Investigation into a Durable and Degradable Binder for the Colouration and Subsequent Recovery of White Cotton Fibres

by

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Thesis

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The candidate confirms that the work submitted is her own and that appropriate credit has been given where reference has been made to the work of others.

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Abstract

Textiles are commonly coloured with dyes or pigments to produce garments with aesthetically pleasing print designs or uniform colouration. However, as a result of historical consumer demands, the colorants used in garment production are designed for durable and long-lasting garments, whilst the average lifetime of fashion garments tends to be only a handful of months. The result is the creation of waste often unsuitable for chemical recycling as the colour content or finishing additives may reduce the efficiency of the chemical processing. In addition, these added chemicals tend to be difficult to remove as they are often cross-linked into the cellulosic textile material.

One approach to this challenge is to investigate the possibility of using a pigment/binder system for the colouration of cotton fabrics. This binder would be sufficiently durable to maintain colour quality during the lifetime of the garment but can be easily removed at the end of first use lifetime hence allowing the recovery of white cotton. The work described in this report is the investigation of using Bunte salt-terminated polymers or a polyamide epichlorohydrin (PAE) as a potential binder material for the pigment colouration of cotton fabrics. The unmodified commercial PAE, Hercosett™ 617 showed the most potential as a binder material. The binder/pigment formulation comprised of Hercosett™ 617 and C.I. Pigment Green 8 was applied to cotton fabrics by a pad/dry/bake method and produced coloured fabrics with excellent colour fastness to washing, assessed according to the ISO 105 C09 standard. Several ′′stripping′′ methods were assessed for the removal of the binder/pigment formulation from the cotton fabrics. A sequential Kybreak™ stripping/reductive bleaching/soaping method was demonstrated to be most efficient in recovering the cotton fabric with its original whiteness and fabric handle. This study has demonstrated the potential of Hercosett™ 617 as a binder material for pigment colouration of cotton and can contribute to the closing of the ′′circular manufacturing loop′′ for cotton fashion apparel.

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Chapter 1 – Introduction

Ever since the industrial revolution in 1800 the global population has been growing rapidly, with the most recent population estimate being over 7.7 billion in 2019 (Worldometers 2019). Since the 1970s the global population has roughly doubled. The growth rates have been declining, but it is still expected that the total number will continue to grow. To support this growth the food, clothing and housing sectors need to similarly grow but this production may impact the environment. It has been suggested that, together with the housing, transport and food sectors, the clothing sector is amongst the highest ranked when it comes to its impact on the environment. These impacts occur at all stages of the clothing life cycle, starting from the production of the raw materials, to the creation of the final garment, in how it is used and taken care of by the end-user and how it is discarded at the end of life (WRAP 2017). Clothing retailers are increasingly driving the development of more fashion seasons within the calendar year and with that consumers are buying more items than they need. In the period of 2000 to 2015 an increasing trend was observed for the global sales of clothing, whilst the trendline for clothing utilisation showed a decline (Ellen MacArthur Foundation 2017). The latter was suggested to be a result of the increased number of fashion seasons or ʻʻfast fashionʼʼ phenomenon. It has been estimated that in 2012 consumers in the UK owned over six billion items of clothing of which 1.7 billion items had not been worn in the last 12 months (WRAP 2012). Fast fashion may lead to the production of garments with a quality lower than general standards and with an accordingly shorter lifetime before disposal by the consumer. Simultaneously, the products of higher value or quality, which are expected to have a relatively longer lifetime, may also become part of the waste stream before even reaching its longer end-of-life, solely because they are no longer considered fashionable. It is difficult to identify the motivations for discarding clothing by consumers and why the products often end up being disposed of rather than re-used or recycled due to a combination of institutional, social, economic, legal and technical factors (Palm 2011).

Within the framework of the garment lifecycle, textile waste can be described as and divided into two categories: industrial or pre-consumer waste and post-consumer waste (Wang 2010; Singh and Ordoñez 2016). When the term pre-consumer waste is used, it is referring to the material that is discarded before it is ready for consumer use which could be in the form of technical errors such as misprints. In contrast, the term post-consumer waste, is used to define the textile products that are discarded after being used by the consumer. These could be in the form of any textile product such as garments and are discarded by consumers who no longer ‘’need’’ them. This may be because the articles are damaged, worn-out, outgrown, or outdated (Hawley 2006).

1.1 Routes for Textile Waste

Once textile products are disposed of by the final consumer and become post-consumer waste, they can follow several processing routes as described below (Palm 2011). If not discarded via the municipal waste system, the products are often reused directly by passing on to family or friends, exchanged or sold between consumers or donated to charity shops or for textile waste collection. Products that are collected will go through a sorting process where they are separated based on the material quality. Typically, garments can either be recycled or end up in landfill or incinerated. Figure 1.1 shows the waste management hierarchy from the waste framework directive for EU member states, with respectively from top to bottom the most favoured to the least favoured route (European Commission 2008).

1.1.1 Disposal and Energy Recovery

Products unsuitable for re-use or recycling or those ending up as part of the municipal solid waste can end up in landfills where they are left to decompose for years under controlled conditions. It has been suggested that an estimated 336,000 tons of clothing ended up in the household residual waste in the UK in 2017, destined for landfill or incineration (WRAP 2019). In 2015 the environmental protection agency estimated that 10.5 million tons of municipal waste textiles was landfilled in the US (EPA 2019b). The decomposition of biodegradable materials in landfills results in the creation of gases such as methane and is therefore a significant potential contributor to local smog and global climate change. Efforts are currently made to capture landfill gas as a renewable energy source (Tsai 2007; Amini and Reinhardt 2011; EPA 2019a). There is also the risk of the release of leachates from the chemical content of waste textiles in landfill, potentially threatening to both ground and surface water (Castillo and Barceló 2001; Renou et al, 2008).

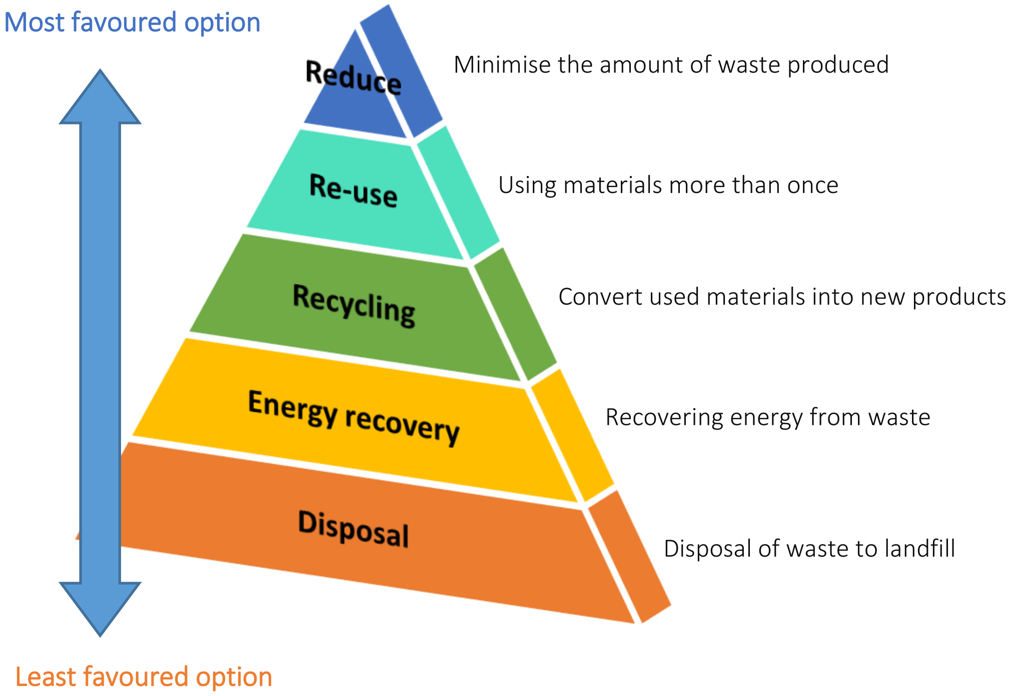


Figure 1.1 EU waste management hierarchy (European Commission 2008)

According to EU legislation, incineration for energy recovery is not classified as recycling but as recovery or disposal (European Commission 2008). Incineration allows partial reclaiming of the energy initially required in the development and processing of the fibrous material. The strategy therefore exhibits advantages over landfill. However, from an ecological and economical point of view, recycling and re-use are more favourable (Bartl 2011).

1.1.2 Reuse and Recycling

Research suggests that for the UK the majority of post-consumer waste collected for re-use or recycling is exported to other countries, predominantly to sub-Saharan Africa, Poland, Hungary, Pakistan and Ukraine (WRAP 2016). Although the donation of clothing to charities with the aim of helping the needy in developing countries may appear to be morally correct, the reality associated with this act of goodwill has recently become a topic of discussion (Bahadur 2018; Kelley 2018; Krauss 2018; Aljazeera 2019; Redfern 2019). It is argued that the large amounts of clothing imported from countries such as the US and UK have contributed to the decline in local manufacturing industries as the local manufacturers could not compete with the cheap imported products and it has created unemployment. In 2015, the heads of states of the East African Community, announced that they were considering a ban on the importation of second-hand clothes and shoes in order to build-up their textile industries to strengthen the countries’ economies. To date no increased duty on second-hand clothing or a ban has been planned, but the EAC ministers have approved a draft for a strategy to promote the textiles and apparels sector in East Africa (Owaka 2019). Despite the complexity of the impact of exporting second-hand clothing for reuse, the concept of reusing items such as garments in general is considered to be a favourable route as it reduces the build-up of waste materials as well as prevents the necessity for (raw) material, energy, water and chemical consumption required for the production of the new products.

Recycling of textile waste is another favoured route for waste management with benefits of minimising the environmental impact of textile products. Collected textile waste can be recycled into new products by mechanically shredding the material back into its fibrous form or chemically converting (depolymerising or dissolving) the material back into its constituent molecular form for the regeneration of new fibres. In most cases textile waste is ʻʻdown-cycledʼʼ producing lower value products such as upholstery, industrial rags, blankets and insulation materials (Morley, Bartlett and McGill 2009; Sandin and Peters 2018). Mechanical recycling involves shredding the material back into fibrous form, followed by optional blending, carding and combing before spinning it back into yarns. For mechanical recycling there is no need to remove any colour or chemicals from the substrate prior to the process, as the textile materials are separated based on their colour. The separation of the different coloured fabrics is labour-intensive, and the process potentially produces products with colour streaks. More importantly, the shredding of the fabrics results in the shortening of the fibre lengths (Lindström et al, 2019). Often the recycled fibres require blending with other materials such as virgin fibres to increase the mechanical properties to a desired level (Merati and Okamura 2004; ; Halimi et al, 2007; Wanassi, Azzouz and Hassen 2016). Chemical recycling is where the textile material is typically depolymerised back to its original monomeric form, and re-extruded or regenerated into new yarns and fibres. A good example is Teijin’s Eco Circle™ fibres programme where polyester products are stripped of additives and colorants, obtaining virgin quality material and hence establishing a closed loop system for polyester (Teijin, n.d.).

