishing agents.

A sample of fibers in water (milliQ) will be surrounded by counter-ions, with opposite charge. When adding solution to the Particle Charge Density (PCD) measuring cell, dissolved sample molecules will attach to the plastic surface of piston and measuring cell wall whilst the counter-ions are relatively free in the liquid. When starting the PCD a piston will start to move up and down, creating a motion of liquid. The counter-ions will be forced to completely separate from the molecules that are attached to the plastic walls. This apparent difference of potential will be measured by the instrument and be displayed in millivolt. Titration with a polyelectrolyte with known charge density, will subsequently neutralize the charge. A zero value would indicate that a neutral charge has been reached and no counter-ions are attached to the molecules at the walls anymore. The rate of titration may impact the results and if several experiments are to be compared, titration should be performed identically [26].

2.6.3 Zeta Potential

Pigment surface charge will be characterized by ζ-potential measurements. It simply determines the particle's surface potential obtained at a distance outside the surface of the particle, referred to as the slipping plane. The $\zeta-$potential indicates the level of attraction or repulsion between the fabric and the pigment that can be obtained, but also gives an indication of the electrostatic stabilization of the pigment. A small ζ-potential could increase the risk of pigment aggregation and flocculation [21].

2.6.4 Dynamic Light Scattering

Dynamic light scattering (DLS) measurements are used to make sure that the pigment formulation is stable, with no large agglomerates. It measures particle sizes in the nanometer range by exposing a sample to a laser beam onto a sample. The laser light interact with the particles in the sample and scatter. A photo detector captures the scattered light and analyzes its scattering angle and intensity [22]. Through the Stokes-Einstein relationship 2.3 the particle sizes are revealed [20].

$$D = \frac{k_B T}{3\pi\eta d} \tag{2.3}$$

D is the diffusion rate that origins from the Brownian motion of the particles and that causes scattering. k_B is Boltzmann's constant, T is the absolute temperature and d is the so called hydrodynamic diameter of the particle [20]. The particle sizes are typically not of identical size. The polydisperisty index (P.I) is indicating the size particle distribution in a given sample.

2.6.5 Colorimetry

The color perception of a human eye is fairly good, but to be able to notice small color differences a color measurement instrument is needed. To be able to express a colorway numerically, a three dimensional (L*a*b*) coordinate system was determined by the Commission Internationale de l'Eclairage (CIE). A color disc, as the one presented in figure 2.4 shows that the most saturated colors are at the far edges, with a maximum value of ±60. The a* values relates to the red/green color intensity and b* to the yellow/blue. As per example, a negative b* value would indicate a blue color. The L*-value is indicating the level of whiteness and runs in the z-direction from 0-100. The higher value, the lighter the color is [23].

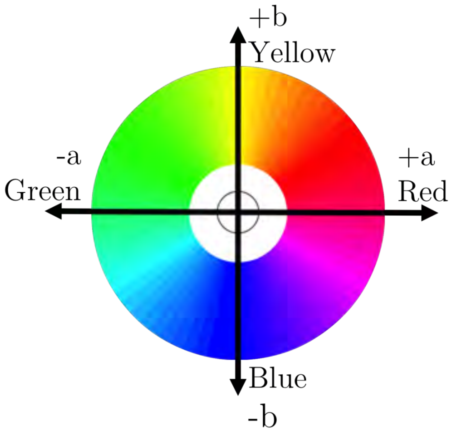

Figure 2.4: Color schematics illustrating the a* and b* values. L* is the z-direction in this coordinate system.

3

Hypothesis

There are many influencing factors that can govern the success of the de-coloring, as the theory chapter has emphasized. In general it is dependent on the chemical, physical and mechanical properties of solely the fiber, the pigment or both. Four hypotheses have been created for the sake of this report, and will be described and explained in this chapter. First, a more detailed description of the pH responsive pigment will be presented.

3.1 pH Responsive Polymer

The On-Off coloring method is based on a "switchable" polymer, where one pigment particle alone is coated with different surface active compounds to enable this functionality. The non-polar surface active compounds are used as wetting and stabilizing agents, whilst the polar ones are carrying the charges that will be at play at different pH and enable the "switches". This will be explained further with illustrations from figure 3.1 as supporting information.

Under alkaline condition (pH 12) the pigment will have a negative charge and is the used condition when coloring a cationic fabric. When lowering the pH to acidic conditions (pH 3) the pigment becomes positive and consequently repels from the positively charged textile surface, see figure 3.2. At neutral pH there will be positive and negative charges present. At this point the pigment formulation will be unstable and flocculate due to the lack of repulsive electrostatic interactions.

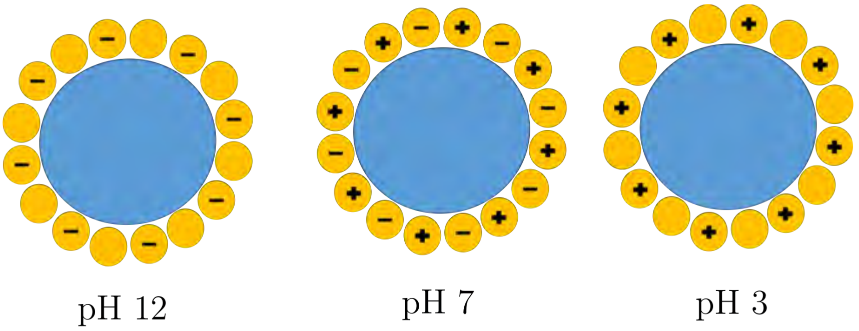

Figure 3.1: The pH responsive pigment showing its electrostatic forces at different conditions.

To further clarify, the interactions between the pH responsive polymer and the fiber surface are based on electrostatic forces, i.e attractive and repulsive forces. A surfactant stabilizes sterically the pigment and prevents agglomeration prior printing and will not have a central part in this report. This clarification naturally leads to the two main hypothesis; the pigment character and the pigment electrostatic charge dependence on the ability to de-color in the de-coloring method.

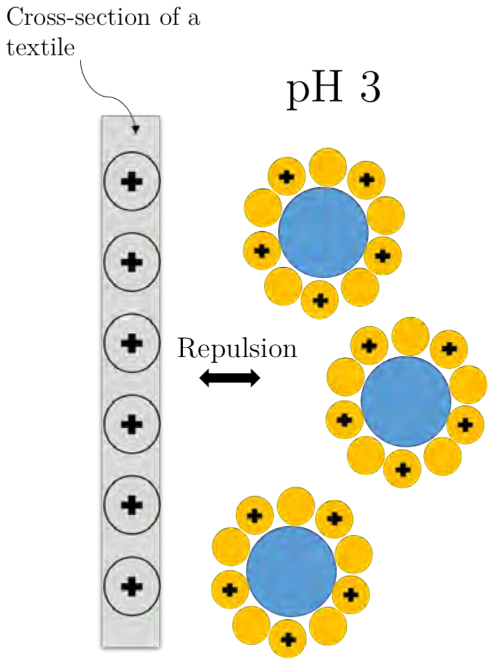

Figure 3.2: The repulsive force causing the pigment to repel from the textile surface.

3.1.1 Pigment Charge and Hydrophobicity

The interactions that are believed to play the comprehensive role in the On-Off coloring method are electrostatic and van der Waals. The strength of the former one is governed by the obtained surface charges of the pigment and fiber. For instance, a high apparent amount of charges on fabric and pigment would lead to stronger electrostatic forces (F) according to Coulomb's law. As it has been explained in 2.5.3 the interactions are long range, and attraction or repulsion between two surfaces can appear at long distances. The interaction is also switchable, the amount of negative charges present at the surfaces will not have a great importance if the corresponding positive charges under acidic condition are equal or greater, see equation 3.1.

$$q_{positive} \geq \mid q_{negative} \mid \tag{3.1}$$

However, as van der Waals interactions are expected to be present it will interfere with this explanation. These interactions will appear unconditionally and solely by the nature of the surface chemistry of the pigment. These interactions are considered short range, and will be present at very short distances between pigment and fibers.

Supposedly a combination of ionic and van der Waals interactions will cause strong attractive interactions and make the fabric harder to de-color as the repulsive forces, caused by positive charges, are not strong enough. To create a repulsive force between pigment and fiber in the acidic condition, the strength of both interaction forces must be overcome.

This is possible by designing the pigment to have dominant positive surface charges than the absolute value of the negative charges, as in equation 3.1 and figure 3.3. However, taking into account that every pigment color has different hydrophobicity, no universal formulation is expected to work.

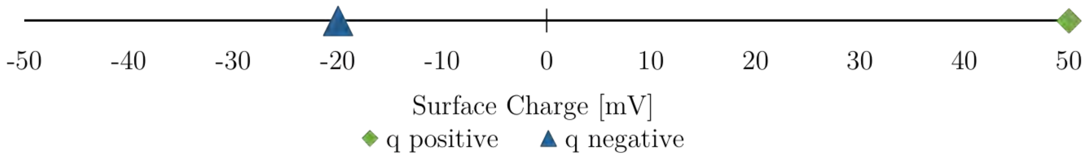

Figure 3.3: Visual illustration of how the charges are distributed.

Given that the van der Waals interactions are considered weak, external mechanical forces may be enough to remove the residue pigment from the fiber surface. This principle is also a part of the produced methodology of the On-Off coloring concept, where sonication of the colored fabric will assist the removal process.

3.1.2 Particle Size

Another occurring hypothesis, is that the pigment size impacts on the de-colorability. Pigments are, compared to dyes, large and will only adsorb on the fiber surface, whilst dyes are small enough to diffuse into its internal structure. However, as mechanical action from a sonicator is applied on the fabric, the pigment particles may reduce in size. With continuous mechanical action the small sized pigments, or perhaps all sizes, might be pushed further into the weave or fiber structure, making it harder to remove with the selected methods.

3.1.3 Fiber's Mechanical Properties

The combination of cationization, sonication and acid environments will of course damage the fibers to some extent. Theoretically, the acid will cause fiber degradation and would perhaps reduce the strength significantly. What is interesting to investigate is where in the system's flow the treatments are most harmful. This is the main aim of the study.