Recycling of textiles is often challenging due to the lengthy and complex nature of the processing of sorting the materials based on their quality and suitability for recycling where each category of waste needs to be processed in a unique way to recycle them into useful products. Limitations are also found in the presence of chemicals in the textile material specifically for the chemical recycling process. Cross-linked chemicals such as easy-care finishes and reactive dyes have been shown to negatively affect the dissolution process for regeneration of cellulose-based fibres by reducing the percentage of fibre dissolution (Haule, Carr and Rigout 2014; Bigambo et al, 2018). Some reactive dyes have been successfully removed through a sequential acid/alkali/peroxide stripping treatment, but this process does not appear to be effective for all types of reactive dyes depending on the dye chromophore. For example, the anthraquinone dye C.I. Reactive Blue 19 showed greater resistance to the stripping sequence in comparison to some azo dyes (Bigambo et al, 2018).

The complexity of removing dyestuff from cellulose suggests that there is a need for an alternative system of colouration to allow simpler and cheaper colour removal. In this study we have reviewed the nature of the current commercial colouration systems and endeavoured to develop a flexible, cheap colouration system for all textiles, but more specifically cotton, that offers the application of satisfactory coloured prints which can be effectively removed when required.

1.2 Cotton

With a market share of almost a quarter of the global fibre production in 2017, cotton is, after polyester, the most important commodity apparel fibre (Textile Exchange 2018). It is one of the most used fibres in clothing due to its physical, mechanical and chemical properties, but also is regarded as having a detrimental environmental impact. The cultivation of cotton involves usage of water, land and pesticides, all of which can have a detrimental impact on the local ecology and the farmers’ livelihoods. The global average water footprint to produce one kilogram of cotton is 10,000 – 20,000 litres, depending on where it is grown (WRAP 2017). Approximately 5% of the world’s arable land is used for cotton cultivation (Zhu and Li 2013). Additionally, as the successful production of cotton depends on specific local climate conditions, the majority of the main cotton-supplying countries are in areas likely to suffer severe water stress and water scarcity into the future. In 2014 images were released by NASA showing that the eastern basin of the once fourth largest lake in the world, the Aral Sea, had completely dried (WRAP 2017; Micklin 2007). The main cause of this was a leaky and inefficient irrigation system for wheat and cotton cultivation drawing from the Aral Sea's two feeding rivers.

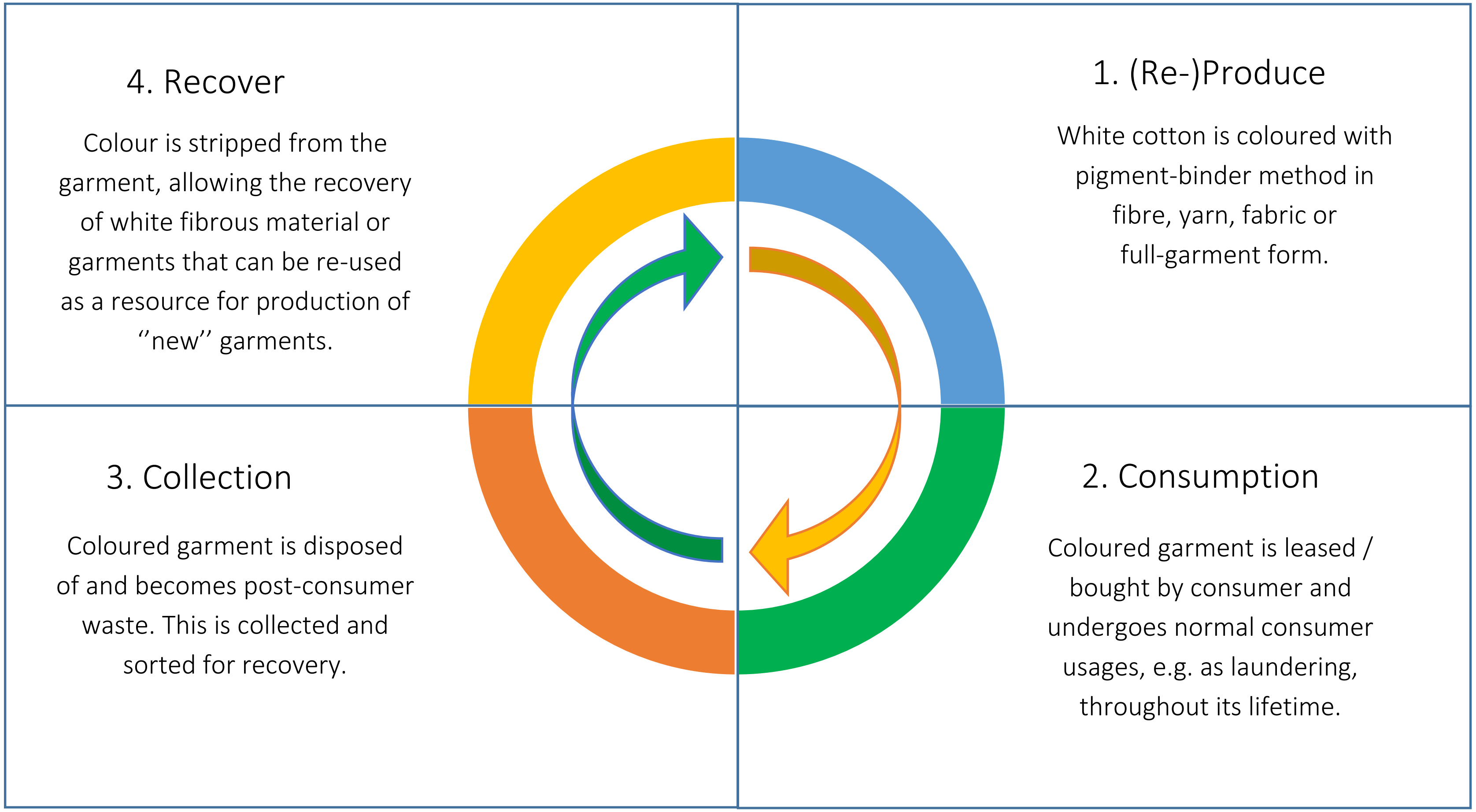
1.3 Colour Removal from Cotton Fabrics

Carbon, water and waste impacts occur in all the different stages in the life cycle of garments. Alongside fibre extraction, spinning/winding and finishing, the colouration process is one of the highest contributors to the carbon footprint of clothing (WRAP 2017). The colouration of cotton generally involves physical entrapment of coloured complexes or some chemical interaction such as hydrogen- or covalent bonding between the dyes and the fibres (Shore 1995) making it difficult to remove the colorants from the textile material and thus posing a problem when it comes to recycling. Previous studies found that the presence of some crosslinked finishes and reactive dyes may potentially pose a problem in the regeneration of cellulose as the crosslinked chemicals reduce the efficiency of cellulose dissolution (Haule, Carr and Rigout 2014; Bigambo et al, 2018; Wedin et al, 2018). There are many ways to remove dyes from cotton including reductive bleaching using sodium hydrosulphite, oxidative bleaching using hydrogen peroxide and even biological stripping using enzymes (Peralta-Zamora et al, 1999; Abadulla et al, 2000; Mechichi, Mhiri and Sayadi 2006). These methods tend to obtain only partial colour removal unless combined with other chemicals, require extra control to prevent decomposition of the fabric or are specific to dye classes (Choudhury 2011; Chatha et al, 2012; Konzewicz and Kozlowski 2012). A sequential acid/alkali/peroxide treatment showed great potential in the removal the easy-care finish dimethylol dihydroxy ethylene urea and some reactive dyes (Haule, Carr and Rigout 2014; Bigambo et al, 2018). It was suggested that the effectiveness of the method could be attributed to the high reduction potential of sodium dithionite, leading to reduction of the dye chromophores and the incorporation of polyvinylpyrrolidone to prevent re-deposition of the dye onto the fibre. However, regardless of the aggressive nature of the stripping method, it was not as effective for the anthraquinone-based dye C.I. Reactive Blue 19. This shows the complexity of designing a stripping method for colour removal from textiles, as the effectiveness may vary with different dye types.

It is of great significance to critically look at the way clothing such as cotton garments can be produced to tackle the land, water and chemical usage issue for the crop production on one side and the (post-consumer) waste production on the other side. Alternatives to conventional cotton such as organic-fair trade cotton already tackle part of the issue with cotton production as the Fair Trade and organic standards require the use of a crop rotation system that helps build soil fertility, protect biodiversity and eliminates the use of any synthetic fertilisers, pesticides or GMOs (Fairtrade International n.d.). However, these alternatives only provide a solution by reducing the amount of resources required to grow the cotton crop to a certain extent.

A different approach is to look at reusing or recycling cotton that is already in existence currently, by developing a method of colouration that allows application of colour which is durable to consumer usage such as laundering but can be removed after its lifetime. In this way waste could be reduced simultaneously as new products can be produced without a need for growing cotton crops. Reusing or recycling could involve reusing waste garments with faulty dyeings created along the production line, leasing or selling garments to companies and/or consumers and reuse the full garments or even allow fibre to fibre recycling through the lyocell process. This approach could also eliminate the complex issue of having to design a dye-specific colour removal method.

The work described in this thesis encompasses the development of a method for the colouration of cotton fabrics designed in a way that imparts durable colouration to the garment in its first lifetime but allows for subsequent colour removal when required. This colour removal at the garments end of life, will allow for the recovery of the fibres for subsequent reuse or recycling. The development of this colour application and removal system could potentially contribute to ‘’closing the manufacturing loop’’ for cotton textile products such as garments (Figure 1.2). Our approach has been to simplify the colorant choice and focus on using the pigment dyeing method, where coloured pigments are applied to the cotton textile material with a polymeric binder as a ‘’fixing’’ agent. The main focus of this report was to investigate the potential of a polyamide epichlorohydrin (PAE) polymer as a binder material for pigment dyeing that will withstand typical domestic laundering but will allow easy removal of the colour after its first lifetime usage. The study aimed to recover the original white cotton fibres which could potentially be reused or recycled, whilst throughout the development and optimisation of the colour removal method considering economic and environmental aspects. The study also included an initial study into the production of Bunte salt-terminated polymers from wool as a biobased precursor material and from PAE as a commercial alternative to function as potential binder materials for cotton colouration.