4

Materials and Methods

4.1 Materials

Both fabric and pigment was chosen due to their commercial availability. A plain weave fabric containing 100% cotton was purchased from Stoff och Stil, Gothenburg, Sweden. The textile had been bleached previous to the purchase. According to ASTM D3775-07 Standard Test Method for Warp (End) and Filling (Pick) Count of Woven Fabrics, the textile has a yarn count of warp $29.04cm^{-1}$ and weft $23.6cm^{-1}$. The fabric was washed twice in a washing machine prior to experiments, once with detergent and second time with water only.

The organic pigments were ordered from SunChemical and had the composition of Heliogen Blue 15:3 (HB) and Pigment Violet 23 (PV), see figure 4.1. Other chemicals, as the cationic agent (technical $\geq$ 90% calc. based on dry substance) (glycidyltrimetyl ammonium chloride) came from Sigma Aldrich. Surface active compounds for pigment formulation were PEG200 (Fluka), Polyethylenimine (Aldrich), TEGO Dispers 556 (Evonik) and Ethylan 1008 (Akzo Nobel). For de-coloring hypophosphorous acid (50% w/w) (Alfa Aesar) and Berol 535 (Akzo Nobel) were used. All chemicals were available at the Department of Chemistry and Chemical Engineering, Chalmers University of Technology.

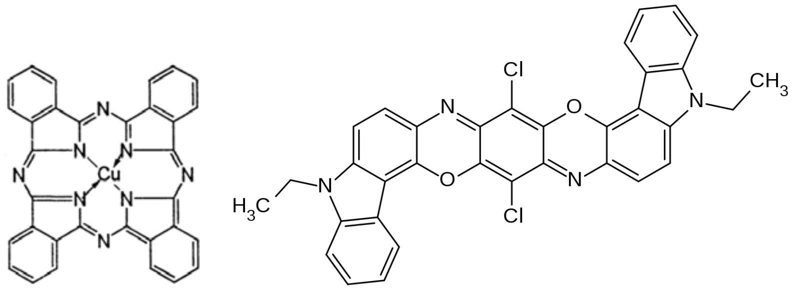

Figure 4.1: Chemical structure of Heliogen Blue 15:3 and Pigment Violet 23.

4.1.1 Pigment Formulation

The design principle is based on the ability of a pigment to be negative at pH 12 and positive at pH 3. As an initial step, characterization of the original pigment particle charge will be determined through zeta potential measurements. The addition of surface active compounds were chosen based on if the charge appeared anionic, cationic or natural. The Heliogen Blue and Pigment Violet pigments were prepared in batches of 40 grams. The pigment concentration was set to 2.0 wt%.

4.2 Cationization of Cotton

The cationization method was established based on a previous study [24] with modification. Schematics of the reaction scheme can be viewed in figure 4.2. The cotton fabric was immersed in sodium hydroxide (0.22 g/l) for 10 minutes at room temperature. In the meantime another bath was prepared with acetone and glycidyltrimetylammonium chloride (82:18). After mercerization, the cotton fabric was added to the cationic solution, where it was stirred (100 rpm) for two hours at 60 °C. Afterwards the fabric was placed in aluminum foil and placed in an oven for another two hours at 80°C.

After cationization, the fabric was washed twice under stirring magnetic stirrer, once with detergent (2g/l) and water and a second time in water, in 40 °C. Water was not circulating readily whereby it was rinsed by hand for one minute to make sure the detergent was completely removed.

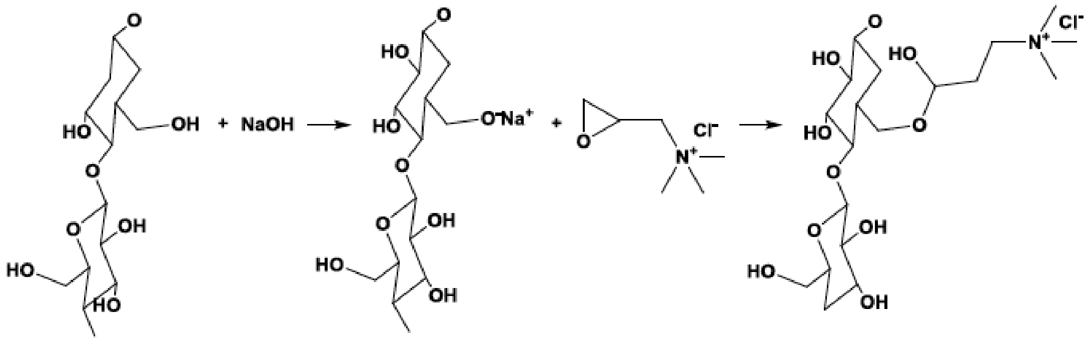

Figure 4.2: Cellulose reacting with sodium hydroxide and glycidyltrimetyl ammonium chloride (GDTAC), respectively.

The level of cationization was verified visually by soaking a smaller piece into an aqueous solution of anionic dye (methyl orange) at pH 10. Lighter orange would indicate less reacted cationic agents. The cationization was also confirmed by colorimetic and particle charge density measurements.

4.3 Pigment Printing

A fabric printer constructed by FabricZoom (USA) was used. The printer head was a RICOH GH2220. Maximum resolution of 150 dpi (dots per inch) could be obtained [25], and corresponds to medium to high color quality on textile.

The provided software enabled experimenting with color intensity by optimizing three different parameters. It simply determines how much ink that would be present in each pixel where value 1<value 2< value 3. The printing program was created manually in order to have a constant color intensity and rectangular dimensions throughout the experiment. The combination of 25-35-50 generated a good color intensity that corresponded well with the maximum. The maximum color intensity was confirmed by dip-dyeing a small piece of fabric. The printing operation including pulse width and pulse delay was set up automatically by the printer. Settings can be viewed in table 4.1.

Table 4.1: Printer settings

Color intensity	25-35-50
Dimensions of printed object (HxW)	31x80mm
Printer speed	6
Number of passes	4
Pulse width	25 nsec
Pulse delay	$25\mu s$

4.4 De-coloring of Textile

Hypophosphorous acid (8 drops/l) and an alcohol ethoxylate surfactant (2ml/l) were added to a 60 °C water bath. The sample was soaking for ten minutes prior sonication with Vibra-Cell 160 processor VC505 at 50% amplitude. The temperature was not kept constant. The tip of the sonicator was placed one centimeter away from the textile surface and was moved back and forth over the textile four times. Its position was changed every ten seconds.

4.5 Analytical Techniques

In the On-Off coloring process, the fiber and fabric's physical properties are expected to change. One of the characterization methods that will be used for identification of these changes are scanning electron microscopy (SEM). Visual inspection of the conducted images will benchmark the original state of the fiber and reveal potential fiber damage and the adsorption of pigment. Tensile testing will reveal the fabric's performance before and after the removal of pigment and the damages the sonicator and acidic condition are causing.

4.5.1 Scanning Electron Microscopy

Pieces of textile were mounted on a metallic holders and then platinum sputtered with EMITECH K550X-J25 for two minutes. Images were conducted with Leo Ultra 55 or JEOL JSM-7800F Prime at three randomly selected places, on each sample.

4.5.2 Particle Charge Density

A total fiber weight of 0.1 gram was extracted from the fabric and cut into the length of 1-3 millimeters. Right before measurements, the fibers were placed in the PCD measuring cell and dwelled in ten milliliter of water (milliQ).

The method was established with inspiration from the operation manual provided by the PCD manufacturer [26]. Polyelectrolyte titration was carried out manually on a non-treated fabric and a cationized fabric. The streaming current (mV) was noted every five minutes followed by $40\mu l$ of cationic polyDADMAC (0.0001N) or anionic sodium polyethersulone (0.0001N), respectively. These steps iterated until 300 mV of opposite potential was obtained. This measurement was repeated three times.

With information about polyelectrolyte consumption (V) and its concentration (C), the specific charge quantity (q) could be calculated, see equation 4.1. The following results was used as a verification method of the obtained level of cationization. A high specific charge would indicate a higher level of cationization.

$$q = \frac{V \times C}{m} [eq/g] \tag{4.1}$$

According to the previous study [10], the measurement of streaming potential is well satisfactory and mostly used when measuring fibers. One of the strongest motivating factors is that the result is linearly dependent on the pressure of the piston, making it reproducible and changes in electrolyte solution will not have any effect. The method will determine the fiber specific surface charge (q) in its original state and after cationization by the use of a particle charge detector (PCD 02) constructed by Mütek. There are no available calibration methods, which means that there are no absolute values. Provided that the procedure for each fabric is carried out identically, the results should be comparable.

4.5.3 Tensile Test

A tensile test was performed on specimens prepared according to the modified grab test, with dimensions inspired by ASTM D5045 illustrated in figure 4.3. The modified grab test [27] is used particularly for high strength fibers, it will create stress concentration and cause fiber breakage at its slits. The test was only conducted in the warp direction.

The method was based on the fact that the fabrics ravel easily, which was prevented by this sample preparation. Another reason was the risk of fabric slippage in the available clamps in the machine that was used. Samples were first cut and then threads were raveled from the sides. This preparation was made in order to ensure exact dimensions and uniform load distributions. To localize the stress concentration, the sample was cut in the middle of the gauge length, creating a waist of ten millimeter, which was considered the width.

An Instron 5565A was used in order to evaluate the mechanical properties of the fabric. It was equipped with a 5kN load cell and pneumatic clamps (25x25mm) pressurized the sample with a pression of 5 bars. Due to previous case of slippage and breakage at clamp, the surface area of the clamps were modified. Sandpaper (25x25mm) were glued together, creating surface roughness facing fabric and clamp surface, which enabled successful testing and no slipping. Rate of extension was set to 100 mm/min. Testing was performed on samples which had been conditioned at 60% relative humidity more than 12 hours, at room temperature. The measurements were repeated three times each per fabric (non-treated, cationized, de-colored) and the total success rate was 100%. The method was also used to benchmark the sonicator's impact on the fabric's properties.

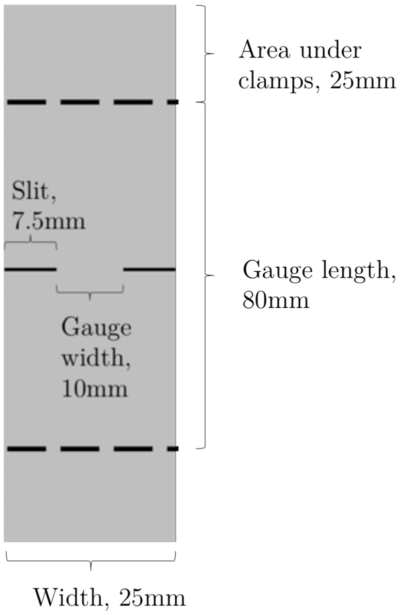

Figure 4.3: Sample dimensions was inspired by ASTM D5045 grab test.

4.5.4 Colorimetry

Colorimetric measurements were performed with a Konica Minolta Spectrophotometer. Five measurements were made on each sample on different spots (non-treated, cationized, pigment printed, de-colored) to verify that similar color intensity was obtained for all samples, but also to understand how much whiteness had been retained after decoloring. The level of cationization was verified by PCD measurements as stated above, but also visually through immersing the cationized fabric in an methyl orange pH indicator. A higher L* value would indicate higher cationization degree.

4.5.5 Dynamic Light Scattering

Measurement of the particle size was controlled with dynamic light scattering measurements. It was performed on a Beckman Coulter N4 Plus Submicron Particle Analyser. Each pigment formulation was diluted with 0.001M sodium hydroxide (pH 12) or hypophosphorous acid (pH 3) until a particle intensity below 1.5×10^6 counts per second was reached. Ideally the samples should have an intensity between $1 \times 10^4 - 1 \times 10^6$ counts per second but as the pigment particles adsorb the laser light, the intensity can be slightly higher. The measurement was carried out at an angle of 90°for 120 seconds.

4.5.6 Zeta Potential

Zeta potential measurements was performed on a ZetaPALS system (Brookhaven Instruments). The same samples from the DLS measurement were used to characterize the charges in basic in acidic condition. Each measurement consisted of three cycles and the mean value with standard deviation was noted.

5

Results and Discussion

During the progress of this report and the evaluation of the de-coloring method it became clear that the coloration of textiles, in general, is complex. Pigments have different chemical structures which influence surface charge, level of hydrophobicity and pigment size among others. These observations led to the previously defined hypotheses and further the comparative studies; effect of pigment charge, effect of pigment hydrophobicity and effect of pigment charge and size.

There are two main treatments in the presented coloring method, cationization and de-coloring with sonication in an acid bath. Another focus area has therefore been to understand to which extent these treatments damage the fibers most. This has been evaluated in a separate study and will be discussed accordingly.

5.1 On-Off Coloring

The de-coloring method relies on a successfully performed cationization of the cotton fabric. In order to verify that the surface charges of the fiber changes previous to the printing operation, charge density measurements were performed with a so called particle charge detector. The non-treated fabric had a surface charge of -103.51 ± 0.28 $\mu eq/g$ whilst the cationized fabric had a surface charge of 102.4 ± 1.53 $\mu eq/g$, which confirms that the cationization was successful. The textile surface was slightly damaged and weakened by the cationization, this could be observed by SEM and results from tensile testing. More about this is reported in section 5.2.

The pigment called Heliogen Blue (HB) was the initial color that was used in this project. It was anionic by nature, meaning that no negative surface active compound was needed to cover the pigment. Removal of both HB1 and HB2 was challenging and the final color shade can be viewed in figure 5.1.

The de-coloring technique was also performed with Pigment Violet (PV) which had a neutral surface charge. This was the original pigment that was used to design the surface of this pH responsive pigment. As the PV pigment does not carry any charge by nature, surface active compounds of positive and negative charges were applied. The cationization was verified with a methyl orange pH indicator. As can be viewed in figure 5.1 the cationization appears weaker in its orange color intensity, which is an indication of a lower obtained cationization.

Light shades of both colorways would still be visible after the de-coloring of HB1, HB2 and PV. Due to these appeared difficulties in the de-coloring of the plain weave, it was out of interest to understand how the pigment was dispersed based on the amount of printing sequences.

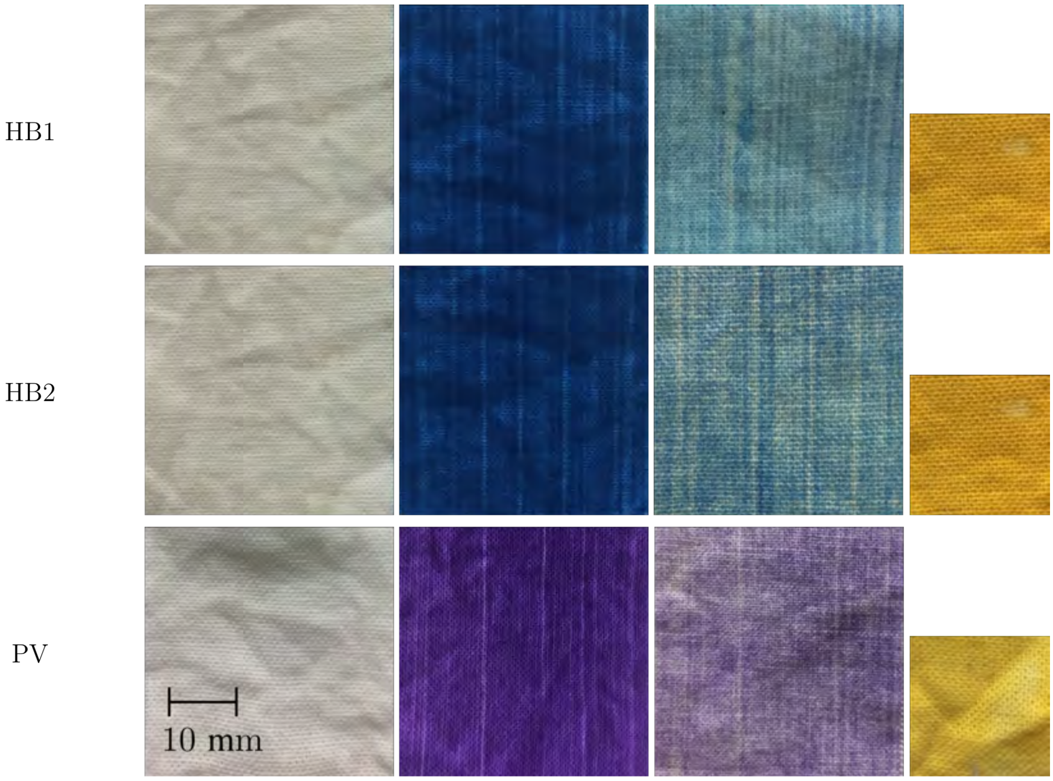

Figure 5.1: Three printing operations have been evaluated in this report. Fabrics in the order from the left; cationized; printed; de-colored; verification of cationization with methyl orange on the right image.

5.1.1 Pigment Dispersion on Fiber

To be able to create a sufficient color depth, each textile was printed four times. Through SEM it became clear that the more pigment that is applied, the more porous the surface is. In figure 5.2 a-c) the porosity of fabrics that have been printed one, two and four times respectively, can be seen. This fact leads to the question if it is the three last layers of pigments that are being stacked on top of each other that gets removed in the de-coloration. Just by visual observation with eyesight a clear difference in color intensity could be seen between a sample that had been printed once and another that had been printed four times and then de-colored. This implies that pigment from the first printing sequence is also being removed which was also confirmed in conducted SEM images, see figure 5.2 c-d). When collecting the images of the de-colored samples, the pigments were hard to find as they were not located on the plain surface of the fiber, but rather on the side. This is also an indication that the concept of the de-coloring method works, but the color intensity of just a few pigments can generate a visible shade for the human eye.

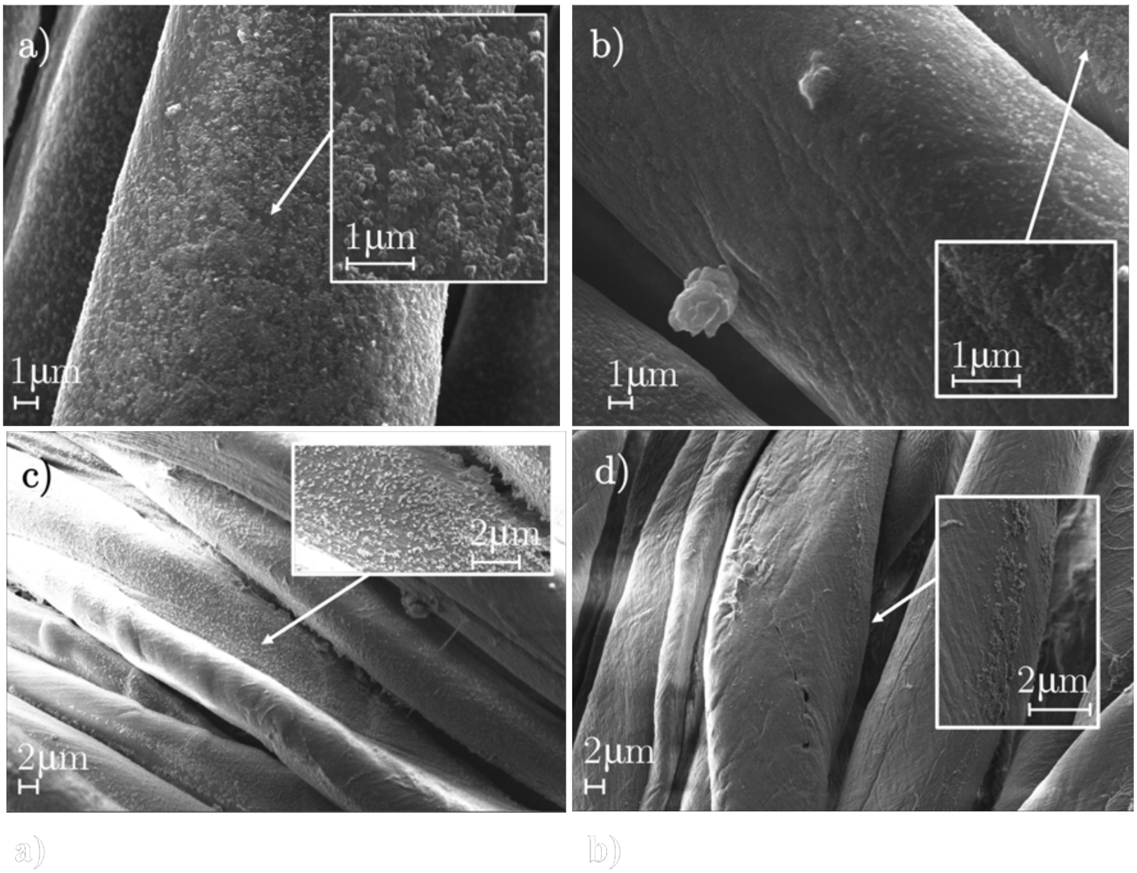

Figure 5.2: Porosity seems to increase with the number of times the fabric gets printed. a) Pigment porosity and dispersion after being printed two times and b) four times c) once and d) four times and then de-colored with four repeated sequences of sonication.