4. Recover

Colour is stripped from the garment, allowing the recovery of white fibrous material or garments that can be re-used as a resource for production of ''new'' garments.

1. (Re-)Produce

White cotton is coloured with pigment-binder method in fibre, yarn, fabric or full-garment form.

3. Collection

Coloured garment is disposed of and becomes post-consumer waste. This is collected and sorted for recovery.

2. Consumption

Coloured garment is leased / bought by consumer and undergoes normal consumer usages, e.g. as laundering, throughout its lifetime.

Figure 1.2 Proposed route for the continuous reuse/recycling of cotton due to implementation of the developed colouration and colour removal method

Chapter 2 – Literature Review

2.1 Cotton

The seed hair of the plant of the genus *Gossypium*, also known as cotton, is the purest form of cellulose available in nature (Hsieh 2007; Alongi and Malucelli 2015). The fibre accounted for almost 25% of the global fibre production in 2017, making it the second most important fibre after polyester, and the most important of all the natural fibre types (Textile Exchange 2018).

2.1.1 Chemistry and Properties

Cotton cellulose comprises a long chain of glucose molecules. Two linked anhydroglucose units form anhydro-beta-cellobiose, which is the repeat unit of the cellulose polymer chain, Figure 2.1 (Alongi and Malucelli 2015). The number of repeat units linked, forming the polymer, is defined as the degree of polymerisation (DP). In comparison to other cellulose fibres, cotton has a high crystallinity and a high DP (>10,000), adding to the strength properties of the fibre (Marx-Figini and Schulz 1966). The abundant hydroxyl groups enable inter-molecular and intra-molecular hydrogen bonding, facilitating the crosslinking reactions in dyeing and finishing applications and serve as the principal sorption sites for water molecules (Cotton Incorporated 2017).

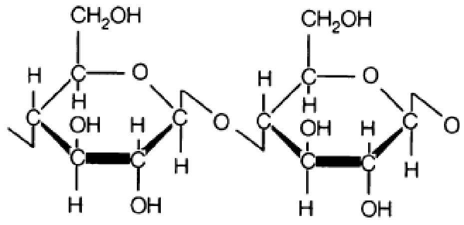


Figure 2.1 Chemical structure of cellulose repeat unit (Alongi and Malucelli 2015)

The cotton fibre has a fibrillar structure and is composed of a primary wall, secondary wall and lumen, Figure 2.2. A typical bale of cotton may comprise 'normal' or mature fibres and also a lower proportion of immature fibres. The maturity of the fibre is related to the thickness of the secondary wall, which influences the fibre quality and value. The lumen is the innermost part of the cotton fibre and contains the hollow space running through the length of the fibre as well as some residual protein. During the growth period of the fibre, it is filled with living protoplast. Once matured, the protoplast dries up and the lumen collapses, leaving a hollow space in each fibre and creating the characteristic twists or convolutions in the cotton fibre (Cotton Incorporated 2017). The convolutions increase the inter-fibre friction and allow the spinning of fine yarns (Dochia et al, 2012).

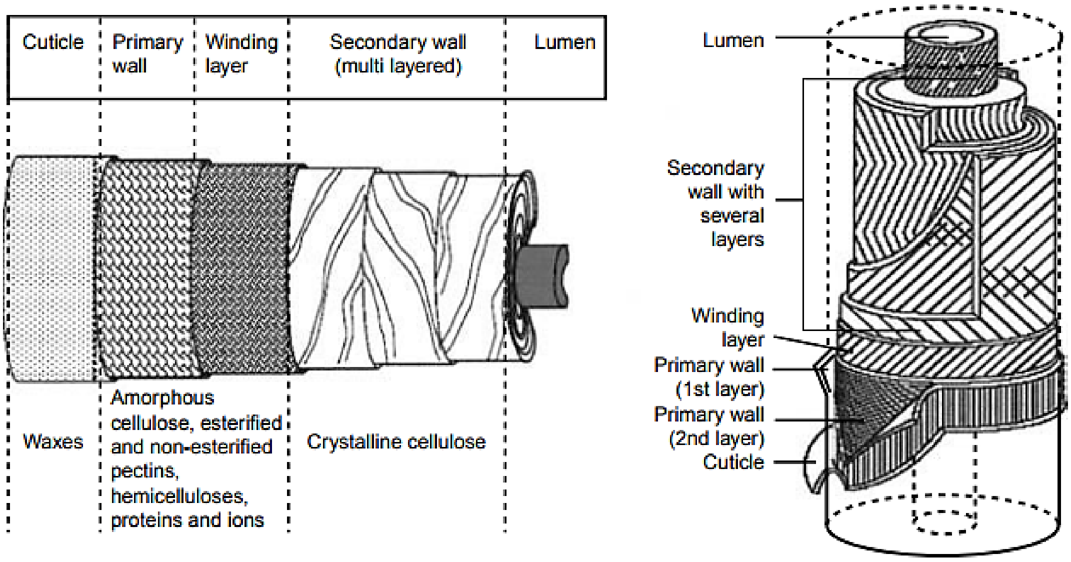


Figure 2.2 Schematic of cotton morphology (Dochia et al, 2012)

The specific composition of cotton fibres depends on a several factors including their varieties, growing environments (soil, climate and weather conditions, etc.) and maturity (Grishanov 2011). The bulk of a mature fibre is comprised of the secondary wall, where the cellulose chain orientation and DP are both high. It consists of multiple layers of almost entirely cellulose fibrils. The primary wall consists of less than 30% cellulose fibrils of low orientation, covered with an outer layer of non-cellulosic materials, including protein, mineral matter, pectin and wax. The latter two materials being responsible for the hydrophobic character of raw cotton fibres (Alongi and Malucelli 2015).

As with the chemical composition of the fibre, the physical properties of cotton vary depending on the type of the fibre, growing environment, harvesting practices and other factors (Grishanov 2011). The staple length for example, can range from 9.5-25 mm for Indian and Asian cottons to 38-63 mm for South American and extra-long Staple cottons. Typically, the fineness of cotton fibres is between 0.13 and 0.21 tex (by linear density), between 2 and 6.5 (by Micronaire reading) or between 12 and 20 µm (by diameter). Cotton's high level of sensorial comfort is related to the tapered ends of the fibre as well as to the fineness. A coarser fibre (related to a larger diameter) will have a stiffer feel. The abundance of hydroxyl groups in the molecular structure of the fibre, as well as the high percentage of voids in the fibre structure both make cotton garments cool to wear. Liquids and vapours can easily be absorbed and wicked away to the environment, keeping the surface of the skin dry. (Grishanov 2011; Zhong 2013). Commercial cotton fibres generally have a creamy yellow to bright white colour appearance. Naturally pigmented and coloured cotton do exist but tend to be regarded as inferior to white cotton due to low yield in production, poor fibre properties such as short fibre length, and non-uniformity of colours (Murthy 2001; Dutt et al, 2004).

2.1.2 Environmental Impact of Cotton Production

Natural fibres such as cotton are often viewed by consumers as superior in eco-friendliness or sustainability in comparison to man-made fibres such as polyester. However, the reality associated with the production of cotton is not clear.

Sustainability in this context is considered as the successful balancing between environmental protection/health, economic profitability and social needs (Wakelyn and Chaudry 2009). The main environmental issues related to cotton fibre production and dyeing processes are well known (Blackburn and Burkinshaw 2002; Khatri et al, 2015; WRAP 2017) and the impact linked to dyeing will be further discussed in section 2.4.

The best growing conditions for the cotton plant are in sub-tropical countries with 6 to 7 months of warm, humid weather (Dochia et al, 2012). Cotton is a relatively drought tolerant crop, but when the plant is grown in semi-arid climates, additional irrigation is required. Cotton producing countries include China, India, USA, Pakistan, Brazil, Turkey, Australia and Uzbekistan with India and Pakistan also likely to suffer water stress and scarcity, Figure 2.3 (WRAP 2017). The global average water footprint to produce 1 kg of cotton, an equivalent to the weight of one t-shirt and a pair of jeans, is 10,000 – 20,000 litres (WRAP 2017). A devastating example of the effect of the water consumption required for cotton cultivation is evident in the drying up of the Aral Sea in 2014 due to ‘‘leaky’’ irrigation systems, affecting the local fishing, ecosystems and general health of the population around the sea (Micklin 2007; Howard 2014).

On top of the large volumes of water, cotton cultivation also requires the use of insecticides, herbicides and fertilisers in order to achieve the required fibre quality and yield (Huang et al, 2003). Irresponsible use of crop production products can lead to serious consequences in agriculture such as health issues of farmers, contamination of surface and ground waters, increase in resistance of pests and severe degradation of the agro-ecosystems (Khan, Mahmood and Damalas 2015). Approaches to solving the problems around cotton include genetic engineering of the crop and the implementation of specific systems to reduce chemical usage during crop production.