5.1.2 Effect of Pigment Charge

The cationization was performed in different batches and every fabric could have small deviations in terms of cationic surface charge. However, two printing sequences had identical level of cationization as they had a fabric from the same batch, which eliminated one parameter from the analysis. The applied pigments (HB1 and HB2) had different charges but the same color origin and where then directly comparable, see the charge differences in figure 5.3.

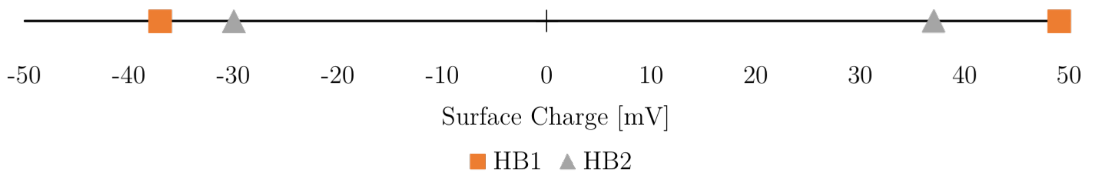

Figure 5.3: Charge distribution of HB1 (-37/+49 mV) and HB2 (-30/+37 mV).

Interestingly, the de-coloring of these printed samples showed a significant variation, with the pigment with higher positive $\zeta-$potential (HB1) being easier to de-color. This was observed by comparing the colorimetric values (L*) before printing and after de-coloring for the two printing sequences, see bar chart 5.4. A lower ΔL* would simply indicate more pigment is removed from the surface and more lightness level is obtained. The ΔL* values are displayed in table 5.1. The previously stated hypothesis claims that the total amount of electrostatic and van der Waals interactions govern the de-colorability. The reason to why HB1 is easier to de-color could then be related to the higher degree of electrostatic repulsive forces obtained by the cationic pigment, thus overcoming easily van der Waals interactions. This observation could confirm this hypothesis.

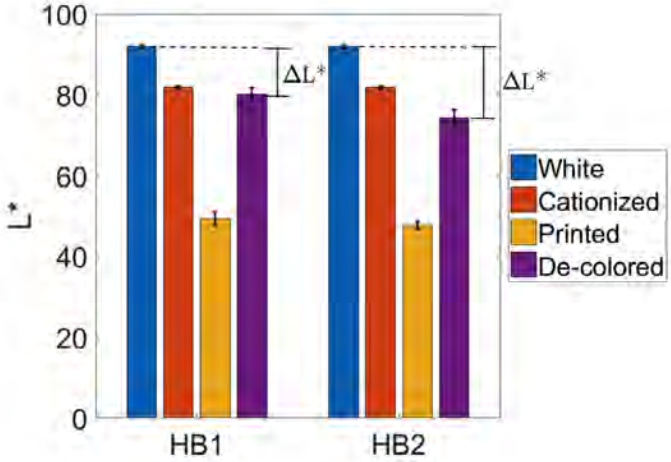

Figure 5.4: The colorimetric lightness intensity (L*) of the plain non-treated fabric, HB printed fabric and after de-coloring. The cationized fabrics have been soaked in a solution of methyl orange prior to measuring.

One could argue that comparing two different pigment charges is not enough to draw conclusions. However three samples per printing sequence went through the same process and gave similar colorimetric results with low standard deviation, thus creating a stable foundation for the analysis. The printed and de-colored fabrics' standard deviation can be obtained in appendix A.

Table 5.1: A low Δ L* value would imply that the de-coloration was easier and enabled more pigment removal.

	L* White	L* De-colored	Δ L*
HB1	92	80	12
HB2	92	74	18
PV	92.5	72	20.5

5.1.3 Effect of Pigment Hydrophobicity

This system allows for comparison between the two different pigments, HB and PV. Ideally the pigment formulations should have the same charge distribution to be directly comparable, see the differences in figure 5.5. The level of cationization of the fabric with PV was also lower than HB2, but some general observations could be made.

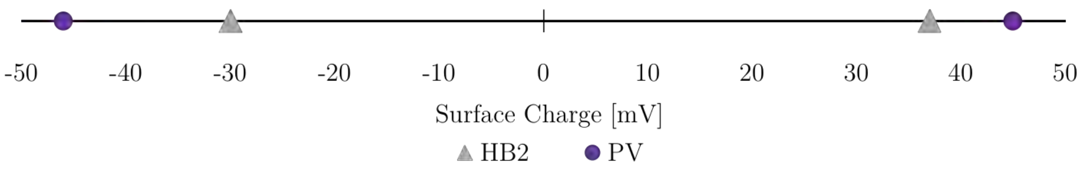

Figure 5.5: Charge distribution of HB2 (-30/+37 mV) and PV (-46/+45 mV).

When preparing the pigment formulation for each color, PV were more prone to agglomerate over time than HB. An observation that indicates that PV is more hydrophobic.

In table 5.1 the ΔL* value appears to be lower for HB2, with a more efficient color removal. In section 2.5.3 the complexity of the fiber-dye interactions was described. One of the described interactions were van der Waals interactions, which are active at a short range and occur between the pigment and fiber due to the hydrophobic character of the pigment, in this case. A more hydrophobic pigment would then find it more energetically beneficial to remain close to the fiber than to be re-dispersed in the acidic water when de-coloring. To compare, the intensity of the van der Waals interactions might have been slightly lower for HB2 due to its lower hydrophobicity, which may have resulted in an easier de-coloration. For the PV pigment on the other hand, the amount of cationic charges and the mechanical action of the sonicator are simply not enough to overcome these stronger, short range interactions. This fact supports the previous observation, that PV was more hydrophobic than HB.

Another fact to consider is the level of cationization that is confirmed through colorimetric measurements to be higher for the HB2 formulation as well, see figure 5.6. Implying that the repulsive forces becomes stronger in the acid bath and will perhaps slightly improve the de-coloration.

In another study [6], where de-coloration was assessed on a reactive dyed lyocell fabric, the blue color was nearly impossible to remove. Even though they used harsh treatments. Noteworthy, de-coloring method use comparably milder treatments, which indicates the level of difficulty for color removal in general.

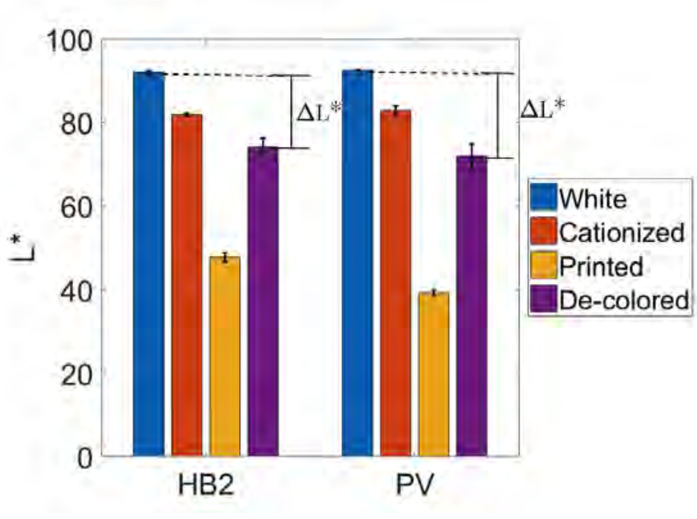

Figure 5.6: The colorimetric lightness intensity (L*) of the plain non-treated fabric, HB and PV printed fabric and after de-coloring. The cationized fabric has been soaked in a solution of methyl orange prior measuring.

5.1.4 Effect of Pigment Charge and Size

Previously in the comparative study of particle charge, it was discussed that a more cationic pigment seems to increase the ability to de-color a printed fabric, based on colorimetric measurements (L*). In this comparative study the pigment size with respect to its charge is evaluated, see figure 5.7. The particle sizes were obtained from DLS measurements and are representing a mean value. To include the polydispersity of each pigment in the plot, the marker size equals the polydispersity index (P.I.), multiplied by a factor of 70.

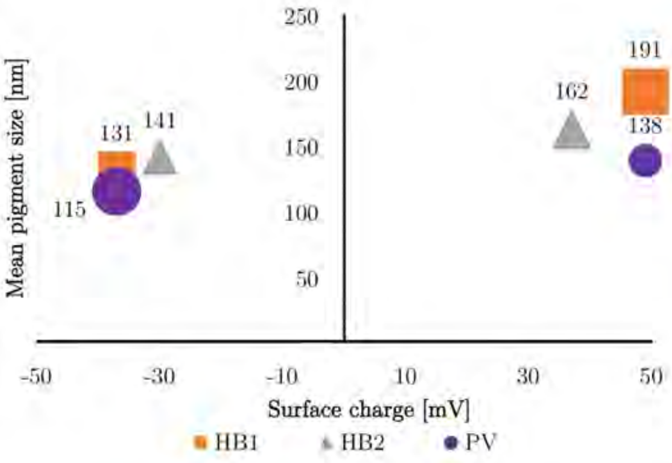

Figure 5.7: When comparing the pigment sizes, HB1 is shown to have the largest particle size and be easier to de-color. The size of the marker indicates the polydispersity of each pigment state.