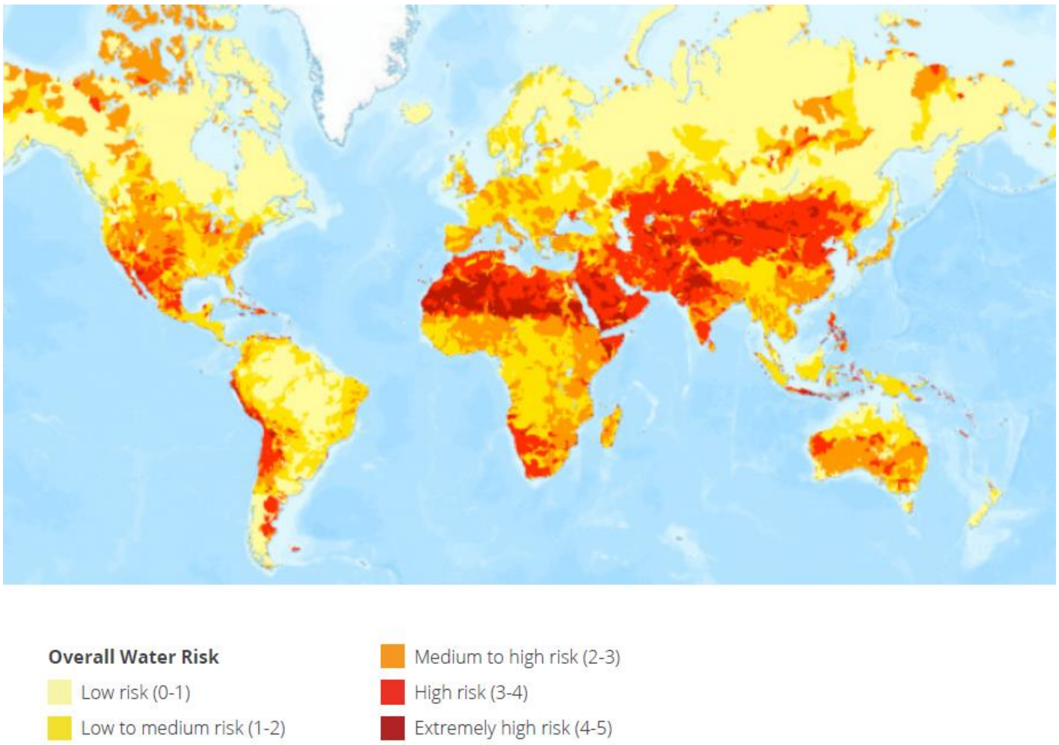


Figure 2.3 Water risk atlas 2015 (WRAP 2017)

In 2017 about 80% of the global cotton area was used for the growing of genetically engineered or biotech cotton (ICAC 2018). Biotech cotton reduces the number of insecticide applications and herbicide spray treatments needed to control insect pests and remove a broad range of weed species (Shaner 2000; Huang et al, 2003; Wan et al, 2017). Insect resistant cotton or Bt-cotton is cotton genetically engineered to produce Bt δ-endotoxin, a natural occurring insect poison from the bacterium *Bacillus thuringiensis.* As the Bt δ-endotoxin targets bollworms and budworms, the adverse effects on non-targeted insects are minimised (Wakelyn 2006). Herbicide-tolerant cotton or HT-cotton is engineered to be tolerant to a specific broad-spectrum herbicide allowing application of this herbicide without damaging the plant itself as well as reducing the number of various sprays needed that each target only one or a few weed species. Even though genetical engineering can provide these excellent advantages for the production of cotton, difficulties are now found in the increasingly rapid evolution of pest resistance to Bt proteins (Wan et al, 2017; Jin et al, 2018).

Another approach to improving the conventional production of cotton is the implementation of organic system standards into the production of the crops (ICAC 2015). Organically produced cotton is often marketed as a more ′′sustainable′′ alternative for conventional cotton. Unfortunately, organic does not necessarily equate to sustainable. Organic cotton production practices mainly differ from those of conventional cotton production in the crop protection products, fertilisers and tillage practices used (Wakelyn and Chaudry 2009). Organic cotton production eliminates the use of synthetically compounded chemicals, and instead uses ′′natural′′ chemicals such as sulphur dust and Bt sprays for pest management and organic acid-based foliar sprays and zinc sulphate for harvest preparation (ICAC 2015). In addition, the fertilisers used to supply nitrogen for the growth of the plants rely on manure from poultry and cattle/dairy instead of commercial fertilisers. With the use of commercial fertilisers, loss of nutrients can occur in the form of leaching, volatilisation and erosion. Organic manure, however, can also present a problem in the form of nutrient run-off into streams and leaching into ground water (Sharpley 1997; Allen et al 2006). Additionally, in contrast to commercial fertilisers, the nutrients in poultry manure are not readily available for plant uptake and difficulty is found in being able to produce enough to meet demands for fertiliser needs (Wakelyn and Chaudry 2009). Looking at the cost of production, it would be expected that the elimination of synthetic chemicals and fertilisers would reduce the costs for organic growing and harvesting of cotton. However, the associated higher costs related to the relatively lower yield obtained by organic cotton production practices in combination with manual labour for weed control and potentially lower lint quality need to be taken into consideration when comparing the sustainability of organic and conventional cotton production practices.

The difficulty of modifying the cotton production in such a way that it minimises environmental impact, as well as allowing economic profitability, shows that there is a need to develop other ways of limiting the disadvantages related to the production of the fibre. One approach is to valorise the material that is already in existence in the form of textile waste to use as a feedstock to produce new cotton products.

2.1.3 Recycling of Cotton

Cotton waste textile can be recycled through breaking the product down into its basic components and using these to produce a product of a lower value in comparison to the constituent, or by converting the material into a product of a similar or even higher value.

Mechanical recycling of textiles involves shredding the textile fabric back into fibrous form. The process is often found to result in shortening of the fibre length as a result of friction between fibres (Lindström et al, 2019). It is well known that shortening of fibre length affects the quality of the resulting yarns due to higher potential of yarn breakage with the amount of times the fibres can wrap around each other having been decreased. To overcome this disadvantage and obtain a yarn strength similar to that of virgin cotton, the recycled fibres need to be blended with virgin fibres (Merati and Okamura 2004; Halimi et al, 2007; Wanassi, Azzouz and Hassen 2016). The challenge in mechanical recycling therefore is found in obtaining yarns of appropriate strength by recovering fibres of appropriate length whilst aiming to reduce the proportion of virgin fibres needed to increase mechanical properties. Recover® (Hilaturas Ferre) in Spain mechanically recycles cotton waste for the production of coloured cotton yarns (Recover 2018). Water, energy and chemical consumption are reduced using solar power in the spinning process and by elimination of dyeing processes. Their fibres are blended with coloured carrier fibres, derived from recycled polyethylene terephthalate bottles or organically produced virgin cotton fibres, to obtain the required strength and colour. The study by Halimi et al. showed the reduction in mechanical properties of cotton yarns with increasing recycled fibre content, especially above 25 % of recycled fibre content (Halimi et al, 2007). Merati and Okamura produced two-component yarns composed of a recycled fibre core (67% cotton, 27% rayon, 4% polyester, 2% acrylic) covered by a virgin cotton sheath and three-component yarns comprising a polyester filament core covered by a middle layer comprised of recycled fibres and a virgin cotton sheath (Merati and Okamura 2004). It was shown that both the two-component as well as the three-component yarns had superior mechanical properties to that of 100% recycled fibre yarn but inferior to that of virgin cotton. However, the three-component yarn spinning method showed good potential for the production of medium count yarns (30 tex) as higher strength and elongation properties were obtained in comparison to virgin cotton yarns. Out of the whole yarn composition, the yarn was composed of 32.8% recycled cotton fibres. Wanassi et al. recycled waste cotton yarns into 50/50 recycled and virgin cotton blended yarns of 10, 15 and 20 Ne (Wanassi, Azzouz and Hassen 2016). The tensile strength of the recycled yarns varied from 73-84% of that virgin cotton yarns of the same count. Aside from managing the short fibre content in yarn spinning, studies have also focussed on how to obtain longer fibres from shredding of textile waste, such as fabric pre-treatment with a lubricant to decrease the inter-fibre friction and (Lindström et al, 2019). The mechanical recycling of materials is further complicated as the quality of the fibre is not just influenced by the feedstock quality in terms of fibre length and by the method of shredding, but also by the use of materials of varying lifetime usage, for example repeated laundering reduces the degree of polymerisation of the cellulose and therefore also reduces the quality of the feedstock in itself (Palme et al, 2014). Mechanical recycling of fibres does not require any chemical processes to remove any non-fibrous ‘contaminants’ such as finishes and colourants. However, this does mean that the textile materials still require sorting based on their colour amongst others. This sorting process is generally done manually and can be labour intensive. The sorting is also prone to human error. Automated sorting machines are currently being developed which can sort textiles based on fibre type and potentially allow sorting based on colour (Valvan Baling Systems 2018; IVL 2017).

Understanding the importance of the design stage and its effect on the properties of the end product, alternative methods of recycling of cotton can contribute to the closing the loop on cotton manufacturing without falling short on the performance of the recycled materials. These alternative processing techniques involve chemical recycling or the regeneration of new fibres. The work by Palme et al*.* showed the potential of cotton waste textiles to be used as a source for regenerated cellulose fibres as laundering tests resulted in a decrease of the molecular mass of the cellulose, to that appropriate for the viscose process (Palme et al, 2014). The number of start-ups focussing on the chemical recycling of textiles is increasing and they are collaborating with big fashion brands incorporating the recycled materials into high-value fashion items. Evrnu® from the US recently launched its consumer-facing brand NuCycl™ in collaboration with Adidas by Stella McCartney with a 100% recyclable hoodie which is said to be infinitely recyclable (Adidas 2019). The garment is composed of 60% NuCycl™ and 40% organic cotton. The company patented a method for the regeneration of cellulose fibres from post-consumer waste, virgin cotton or wood pulp and pre-consumer waste. This method comprises a multi-stage process with one or multiple pre-treatments of the materials, followed by dissolution for the isolation of the cellulose molecules from the non-cellulose material and subsequent extrusion of the fibres (Flynn and Stanev 2016). The Infinited Fiber Company in collaboration with H&M group recently debuted a proof-of-concept garment made from recycled cellulose (Chua 2019). The Finnish manufacturer uses a modified viscose technology that converts cotton waste into cellulose carbamate (European Commission 2018; Fontell et al, 2018). H&M also supports the Swedish startup Re:newcell and its Circulose fibres, with the first garments made from the recycled fibres planned for debut by spring 2020 (Re:newcell 2019). These methods for regeneration of fibres from cellulose waste are based on the process that has been used for over a century to produce fibres from a viscous solution of natural cellulose, also known as viscose. Only now the feedstock is not just composed of wood pulp, but partially consisting of cellulose from waste products. Chemical recycling of cotton and other cellulose-containing materials can obtain regenerated fibres with properties similar or even superior to those of the virgin material (Haule, Carr and Rigout 2016).

Viscose

A longstanding method for cellulose regeneration is the viscose (rayon) process (Newcomb and Chae 2018). For the recycling of cotton, the fibres are mixed with wood pulp and the mixture is immersed in sodium hydroxide and reacted with carbon disulphide to produce cellulose xanthate. The cellulose xanthate is then dissolved in dilute sodium hydroxide, which is the viscose solution from which the fibres are wet-spun. The spinning bath containing sulfuric acid, sodium sulphate and zinc sulphate facilitates acidification of the sodium cellulose xanthate, coagulation to form the fibres and cross-linking of the macromolecules. The complexity of the viscose process and the potential of carbon disulphide to cause adverse effects on the health of the plant workers and on the environment are reasons for the emergence of alternative methods for the dissolution of cellulose (WHO 2002).

Lyocell

A less complex and less chemical consuming alternative to the viscose process is the direct dissolution of cellulose in N-methylmorpholine-N-oxide (NMMO) producing fibres known under the name of Tencel or Lyocell (Perepelkin 2007; Haule, Carr and Rigout 2016). The direct dissolution into NMMO has a lower impact on the environment as the solvent is non-toxic and biodegradable and both the water and solvent used in the spinning process can be reused. The Lyocell process involves dissolving the feedstock material into an aqueous NMMO solution to form a concentrated solution of cellulose also called a dope. This viscous cellulose solution is then filtered and extruded through an air-gap into a precipitation bath for the coagulation of the cellulose fibres (dry jet-wet spinning) before washing and drying and post-treatments of the fibres. The viscosity, related to the degree of polymerisation or cellulose concentration, of the cellulose solution is an important parameter which needs to be controlled in order to minimise difficulties when processing the dope (Fink et al, 2001; Petrovan, Collier and Negulescu 2001). Crosslinking of the cotton cellulose that occurs with some finishes and dyes do pose a challenge in the efficiency of the cellulose dissolution (Haule, Carr and Rigout 2014; Bigambo 2016; Wedin et al 2018). The removal of these chemicals from the cellulose material prior to dissolution is therefore of importance.

The complexity found in recycling systems together with the disadvantages of cotton production show that there is a need for a different approach. Instead of developing colour removal methods based on the waste material, another approach could be to start further back in the product manufacturing line and investigate the design of a relatively simple colouration mechanism, which in turn allows simplifying the removal of these colours from the textiles. This concept could not only be applied to post-consumer waste, but potentially allow implementation into garment-lease systems, where garment designs can be rapidly changed when needed. This way the production of textile waste can be reduced and prevented in a most efficient way.

2.2 Bunte Salts

Bunte salts are compounds with the formula $R\text{-}SSO_3^-Na^+$ and can be derived from alkyl halides and sodium thiosulfate and also by the direct addition of sodium thiosulphate to compounds containing activated multiple bonds (Distler 1967). Bunte first prepared the S-ethyl thiosulfate sodium salt aiming to clarify the structure of sodium thiosulfate (Bunte 1874). Since that synthesis study, the S-alkyl and S-aryl thiosulfate salts bearing his name, have been shown to be valuable for pharmaceutical as well as for textile applications.

Bunte salt-terminated polyethers have been studied for their potential as pigment binders for the pigment dyeing and shrinkproofing of wool (Hinks and Lewis 1993; Lewis 1999). Synthesis of the Bunte salt -terminated polyethers involved esterification reaction with chloroacetic acid, followed by Bunte salt formation using sodium thiosulphate. The crosslinking mechanism for polymer/wool crosslinking relied on the Bunte salt groups readily reacting with thiol residues (cysteine) in wool, forming covalent disulphide bonds. The Bunte salt-terminated polyethers showed excellent potential for application as shrinkproofing agents and pigment binders as well as for their use as wetting agents and dispersants.

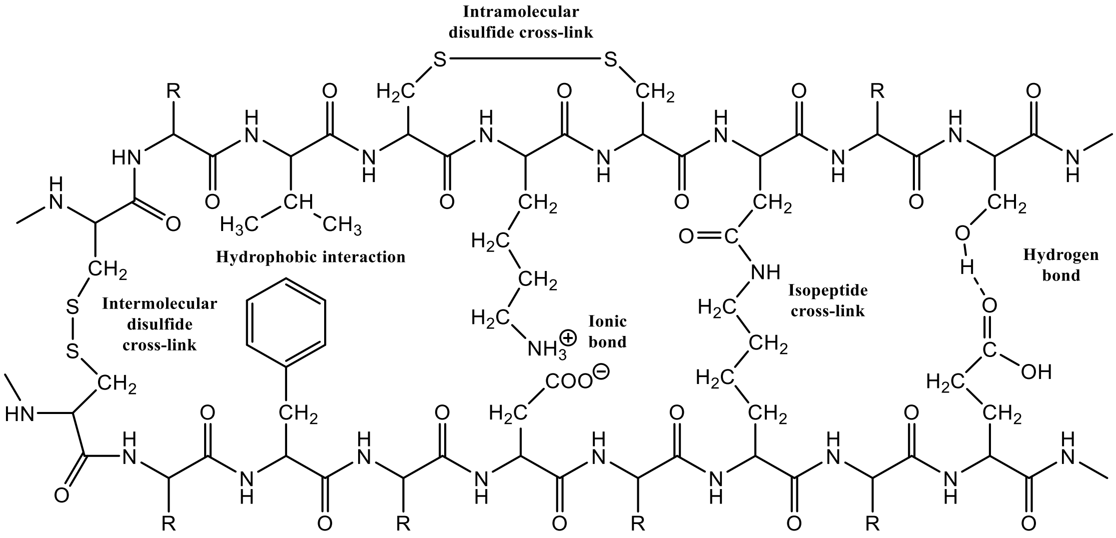
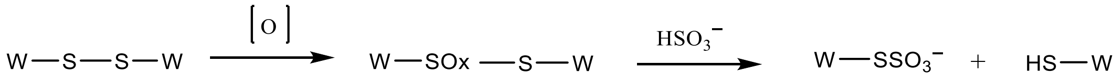


Figure 2.4 Covalent and non-covalent interactions in wool α-keratin (Rippon 2013)

It has been shown that acid hydrolysis of Bunte Salts yields thiols, whilst alkaline degradation may yield sodium sulphite, sulphenic acids and disulphides amongst others (Price and Twiss 1908; Lecher and Hardy 1955; Milligan and Swan 1963; Kice, Anderson and Pawlowski 1966). Thiols are sensitive to air and readily oxidise to disulphides in the presence of atmospheric oxygen (Ruano, Parra, Alemán 2008). For the study described in this thesis, the value of the Bunte salt chemistry is therefore found in their role as intermediates for their potential for thiol formation and oxidation to produce disulphides for the fixation of compounds onto fibres.

Douthwaite and Lewis studied the preparation of Bunte salt functional groups from wool (Douthwaite and Lewis 1994). Keratin proteins such as wool contain a relatively high content of sulphur and is found mainly in the form of the amino acid cystine. The crosslinked disulphide bonds of cystine are responsible for the stability and low solubility of wool, Figure 2.4 (Rippon 2013). The study of the formation of Bunte salt groups in wool involved oxidation using potassium peroxymonosulphate to convert cystine residues into cystine intermediate oxidation products, followed by a reaction with bisulphite to form the cysteine-S-sulphonate groups. The proposed reaction is given in Scheme 2.1 where ‘‘W’’ represents the wool protein chain. This chemistry shows value for the production of a binder for the colouration of textile fabrics such as cotton, from bio-based resources such as wool containing readily available cystine residues.

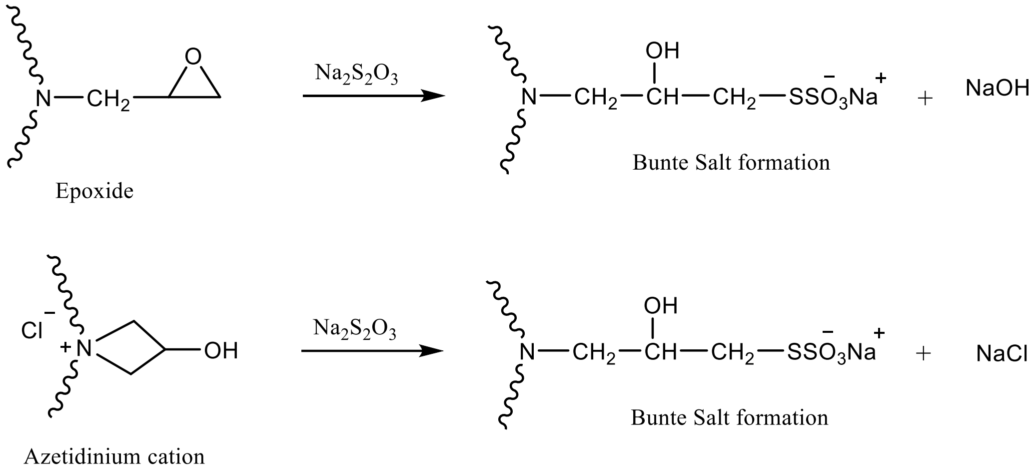


$$W{-}S{-}S{-}W \xrightarrow{[O]} W{-}SO_x{-}S{-}W \xrightarrow{HSO_3^-} W{-}SSO_3^- + HS{-}W$$

Scheme 2.1 Preparation of Bunte salts from wool (Douthwaite and Lewis 1994)

Bunte salt-terminated polymers have also been prepared from polyamide polymers (Cockett and Lewis 1976). A cationic polyamide prepolymer, Hercosett™ 57 was converted into a Bunte salt-terminated polymer with an overall anionic character, for the chlorination of wool tops. Hercosett™ 57 was reacted with sodium thiosulfate to give the Bunte salt-terminated polymer. The proposed reaction of the thiosulphate nucleophile with reactive groups in the cationic polymer was described as given in

Scheme 2.2. However, recent published studies could only find evidence for the presence of the azetidinium reactive groups in polyamide epichlorohydrin resins, hence for the knowledge of the current work it is assumed that the Bunte salts in this context were only produced in reaction with the azetidinium cation and not with the epoxide reactive group (Kricheldorf 1981; Guise and Smith 1985; Obokata and Isogai 2004). This chemistry is of interest for the potential of polyamide epichlorohydrin resins such as Hercosett™ 57 to produce Bunte-salt terminated polymers which can function as a polymeric binder for the colouration of textile fabrics such as cotton.



Scheme 2.2 Proposed reactions of sodium thiosulphate with Hercosett™ 57 (Cockett and Lewis 1976)

Bunte salt chemistry has also been studied for its potential in the finishing of cotton fabrics (Belot 2005). Wool was subjected to a two-step treatment to produce Bunte salt-terminated protein derivatives. First, the wool was ′′sensitised′′ with a hydrochloric acid solution to partially hydrolyse the amide linkages of the chemically resistant wool keratin, producing two fractions: dissolved proteins and undissolved but partially hydrolysed proteins. The latter were subjected to following oxidative sulphitolysis treatment with a sodium bisulphite solution. Oxidative sulphitolysis involved oxidation of the cystine disulphide bridges to produce cysteine-S-sulphonate and cysteine. The introduction of air into the mixture allowed simultaneous oxidation of the unstable cysteine to re-produce cystine which could then in turn produce cysteine-S-sulphonate and cysteine and so on until no cystine is left.