Interestingly, the pigment formulation with a mean size that appeared larger in the acid condition (HB1) was the easiest to remove. This observation opens up for further analysis. Based on the fact that smaller pigments have more available surface areas, it means that more van der Waals interactions will be present and impede the repulsion in the acidic bath. Consequently, smaller pigment particles need to be compensated through even higher repulsive electrostatic forces. Through this analysis, one can not stress enough the complexity of the fiber-pigment interactions.

Additionally, one can note that PV and HB pigments can not be directly compared, due to their different hydrophobic characters but were included in below graph for illustration purpose.

P.I. is an indication of the size uniformity of the pigment, in this case at pH 12 and pH 3 respectively. For HB1 one can observe a larger marker size, which would mean that the pigment has larger size variations. Ideally, the pigments at pH 3 should have large mean size and low P.I., to have the optimal de-coloring ability. This implies that if the pigment formulation had a lower P.I, the de-coloration may have been even more successful. This would be an area to study further in future work.

5.2 Mechanical Properties

The tensile tests reveals information about the textile's mechanical properties before and after every treatment, see figure 5.8. Three to four samples per treatment were tested which is not the optimal number of samples to get enough data for a final conclusion. However, the tests were performed identically and the results are considered reliable as the standard deviation of ultimate strength and elongation at ultimate strength were considered small, see appendix B. Thickness and cover of the fabric was measured to identify the level of shrinkage that could influence these results. The measurements of fabric cover and thickness can be found in appendix C.

Following key findings will be discussed accordingly:

- Reduced strength and increased elongation for cationized fabric.
- Increased strength and reduction in elongation in de-colored fabric.
- Number of threads per square centimeter increased in both warp en weft direction after cationization. Creating a more compact fabric. Average thickness of the fabric increased accordingly.
- After de-coloring, the number of threads per square centimeter and average thickness of fabric almost returned back to origin.

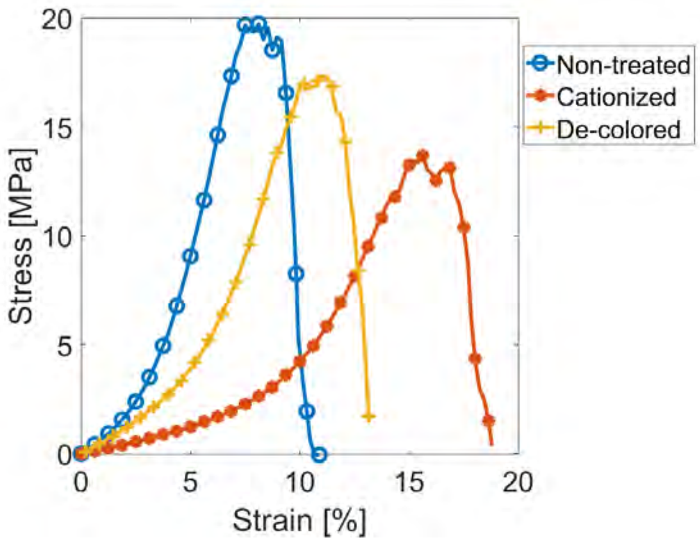

Figure 5.8: Changes of mechanical properties of the textile before and after each treatment; non-treated, cationized, de-colored.

After cationization there is a clear breaking strength reduction but also an increase in elongation at break. Cationization is performed in a reactor with the fabric in a non-stretched condition, which allows it to shrink due to the heat exposure and the soaking in liquid. In appendix C the warp and weft count reveals the level of shrinkage before and after every treatment. Where the count had increased in both directions. In the meantime, a thickness increase of 0.05 millimeter after cationization was also observed. Supposedly induced by swelling of the amorphous regions of the fiber's fibrils. Literature reports [7], that this is usually what happens when fabrics are exposed to wet and warm conditions as fabrics usually are wet processed under tension. Essentially the fibers will try to return to its original position. The shrinkage may then be the reason of the appeared elongation increase after cationization, as the amorphous regions in the polymer chains have slightly curled up after cationization and thus have space to extend when tension once again is applied. In appendix C images of how the warp and weft count were conducted can be seen.

In the reactor there are also blades that stir the fabric in the solution at a hundred routs per minute for two hours. In the conducted SEM images abrasion on the textile surface could be seen, whilst the non-treated textile had none. This fact leads to the conclusion that the method of cationization fractures the fibers, causes abrasion and could be the explaining reason of the declining fabric strength. The impact of the cationizing agent (GDTAC) has not been studied.

The fabric was slightly in tension when treated in a 60°C acidic bath. Literature explains that a textile in under tension will exhibit stretching. This in combination of mechanical action from the sonicator at the surface of the fabric would mean that the amorphous regions of the fibrils will readjust and become more aligned with the fiber axis [7]. This will create stronger and stiffer fibers, which accordingly is observed in the stress-strain curve, see figure 5.8. The acid is expected to degrade the fiber slightly [2], but does not have a visible impact on the fabric's breaking strength. However, this will be discussed further in section 5.2.3.

Sonication was performed from one side alone which opens up for the question if there is a significant difference between the front and back of the fabric after mechanical treatment. Through SEM this was further analyzed and the cationized fabric showed no major difference between front and back. Images of this analysis are located in appendix D. For the non-treated fabrics, the backside appeared more damaged than the front. The different outcome may be explained that the latter have been mercerized and cationized, which will increase the elongation to break as the tensile test in figure 5.8 pinpoints. Consequently it will be more ductile and resistant to the mechanical forces from the sonicator. The fabric cover of the cationic fabric showed that it had exhibit shrinking. A more compact fabric would resist the mechanical forces better.

5.2.1 Control of Fiber Damage Caused by Sonicator and Acidic Bath

Bleaching is a chemical treatment that is commonly being used in terms of stain and color removal [2]. This de-coloring technique opens up for more sustainable treatments with only acidic pH and some mechanical action as requirements for the color removal. Main focus was to evaluate whether the de-coloring method was reproducible on cotton fibers, meaning that the constructed de-coloring method have not yet been optimized. The impact from the used treatments has however been investigated through scanning electron microscopy and tensile tests, to verify the damage caused by the sonicator and acidic condition.

Below listed samples are going to be analyzed and compared. Note that the later four samples were sonicated identically and according to the de-coloring method. This means that fabric shrinkage will be a set parameter and will not influence the analysis. The alphabetical order is also corresponding to the images in figure 5.9.

(a) Non-treated cotton fabric
(b) Cationized cotton fabric
(c) Non-treated cotton fabric sonicated in pH 7
(d) Cationized cotton fabric sonicated in pH 7
(e) Non-treated cotton fabric sonicated in pH 3
(f) Cationized cotton fabric sonicated in pH 3

5.2.2 Effect of Sonicator on Fiber Properties

The impact of sonication treatment on the fiber properties were evaluated by observing SEM images and the stress-strain curves of sample a-d). To clarify, non-treated and cationized fabrics that had been sonicated at pH 7 were compared to samples that had not been sonicated. When comparing the non-treated fabrics in image a) and c) of figure 5.9, evidence of some abrasion was visible. In figure 5.9 b) and d), it was harder to visually distinguish between the fiber damage caused by the cationization and the sonication. Visual observations in SEM were simply not enough to draw any conclusions of the effect of the sonication treatments on the fabric. The performed tensile test does however reveal a similar trend as the previous stress-strain curve (figure 5.8). The mechanical action from the sonicator, without acid in this case, will increase the strength at break and the fiber seems to become more brittle as the elongation to break is also reduced, see figure 5.10.

When analyzing the stress-strain curve of the samples, the sonication seem to cause a strength increase, see figure 5.8. Where the non-treated samples increased from 21.5 to 22 MPa after sonication and the cationized samples increased from 14.2 to 15.8 MPa accordingly, standard deviations can be obtained in appendix B. This could be due to the mechanical action from the sonicator that causes elongation of the amorphous regions in the fibrils, that would be somewhat curled after shrinkage. More aligned fibrils would create a uniform load distribution when the load from the tensile tester is applied. This alignment would ultimately result in higher strength at break (UTS).

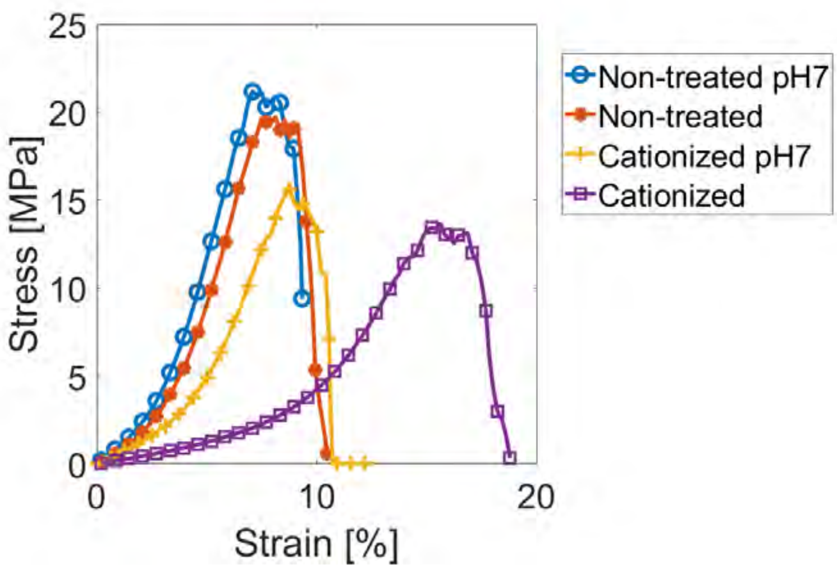

Figure 5.10: Non-treated and cationized sample have not been sonicated, whilst the non-treated pH 7 and cationized pH 7 have. Sonication is slightly increasing the strength at breat.

A second influencing factor that may have a sufficient impact on the fiber strength after cationization and de-coloring is the apparent fibrillation. This occurs when small fibrils from the fiber delaminates and cross over to adjacent fibers. These additional contact points will prevent fiber sliding once tension is applied from the load cell in the tensile tester and further increase the overall strength properties. This observation has also been supported in literature [7] and is explained in the theory section. See examples of the delamination and fibrillation in figure 5.11.

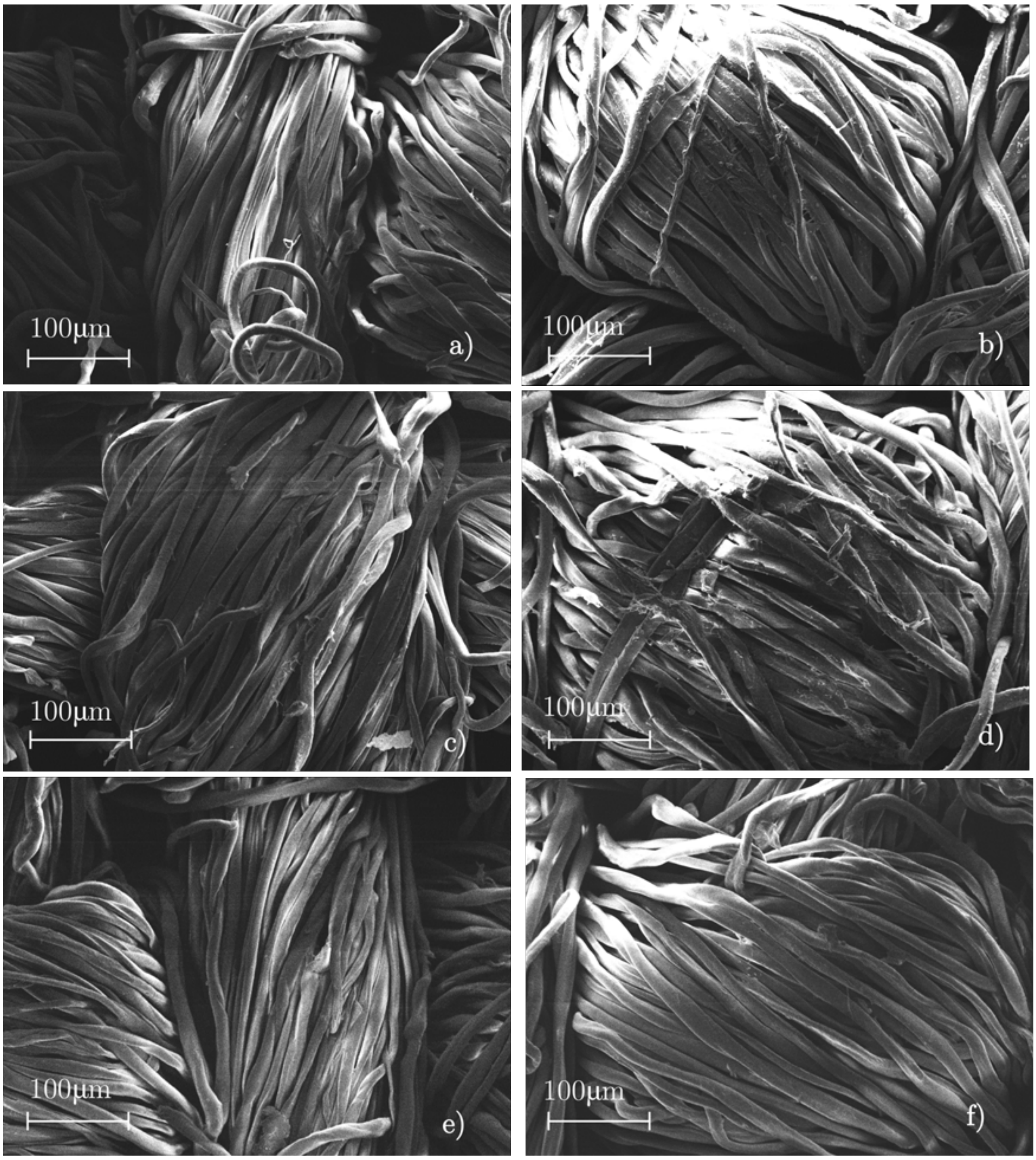
100μm
a)
100μm
b)
100μm
c)
100μm
d)
100μm
e)
100μm
f)

Figure 5.9: Sonicator may cause some abrasion on fibers when comparing fabrics before and after treatments of different pH. a) Non-treated fabric. b) Cationized fabric. c) Non-treated fabric sonicated four times in pH7. d) Cationized fabric sonicated four times of pH 7. e) Non-treated fabric sonicated four times of pH 3. f) Cationized fabric sonicated four times of pH 3.

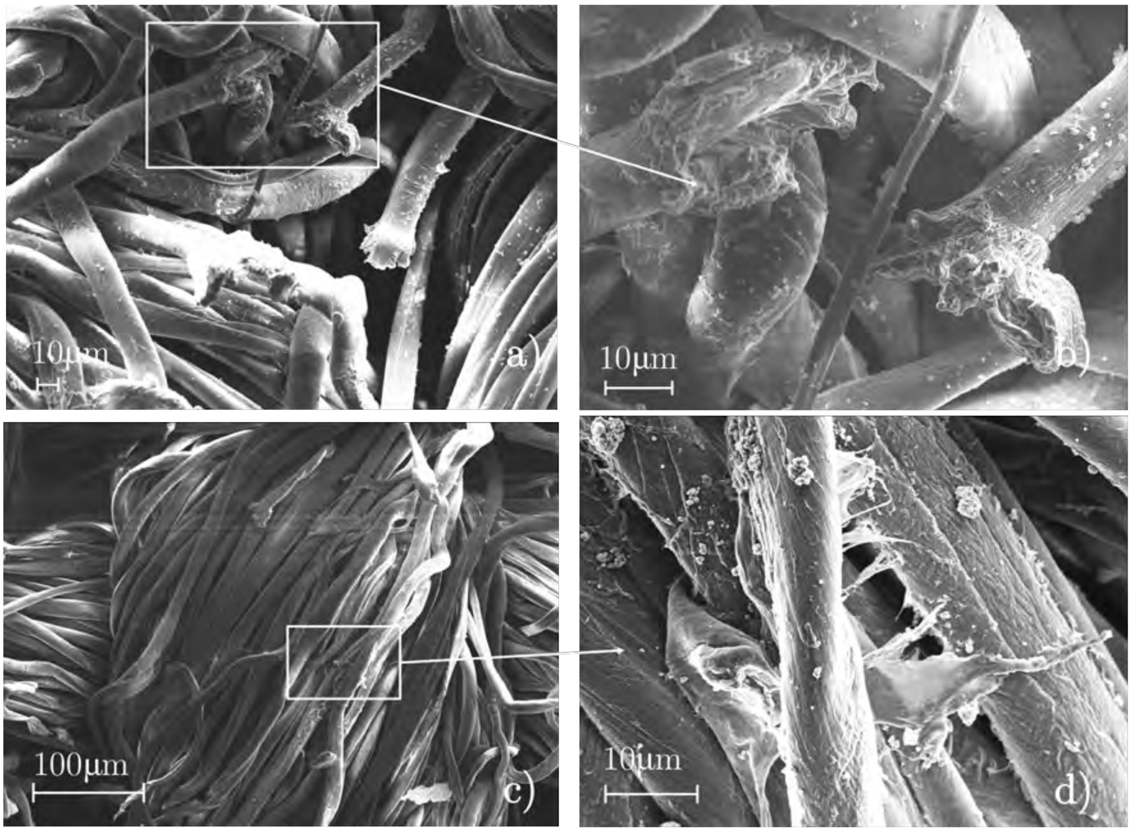

Figure 5.11: Appearance on textile after sonication and cationization. a-b) Fiber fracture. c) Abrasion caused by sonication and cationizing treatments. d) Fibrillation

5.2.3 Effect of Acid on Fiber Properties

To analyze the fiber damage caused by the acidic condition, sample e) and f) were analyzed and compared towards sample c) and d) respectively. Based on SEM images, no additional damages were observed on the sonicated samples that had been treated in a acidic condition. Instead it seemed that the surfaces were smoother, for both non-treated and cationized fabrics. In theory the acid will degrade the fibers [2], perhaps the images indicates that the acid and sonication causes fiber breakage and thereon will leave the fabric completely. If this were true, a reduction of breaking strength should be visible in the stress-strain curve, but it is the opposite. Both the non-treated and cationized fabric after sonication in pH 3 seem to have a slightly higher strength and no evidence of embrittlement. In terms of materials in general and metals in particular, the surface roughness plays an important role for the mechanical properties. More rough surfaces would create more stress concentration and weaken the material. Due to this fact, the absence of the abrasion that were seen after cationization and sonication in pH 7, could cause a slight strength increase.

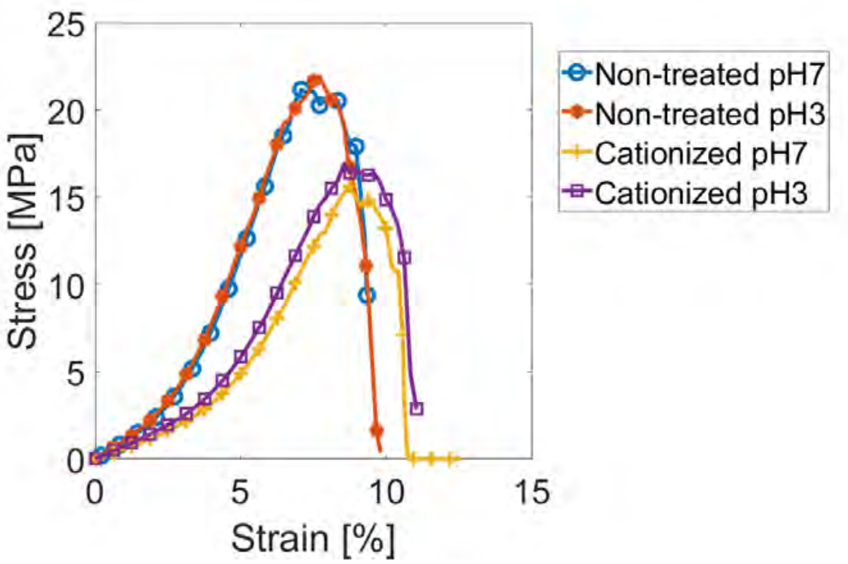

Figure 5.12: The acid bath does not seem to degrade the fabric as the breaking strength remains more or less the same for both the non-treated and cationized samples. All samples have been sonicated equally.