Keratinous waste is generated by the textile, breeding and butchery industries in the form of wool, hair, feather, beaks, hooves, horns and nails. The disulphide bonds and the extensive crosslinking in keratinous materials, provide them with a rigid structure and make them difficult to degrade. Various studies have already investigated numerous degradation methods for keratin-rich materials (Mokrejs, Krejci and Svoboda 2011; Ayutthaya, Tanpichai and Wootthikanokkhan 2015; Shavandi et al, 2017; Peng et al, 2019) and their potential as a resource for medical applications (Reichl 2009; Wang et al, 2017) and cosmetic products (Villa et al, 2013; Mokrejs et al, 2017). For the current work the use of keratin waste as a sustainable resource material was of interest when a key objective was to minimise the environmental impact of colouration processes. Of specific interest was the potential for the use of wool waste, containing a high amount of cystine (Zoccola, Aluigi and Tonin 2009) which could be converted to produce Bunte salt-terminated polymer binder materials by cleaving the inter- and intramolecular bonds of cystine. Fixation of colour onto cotton was expected to be achieved due to the crosslinking mechanism in the form of the formation of disulphide bonds from these Bunte salt groups.

2.3 Polyamidoamine Epichlorohydrin

2.3.1 Chemistry

Polyamidoamine epichlorohydrin (PAE) is a neutral/alkaline curing resin known for its use as an excellent wet-strength agent in the papermaking process (Kymene™), for its use to shrink-resist wool (Hercosett™) and has also been used to improve the dyeability of cellulose fibres (Guise and Smith 1985; Burkinshaw, Lei and Lewis 1989;

Burkinshaw et al, 1990; Dunlop-Jones 1991; Obokata and Isogai 2007; Hassan and Carr 2019). Its chemical structure generally comprises a polyamide backbone with reactive side chains. The PAE solutions (generally 10-30%) are produced by condensation of a dicarboxylic acid or its ester with a polyamine (e.g. diethylene triamine) to produce a water soluble polyamidoamine. The polyamidoamine mainly contains secondary amines, but also a small quantity of primary amines and carboxylic end groups. The addition of epichlorohydrin most importantly to the secondary amine groups results in the formation of tertiary aminochlorohydrins, which can self-alkylate to form 3-hydroxyazetidinium ring (AZR) groups, Figure 2.5 (Siqueira 2012). A minor reaction occurs in the form of crosslinking between polyamidoamine chains during the azetidinium ring formation. The four-membered AZR groups are responsible for the reactivity and the cationic charge of the resin due to the strained and therefore highly reactive nature of the rings (Dunlop-Jones 1991; Obokata and Isogai 2004). One study concluded the presence of AZR, epoxy and chlorohydrin groups in a commercial PAE resin (Carr et al, 1973). However, later studies confirmed only the presence of the azetidinium groups (Kricheldorf 1981, Guise and Smith 1985; Obokata and Isogai 2004).

Typically, commercial PAE solutions are kept at pH 3 – 4 to maintain the stability of the polymer after synthesis. The addition of sulfuric acid and formic acid for this purpose may result in the formation of HCl as a reaction between the acids and the chlorine ions at the quaternary ammonium groups. Any free epichlorohydrin present in the solution could then be partially converted into the toxic by-product 1,3-dichloro-2-propanol and 3-monochloropropan-2-ol (Obokata and Isogai 2005; Solenis 2014b). Therefore, innovative process solutions have been designed to limit the production of harmful by-products through for example biohalogenation or membrane separation technologies (Solenis 2014b). Biohalogenation involves using naturally occurring microorganisms to consume the by-products. This process uses little energy, requires no additional chemicals and no additional waste is produced. It does however affect the level of functionality in the polymer resins. Membrane

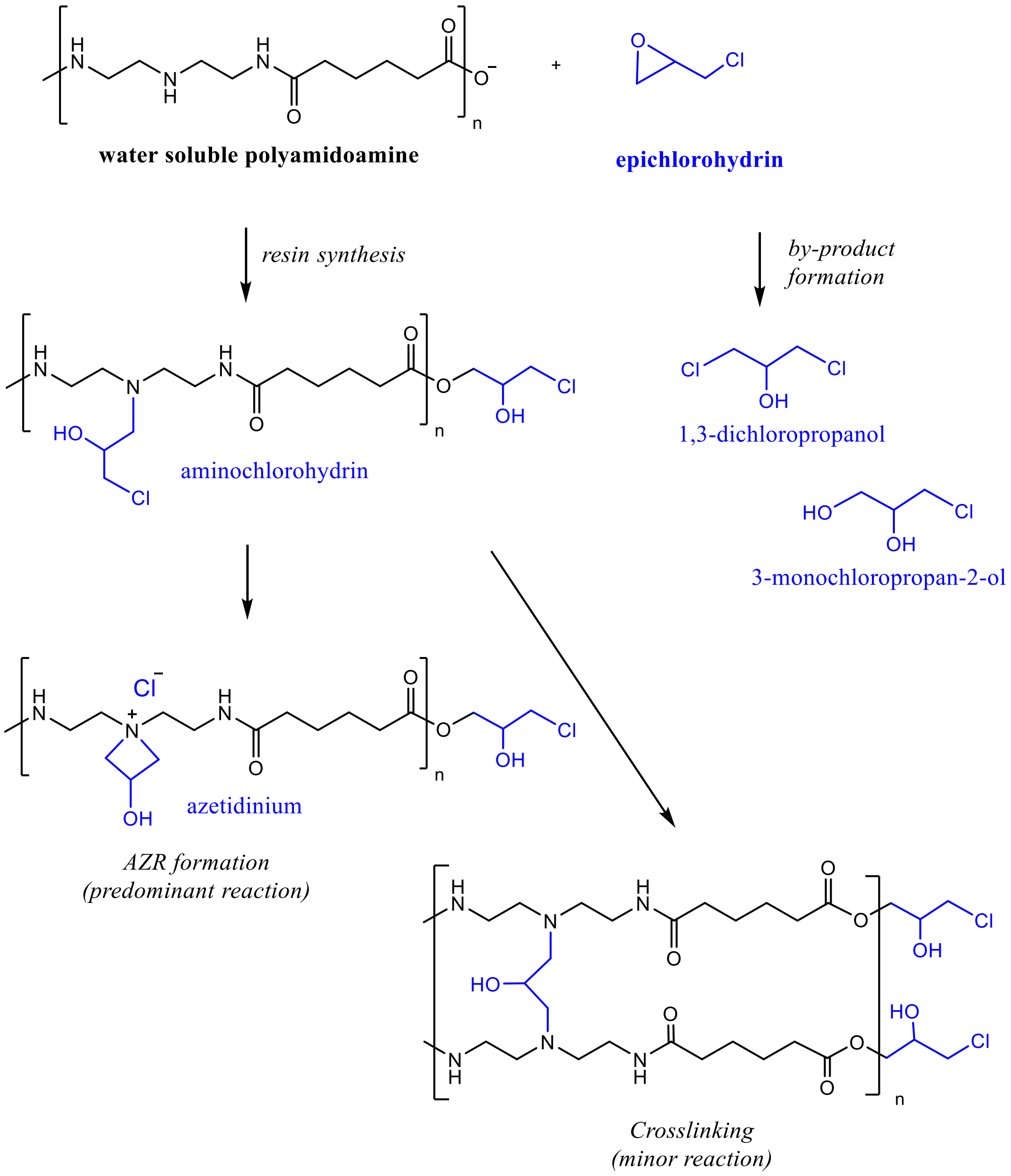


Figure 2.5 PAE synthesis (Obokata and Isogai 2004; Solenis 2014b)

separation involves nanofiltration to remove all by-products allowing the production of solutions without compromising on AZR functionality (Riehle and Vinciguerra 2011). Care still needs to be taken with regards to shelf-life, due to the instability of the AZR groups, with PAE tending to lose its activity during prolonged storage or storage at storage temperatures higher than recommended, causing the PAE to react with itself.

2.3.2 PAE and Cellulose

PAE is used in the paper industry as a wet-strength agent, useful for applications that involve contact with liquids such as milk cartons. Paper is a sheet of cellulose fibres, derived mainly from wood, with a number of added components to obtain the properties required for the specific application purposes. In dry paper the fibres are predominantly held together by hydrogen bonding (Gardner et al, 2008; Su et al, 2012). These bonds are broken when the fibres are wetted as a result of swelling of the fibres. When wetted, paper generally loses most of its strength, keeping approximately 3 to 10% of its original dry strength (Dunlop-Jones 1991). With the addition of reactive polymeric materials such as PAE, the wet-strength of the cellulose fibres can be reinforced to be at least 10 to 15% of the dry strength (Hubbe n.d.). The crosslinking between the polyamidoamine backbones through the AZR groups is accountable for the increase in molecular mass of the PAE intermediates. An increase in higher molecular mass has been linked to the increase in wet-strength of paper (Obokata, Yanagisawa and Isogai 2005). The mechanism of wet-strength development in the papermaking process is primarily ascribed to the covalent bonding between PAE and the cellulose. The carboxyl groups in cellulose behave as anionic retention sites for the cationic PAE molecules facilitating ester bond formation between the carboxyl groups of the cellulose and the AZR groups of the PAE during curing of the sheets (Obokata and Isogai 2007; Siqueira 2012). In this way, wet-strength additives such as PAE-based additives provide strength to the paper when it is wetted, but also increases strength in dry state as existing fibre-fibre bonds are reinforced (Solenis 2019). Su et al showed that the wet-strength of cellulose can be increased with increasing add-on concentrations of PAE (Su et al, 2012). The maximum concentration of PAE was 10 mg per g of oven dried cellulose after which the ratio of increased wet strength to dry strength of the paper levelled off. It was also found that the increase in PAE concentration correlated with a decrease in recyclability of the paper, which was assessed by proportion of the fraction of the mechanically re-pulped slurry that did not pass the slot screen. It was shown that with increasing PAE dosage, wet-tensile properties increased and simultaneously, recyclability decreased. In recycling conditions, when paper is wetted, the hydrogen bonds between the fibres are disrupted by competing water molecules, thus weakening the inter-fibre bonds and allowing easy breaking down of the paper into individual fibres using mechanical shear force. As the addition of PAE increases inter-fibre bonding, the breakdown of the fibre network is inhibited, and recycling becomes much more difficult.

2.3.3 Degradation of PAE-Containing Cellulose

When considering PAE to be selected as a potential binder material for the colouration of and colour removal methods to be developed, it is important to not only understand its potential to fix colour particles onto cellulose substrates, but also its potential to be removed from the substrates.