6

Conclusion

The complexity of the fiber-pigment interactions has repeatedly been emphasized throughout the report. These interactions are the reasons why the de-coloration of the printed textiles appeared difficult. A great amount of pigment was successfully removed but the remains generated a light, but still visible, shade of blue or violet, even though in SEM they appeared to be located sparsely over the textile and on the sides of the fibers.

Through comparative studies the pigment's charge, hydrophobic character and size was shown to be of significant importance. When comparing two de-colored samples that had been printed with pigments of different charges, it became clear that the pigments with most positive charges were easier to de-color. This observation simply opens up for more research as it might be a key feature for being able to remove the remaining pigments. It also became evident that the blue pigment (HB) was easier to de-color than the violet (PV), with a probable reason being their hydrophobic differences. PV appeared more hydrophobic as the pigment made for printing seemed to be more unstable over time from a colloidal perspective. A trend between pigment particle size and the obtained shade after de-coloring was also observed, meaning that a smaller pigment could potentially be harder to remove due to the more available surface areas which further enables for more van der Waals interactions.

When it comes to the mechanical properties, the cationized fabric had an expected reduction in strength. Surprisingly the stress-strain curve of the de-colored fabric showed a strength increase after sonication in acid. SEM images indicated an increase of fiber delamination and fibrillation. Additionally, the warp and weft count and thickness were measured between each treatment, which confirmed that shrinkage occurs during cationization and stretching of fibers when de-coloring. This is due to the selected methods for each treatment where de-coloring is performed in tension and the cationization in an un-stretched condition. This observation would have an significant impact on the result of the mechanical properties and is important when interpreting the results.

The mechanical action in terms of sonication and the acid were expected to damage the fibers in the de-coloration process. Conducted images in SEM showed few indications of fiber damage caused by the sonicator on both cationized and non-treated fabric. However, the tensile testing analyses revealed a slight increase of breaking strength and a more obvious decrease in elongation at break, indicating fabric embrittlement. The acid did not seem to have a severe impact on the fabric, as no damage could be observed in SEM. The mechanical properties remained more or less the same according to the performed tensile test.

These results may be a step in the right direction to create a successful de-coloring method. More work is required to establish any final conclusions. A suggestion would be to complement the study of pigment charge with a pigment where the positive charges were even more dominant. Another interesting aspect is the textile, perhaps a textile with less crystalline fibers would be easier to de-color, due to the fact that it is the amorphous regions that adsorbs moisture and swells. A slight increase of swelling might help the fiber to repel the remaining pigments. In order to further understand why the de-colored fabric has higher breaking strength and lower elongation at break than the cationic fabric, crystallinity of the fiber could be determined through XRD measurements before and after treatments.

This report is only focusing on Heliogen Blue and Pigment Violet, but in order to create a new coloring technique a lot more colors need to be synthesized and tested. Every individual color have its own character and has to be evaluated separately. Another observation that was made, but was not discussed, is the fabric weave impact on the de-coloring method. The question still remains if weave type has any significant impact on the de-coloring or if it is mostly the pre-treatments of the fabric, as mercerization and bleaching among others, that govern this.

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A

Standard Deviation Colorimetry

Table A.1: L*-values and standard deviation of white, printed, de-colored and cationized fabric in 5.1.

		L*	Std
HB1	White	91.99	0.46
	Printed	49.32	1.59
	De-colored	80.04	1.50
	Cationized	81.83	0.31
HB2	White	91.99	0.46
	Printed	47.72	1.04
	De-colored	74.21	2.03
	Cationized	81.83	0.31
PV	White	92.51	0.18
	Printed	39.27	0.8
	De-colored	71.86	3.06
	Cationized	82.96	1.11

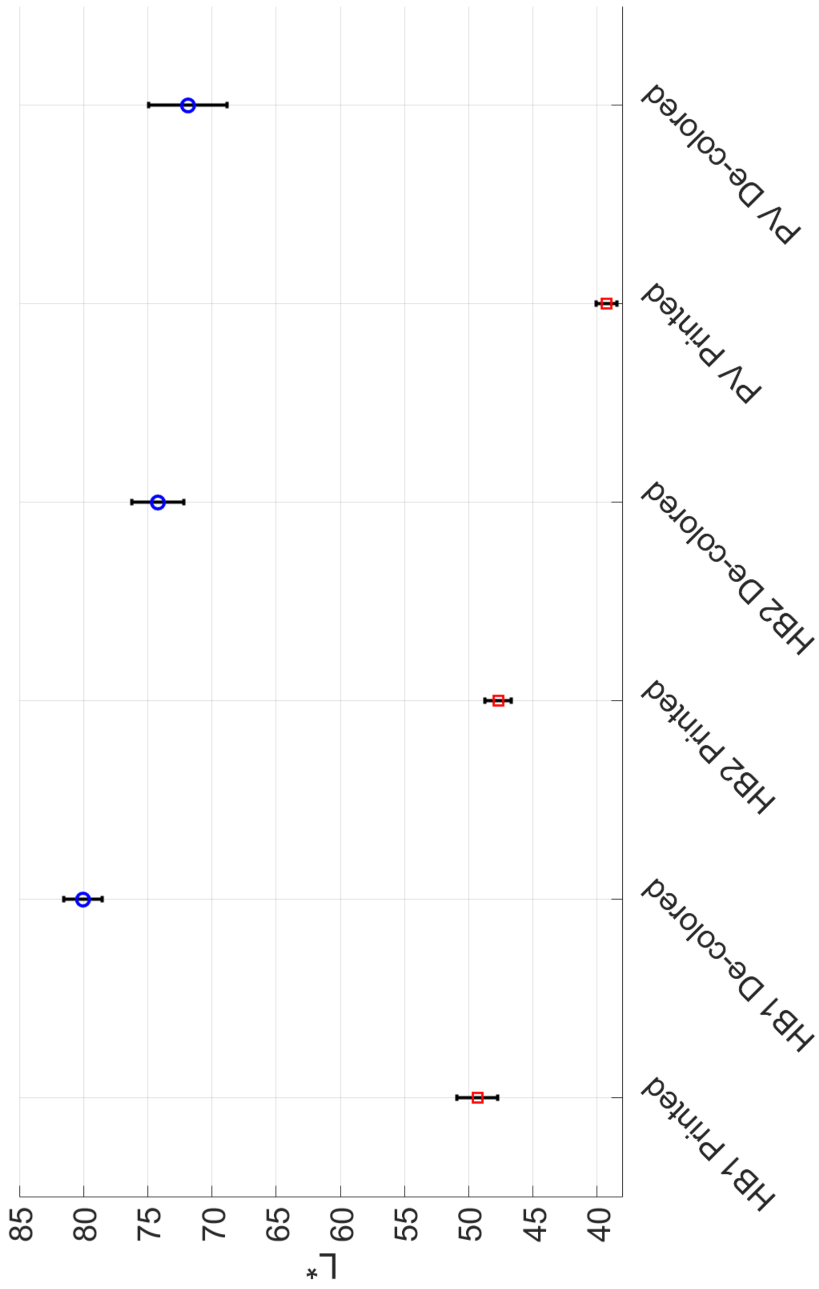

Figure A.1: Standard deviation of printed and de-colored fabrics were considered low, implying that the methods repeatability were good.

B

Standard Deviation of UTS and Elongation at UTS

Table B.1: Ultimate strength (UTS) and elongation at UTS before and after every treatment.

	UTS [MPa]	std	Elongation at UTS [%]	std
Non-treated	21.5	0.8	8.2	1.2
Cationized	14.2	1.0	16.0	0.9
De-colored	18.6	1.1	11.2	0.3
NT pH 7	22.0	0.5	7.4	0.4
Cat pH 7	15.8	0.6	8.7	0.1
NT pH 3	22.4	0.6	7.8	0.3
Cat pH 3	17.1	0.3	9.3	0.7