In published literature, the degradation of PAE present in cellulose substrates was mainly studied in the context of degradation or re-pulping of PAE-based sheets. Re-pulping involves separation of the fibres from the sheet form and dispersing them in water for reformation into a web. Pulping processes can rely on chemicals, mechanical action or a combination of both for fibre separation. During pulping in a recycled fibre recovery process, wet-strength paper is separated from the aqueous slurry as a contaminant material along with others such as wires and plastic sheeting (Bajpai 2018).

Traditionally sodium hypochlorite was used by paper mills to enable the recycling of wet-strength modified paper, but these reagents are now regarded as less desirable due to environmental concerns arising from the formation of organic halides during processing and adding chlorinated derivatives to the effluent streams (Bjørseth, Carlberg, and Møller 1979; Gelman and Hyunh-Ba 1999; Fukazawa et al, 2001). Non-halogen containing compounds such as persulphate salts have also been used as alternatives for the re-pulping of wet-strength paper (Espy 1997; Caropreso, Thorp and Tieckelmann 1999; Gelman and Hyunh-Ba 1999). The mechanism of the re-pulping methods relying on oxidation of the wet-strength PAE agent leading to fibre separation. United States Patent US5585456A describes a method to prepare a polyamidoamine epichlorohydrin resin that allows imparting of wet-strength to paper but also allows a reduction of the re-pulping time (Dulany et al, 1996). Re-pulping was carried out by adding the wet-strength paper product to an aqueous solution, of pH 4-12, before stirring and heating up to a temperature of 70°C. It was claimed that when the re-pulping process was performed at pH 10, paper products can be re-pulped in 20-70% shorter time compared to other commercially available polyazetidinium chloride resins. The re-pulping process patented by Balos et al involved using a two-step pH method for the re-pulping of wet-strength paper (Balos et al, 1997). The invention describes the first step of the process with the initial pH environment of the paper slurry of pH ≤8, followed by heating of the slurry up to an ideal temperature of 70°C and addition of a non-chlorinating oxidising agent such as sodium persulphate, sodium peroxymonosulphate, hydrogen peroxide and peracetic acid. The slurry is then mixed for 30 to 60 minutes to initiate breakdown of the fibres, followed by adjusting the pH to pH ≥10. The slurry was left for another 15 minutes minimum to substantially complete the breakdown of the paper. Kanie et al investigated the biodegradability of composite paper sheets with and without addition of PAE and polyvinylamines and genuine paper sheets (Kanie et al, 2005). After 30 days of degradation in soil, the composite sheets prepared with PAE and polyvinylamines had a weight loss of 65%, whereas the sheets without addition of PAE and polyvinylamines and genuine paper sheets had 82% and 90% weight losses, respectively, over the same time period. Siqueira examined a variety of different methods for the degradation of PAE films and PAE-based industrial papers (Siqueira 2012). Degradative treatments were carried out using water, and aqueous solutions of sodium hydroxide, hydrogen peroxide, potassium persulphate ($K_2S_2O_8$), and sulphuric acid. Using $K_2S_2O_8$ as the degradative agent, obtained the best results in terms of relative weight difference and tensile properties before and after the treatments. The method, based on the work by Fischer (Fischer 1997), involved a 2-step pH process. The PAE containing material was initially stirred in a $K_2S_2O_8$ solution at an acid pH (pH <7) at 80°C for 60 minutes, followed by 120 minutes stirring at alkaline pH (pH = 11).

The crosslinking ability of PAE and the established efficiency for application on textiles such as wool and on cellulose in the form of paper as well as its potential use for targeted degradation, are reasons to believe that the polymer resin could be suitable for application as a binder material for the colouration of cotton fabrics.

2.4 Pigment Colouration

2.4.1 Pigments as an Alternative Colorant to Dyes

Textiles can be changed aesthetically by applying colour onto the fibrous substrate in the form of dyes or pigments (Broadbent 2001; Gutjahr and Koch 2003). Using dyes for textile colouration can provide a product of the desired colour or colour pattern that is able to withstand repeated laundering cycles and exposure to light or friction. In contrast to pigments, dyes are generally water soluble and have a substantivity for textile fibres, either inherently or induced with the use of reactants. Dyes are fixed onto fibres as a result of reactions specific to the dye type. Dyes used for cotton include vat, azoic, sulphur, reactive and direct dyes (Broadbent 2001). The application mechanism for vat, azoic and sulphur dyes involves reduction of the water-insoluble dye (Koh 2011). The reduced (leuco) form of the dye has an increased water solubility and has a degree of substantivity towards the fibre which enables adsorption of the leuco dye molecules by the fibre. Once adsorbed by the fibre, the dye oxidises *in situ* back to its insoluble form and is thus mechanically trapped within the fibre. The initial adsorption is based on hydrogen bonding, Van der Waals forces and hydrophobic interactions. Reactive dyes are attached to the cotton fibre by forming strong covalent bonds between the dye and the fibre through reactions between the functional groups of the dye chromophores and the hydroxyl groups of cellulose (Blackburn and Burkinshaw 2002; Koh 2011). Direct dyes are retained on the fibre surface through hydrogen bonds and Van de Waals forces (Koh 2011). Direct dyes have a substantivity for cellulose, but due to their anionic nature and the negative charge of cotton fibres in water, salt needs to be added to overcome the repulsion between the fibre and dye molecules and control dye uptake in combination with an increase in temperature. An additional aftertreatment is generally required to improve fastness properties. What all these dyes have in common is that they rely on the physical and chemical interactions between the fibre and the dye or on mechanical entrapment of the dye within the fibre. In looking to obtain maximum durability of the colour on textiles, this multi-faceted binding needs to be overcome in order to affect the removal of the colour in order to recover the original textile material. Additionally, the most important dye class for dyeing cellulose, reactive dyes, requires large quantities of salts to improve exhaustion and fixation of the dye. The process results in the production of effluent contaminated with high amounts of salts and hydrolysed dyestuff, which could in turn affect aquatic life if the effluent is not treated appropriately. Numerous investigations have been aiming to improve the reactive dyeing process including the pre-treatment of cotton (Blackburn and Burkinshaw 2002; Ma et al 2005). An alternative approach of colouration, when keeping in mind the potential of the material for subsequent colour removal is using the pigment colouration system.

Pigments can provide colour to textiles, but this colour application often goes hand in hand with making the substrate more rigid, especially noticeable on light weight-, knitted- or voluminous textiles. This effect on the fabric handle is due to the properties of the ʹʹpigment fixation vehicleʹʹ or binder material required to transport and fix the dispersed pigment particles onto the fibre surface (Schwindt and

Faulhaber 1984). The procedure for applying pigments to textiles is relatively simple, starting with the application of the ink, through printing or padding, followed by drying and fixation. Since pigments have no affinity for the textile fibres, the fixation of the particles relies on the properties of the binder material and the fixation process, allowing the enveloping of the particles by the binder material and the thin conformal coating of the fibre or yarn surface (Miles 2003). In comparison to dyes, the use of pigments eliminates the need for a wash-off step following colour application, since the process is essentially pad/dry/bake. Pigments can provide textiles with superior light fastness but tend to be prone to relatively low wet rubbing fastness. Due to the nature of the pigment colouration mechanism not relying on any affinity between the pigments and the fibres, they can be applied to almost any fibre, which is convenient for application onto fibre blends (Schwindt and Faulhaber 1984).

2.4.2 Pigment-Binder System

A successful pigment printing formulation is generally comprised of a pigment dispersion, binders and crosslinking agents and thickeners and auxiliary agents for obtaining the required rheology (Gutjahr and Koch 2003). With the thesis study focussing on the development of a simple pigment formulation, it is of importance to have a general understanding of pigments and binders and the crosslinking mechanism.

Pigments are inorganic, organic, coloured, white or black materials that, in contrast to dyes, are generally insoluble in most media. Even though in many cases the basic chemical structure of pigments is similar to that of dyes, pigments do not have any affinity for specific fibres due to their lack of chemical groups to react with the fibres (Schwindt and Faulhaber 1984). Examples are titanium dioxide (white), carbon black and ultramarine for inorganic pigments, and azo, anthraquinone and dioxazine for organic pigments (Herbst & Hunger 2006; Buxbaum 2008). For their fixation onto fibres, pigments can be dispersed in water and attached onto fabrics with the use of binder systems (El-Molla and Schneider 2006; El-Molla 2007). Some pigments are partially or even completely soluble in certain solvents, such as perchlorethylene, a dry-cleaning medium. Therefore, appropriate selection of the pigments is important for the required end-application (Schwindt and Faulhaber 1984). Pigments for textile application are generally synthetic organic materials which can be classified into the same chemical classes as soluble dyestuffs but have no ionic groups (Broadbent 2001). The particle size, particle size distribution and the refractive index of pigments influences the final colour in terms of intensity and opacity of the print and therefore needs to be of a specific size range (generally 0.03–0.5 µm) to obtain appropriate colouration results (Gutjahr and Koch 2003). Due to the water-insolubility of pigments, the wash and rubbing fastness of pigment prints is mainly dependent on the binder material, although the pigment particle properties also influence rub fastness to a certain extent (Schwindt and Faulhaber 1984).

Binders are the link between the pigments and the substrate to be coloured, by ‘’gluing’’ the particles onto the fibres. The binder encloses the pigment particles and forms a thin layer or film that adheres to the substrate surface. Most binders are applicable in aqueous systems and generally comprise dispersions of water insoluble acrylate-, styrene acrylate, styrene butadienes- or vinylacrylate-based prepolymers of comparable size to that of the pigment particles (≤5 µm) (Aspland 1993). The binder material is preferably colourless and transparent to allow application of the desired colour. Depending on the end application, the binder should be able to endure exposure to light or to mechanical or chemical stresses and hydrolysis to washing liquors, body sweat or industrial atmospheres (Gutjahr and Koch 2003). The fixed form of the binder-pigment onto the textile is in the form of a three-dimensionally linked network, usually through self-crosslinking of the binder material caused by the exposure to heat or a change in pH (Schwindt and Faulhaber 1984; Giesen and Eisenlohr 1994). The binder therefore needs to be able to withstand elevated temperatures. To further ensure that the binder-pigment system is resistant to wear and cleaning, it is of importance that crosslinking is limited to the degree that elasticity/handle is maintained whilst facilitating appropriate cohesion and adhesion to the substrate. The crosslinking reaction should only occur under specific fixation conditions and not during storage (Gutjahr and Koch 2003). Crosslinking of the polymeric binder material may occur through internal or external crosslinking. With internal crosslinking occurring, a small amount of a copolymer with residual reactive groups such as a N-methylol groups incorporated into the binder polymer, will undergo intermolecular condensation reactions during hot dry air curing. The crosslinks are reasonably stable to hydrolysis as a result of the reaction of methylol groups with each other or with hydroxyl groups, Scheme 2.3, with B representing the principal part of the binder molecule (Broadbent 2001; Gutjahr and Koch 2003.

$$\mathrm{B\text{-}CH_2OH + HO\text{-}CH_2\text{-}B} \xrightleftharpoons{\text{pH} <5} \mathrm{B\text{-}CH_2OCH_2\text{-}B + HOH}$$

or

$$\mathrm{B\text{-}CH_2OH + HO\text{-}B} \xrightleftharpoons{\text{pH} <5} \mathrm{BCH_2\text{-}OB + HOH}$$

Scheme 2.3 Binder crosslinking mechanism in mild (acid) conditions (Gutjahr and Koch 2003)

Poly-N-methylol compounds can be added to react with the N-methylol-containing copolymer binder material as well as with the fibre and other chemicals in the printing paste for external crosslinking. This is especially suitable for synthetic fibres because of the improved adhesion (Broadbent 2001). Other crosslinking mechanisms are based on epoxy and chloromethyl groups, where the limited stability of these crosslinking groups is overcome by including an excess of volatile organic acid. Crosslinking subsequently occurs upon vaporisation or neutralisation of the acid with aqueous alkali (Schwindt and Faulhaber 1984; Gutjahr and Koch 2003).