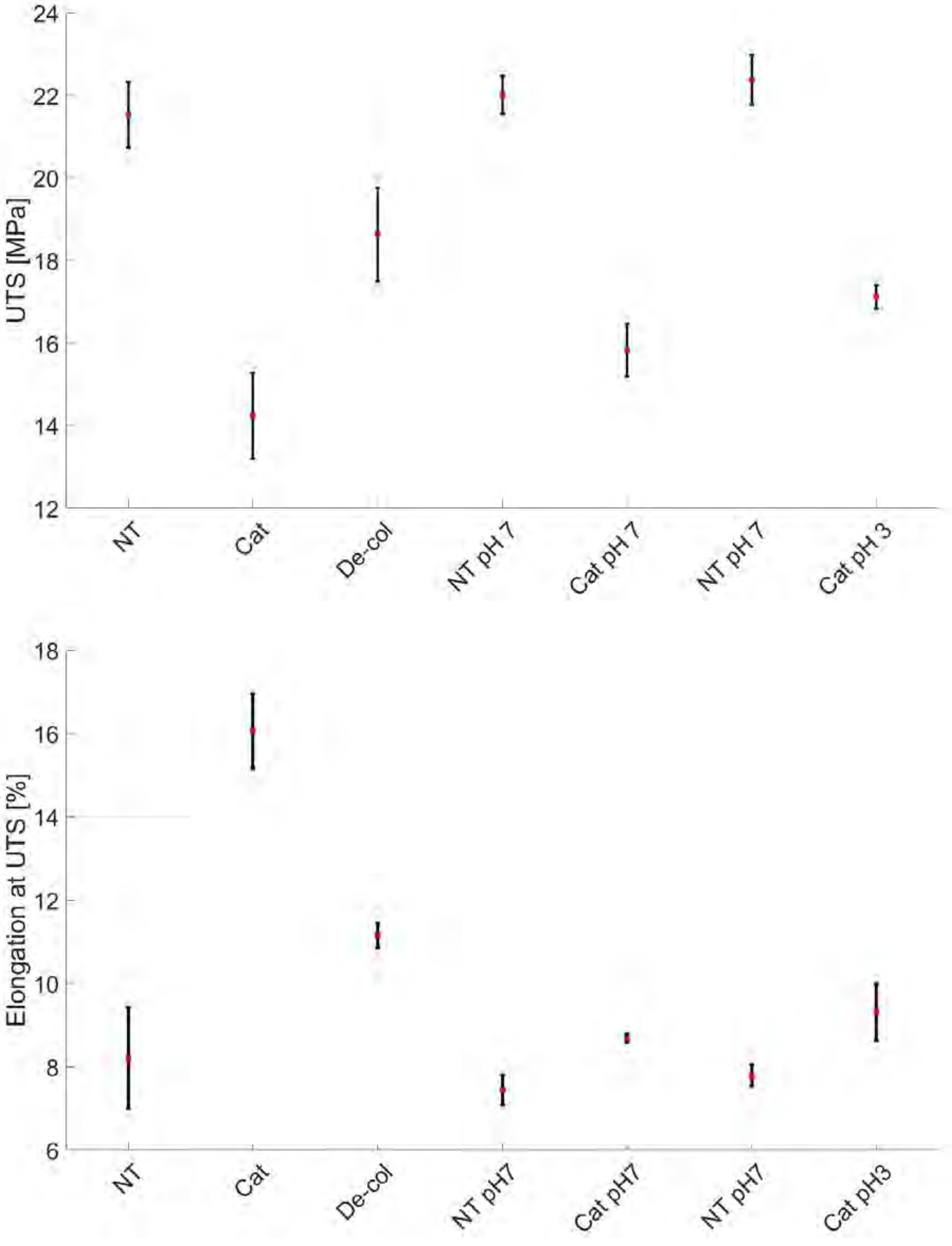

Figure B.1: Standard deviation of Ultimate Strength (UTS) and Elongation at UTS.

C

Warp and Weft Count of Plain Weave Fabric

Table C.1: Warp and weft count and thickness as an indication of shrinkage due to the different treatments.

		Count	**Distance (cm)**	**Counts/cm (cm^{-1})**	**Thickness (mm)**
Non treated	Weft	19	0.8047	23.6	0.32
	Warp	31	1.0672	29.0	
Cationized	Weft	20	0.7815	25.6	0.37
	Warp	30	1.0105	29.7	
De-colored	Weft	19	0.7899	24.1	0.31
	Warp	30	1.0294	29.1	

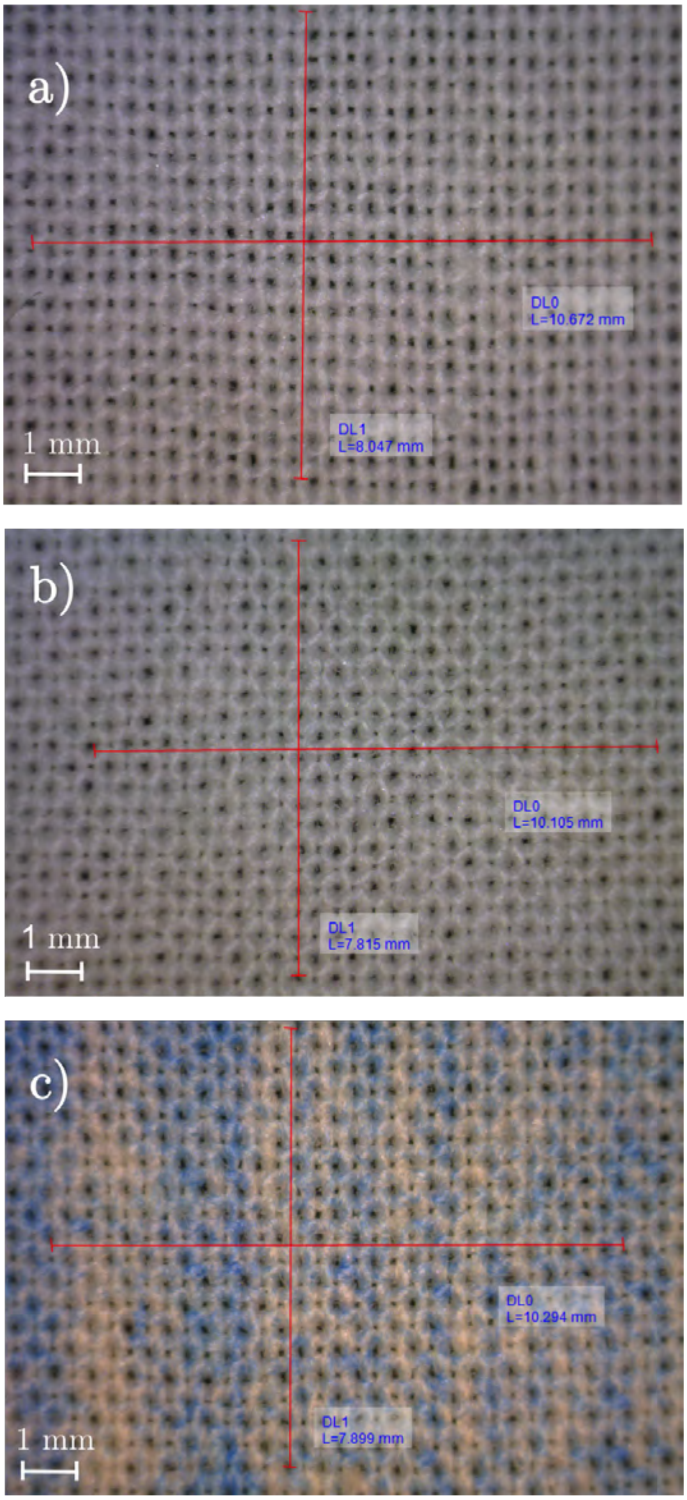
a)
DL0
L=10.672 mm
DL1
L=8.047 mm
1 mm
b)
DL0
L=10.105 mm
DL1
L=7.815 mm
1 mm
c)
DL0
L=10.294 mm
DL1
L=7.899 mm
1 mm

Figure C.1: Images were used to determine the warp and weft count and the shrinkage caused by treatments. a) Non-treated b) Cationized c) De-colored.

D

SEM on Front and Back of Sonicated Fabric

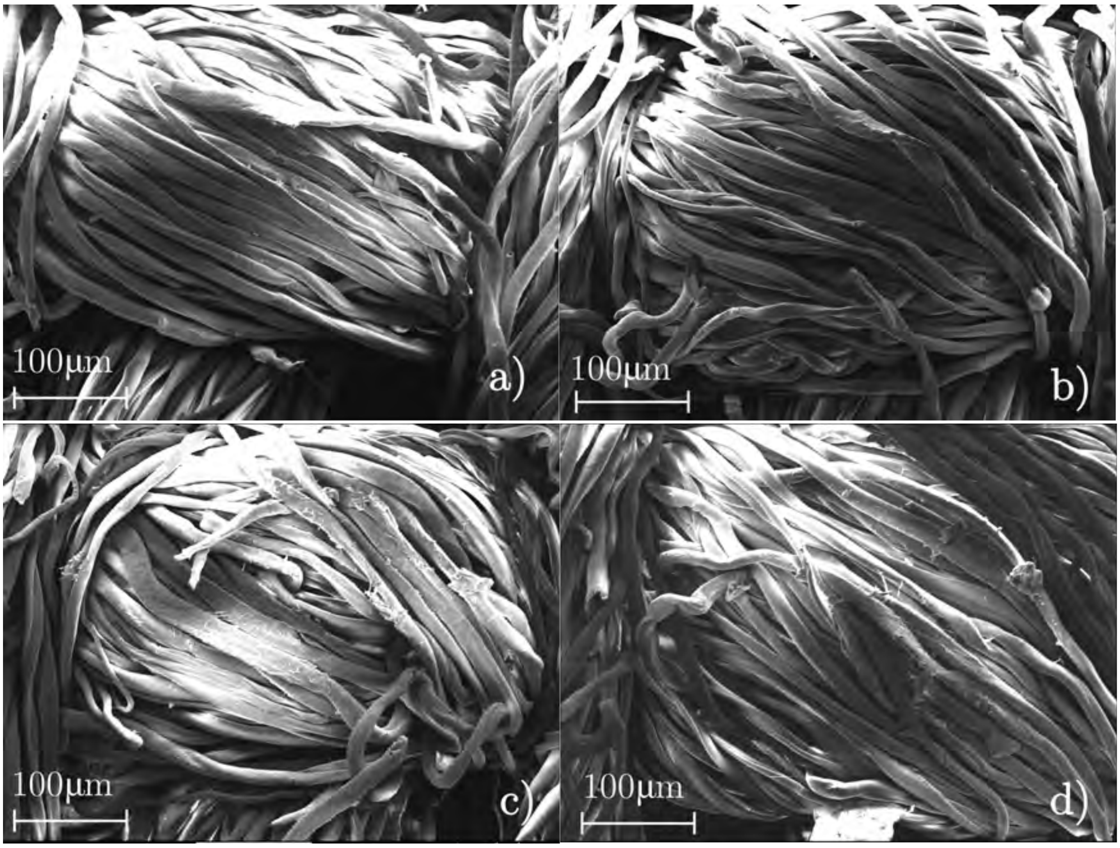
100µm
a)
100µm
b)
100µm
c)
100µm
d)

Figure D.1: Sonicator and acid impact on fibers front and back. a) Non-treated fabric front and b) back. c) Cationized fabric front and d) back.