2.5 Gaps Identified

Cotton is the second-most important fibre and the most used natural fibre. However, the process from crop to finalised item made from cotton are related to negative impacts on the environment. Despite regulated irrigation systems and improved technology such as genetic engineering to reduce the amount of fertilisers and pesticides needed, the production of cotton still remains a contentious issue mostly due to the high levels of water usage and the environmental impact. Therefore, any process developments that can reduce water usage is beneficial and welcome.

Of all the dyeing processes, the reactive dyeing of cotton is the most prevalent and potentially poses a threat to the environment due to the process producing effluent contaminated with salts and hydrolysed dyestuff. The attraction of reactive dyeing is in its high colour durability, with the reactive dye strongly bound to the fibre through covalent bonds. However, for fashion garments where there is a relatively short lifetime, this high degree of colour fastness is often unnecessary. Furthermore, when it comes to recycling of the garments after their end-of-life, the covalently bound dyes are considered contaminants which may pose a problem to the fibre recycling process in terms of colour-based sorting for mechanical recycling or in terms of re-pulping efficiency for chemical recycling. Published studies have demonstrated the complexity of removing colorants from cotton, where dye class, the chemical nature of the dye as well as the composition of pigment formulations may affect the colour removal efficiency.

Colouration of cotton with a pigment printing method using a simple two component formulation (binder + pigment) may provide a solution overcoming the complexity of the removal of colour from cotton. The low number of formulation components allows the development of a more targeted colour removal or ‘stripping’ mechanism. With pigments possessing no affinity for the fibres to be coloured, the fixation and colour durability would rely on the binder material. Thus, the selection of an appropriate binder material for the pigment colouration of cotton could affect both the colouration and colour removal efficiency.

Potential binder materials can be found in the form of Bunte salt-terminated polymers or polyamidoamine epichlorohydrin (PAE). The potential of Bunte salt-terminated polymers lies in their ability to form disulphide linkages, advantageous for fixation of the pigment onto cotton substrates. Additionally, using Bunte salt-terminated polymers could address the use of waste materials as the Bunte salt polymers can be produced from wool. By demonstrating the potential of producing Bunte salt-terminated polymers from wool and the potential of these wool derivatives as a binder material for pigment colouration of cotton could potentially set the platform for future closed loop manufacturing of cotton as waste wool or even other waste keratinous materials could be utilised for the production of binder materials. Bunte salt-terminated polymers can also be produced from PAE, which is commercially available. Furthermore, unmodified polyamidoamine epichlorohydrin shows potential as a binder material since crosslinks can be formed on their reactive AZR groups. Understanding the crosslinking mechanisms of the potential binder materials could allow for controlled or targeted ‘degradation’ of the material for colour removal.

2.6 Objectives of the Thesis Research

Based on the abovementioned gaps found in the literature and the opportunities arising from those, the main objectives of this thesis work were:

Objective I. Assessing the use of bio-based resources and exploring Bunte salt chemistry for the production of potential binder materials

A fundamental objective was to deliver a more environmentally sustainable colouration system for cotton and for its end-of-life colour removal. Initial work investigated the colouration of cotton fabrics using ''eco-friendly'' materials and processing.

- Assess wool as a bio-based starting material for the development of a functional binder material that will allow the deposition and fixation of colour onto cotton fabrics
- Assess polyamide epichlorohydrin (PAE) as a starting material for the development of a functional binder material
- Explore Bunte salt chemistry for the development of a functional binder material, through the production of Bunte salt-terminated polymers from wool and PAE
- Select an appropriate ''sustainable'' colour application method

Objective II. Assessing the suitability of unmodified PAE as a binder material for pigment colouration

A commercial PAE, Hercosett™ 617, was evaluated as a potential binder material for the pigment colouration of cotton fabrics. The durability of the pigment colorants onto the fabrics was used as an indication of crosslinking of the polymer binder onto the cotton.

- Colour fastness to washing was identified as a key performance criterion, as it reflects the garments actual lifetime usage and durability to multiple domestic laundering cycles.
- Monitor the durability of the binder material indirectly through colorimetric assessment
- The in-use perception of the binder application was assessed through subjective fabric handle as well as by objective Kawabata Evaluation System

measurements. Ideally, complete removal of the PAE binder will return the cotton fabric back to its original mechanical properties.

Objective III. Stripping of the binder/pigment formulation from cotton fabrics

In order to recover ‘’white’’ cotton fabrics, the pigment-binder material needs to be removed from the cotton fabrics. Therefore, it was necessary to develop a method that allows removal of the material. In terms of ‘whiteness’, the standard used for comparison of the stripped fabrics was the white colour of the bleached and washed cotton fabrics before application of colour. It was of importance to assess the effect of the removal on the following points:

- The stripping method should be effective for the removal of the pigment-binder system, aiming for the resultant fabric properties to be similar to that of the original bleached and washed cotton fabric.
- The stripping method should adhere to best commercial practices and be optimised (processing time, chemicals and temperature) in order to achieve environmental and financial viability.

Chapter 3 – Analysis Techniques

3.1 Vibrational Spectroscopy

3.1.1 Principles of FTIR and Raman Spectroscopy

Vibrational spectroscopy such as Fourier-Transform Infrared spectroscopy (FT-IR) is useful for the analysis of the chemical composition and functionalities of textile substrates. The FT-IR spectroscopic technique relies on molecules absorbing radiation in the mid-IR region (approximately 4000-400 cm^{-1}), with the vibrations being related to the nature of the functionalities present in the molecules (Wartewig 2003; Bell 2013). During exposure of a sample to the IR radiation, some of the radiation is absorbed by and some passes through the sample (is transmitted). The result of the IR absorption, superimposed on the background of IR transmission, is a vibrational 'fingerprint' of the sample represented by a spectrum of wavenumber, in cm^{-1}, against the intensity of absorbance or transmittance (Larkin 2011). Different chemical structures produce different spectral fingerprints allowing the user to characterise the sample's chemical composition and any processing modifications.

The interaction between the molecules in the sample and the IR radiation can be described in terms of amplification or resonance, where the specific oscillation radiation frequency matches that of the natural frequency of the molecule (Larkin 2011). The molecular bond vibration produced by absorption of the IR is due to a change in the dipole moment of the bond. The dipole moment of a molecular bond is the difference in polarity or charge along the axis of a bond between the atoms involved, Figure 3.1. The molecule absorbs the IR light and is excited to a higher vibrational energy state (Ramaiah and Bhatia 2017). The frequency of the vibration is influenced by the ''stiffness'' of the bond, which in turn is affected by the electronic environment of the functionality and nearby substituents. Within the FTIR spectrophotometer the IR radiation initially passes through a Michelson interferometer, the IR frequencies ''mixed'' and then impacted onto the sample.

Following selective absorption in the sample material the resultant interferogram is collected and processed using a mathematical operation called Fourier Transform to yield the IR spectrum we can recognise and analyse (Bell 2013).

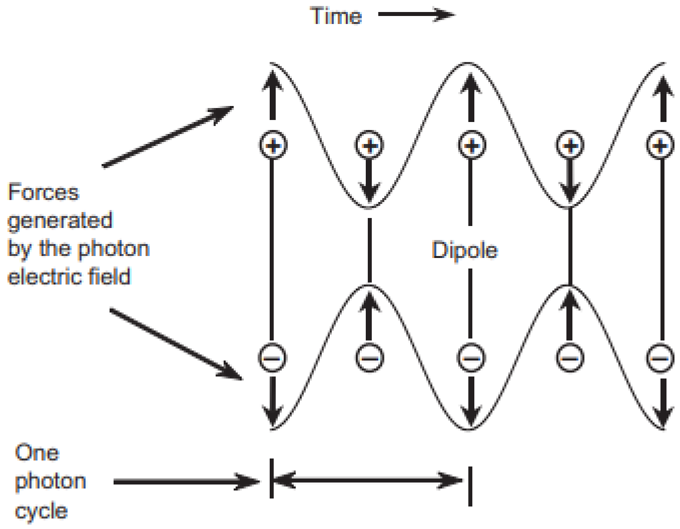


Figure 3.1 IR absorption process, where the IR photon generates oscillation of the molecular dipole and the dipole spacing oscillates with the same frequency as the IR photon (Larkin 2011)

Raman spectroscopy is an alternative method of analysis to obtain information about a sample's chemical composition and can be used as a complementary technique to IR spectroscopy. Where IR spectroscopy is most-commonly used for analysis of asymmetric vibrations of polar groups, Raman spectroscopy is used for analysis of symmetric vibrations of non-polar groups (Larkin 2011). The interaction between light and matter in Raman spectroscopy is that of an off-resonance condition involving the Raman polarisability of the molecule.

In Raman spectroscopy a sample is exposed to a monochromatic visible light source, where part of the light is transmitted through the sample and part of it is scattered in all directions by the sample. Two types of light scattering are observed: Rayleigh scattering, where the scattering frequency matches that of the incident light, and

Raman scattering, where the frequencies don’t match. The Raman effect can be regarded as a two-photon process. Upon interaction of the incident photon from the light source with an electron in the sample, the photon loses some of its energy through absorption by the electron resulting in the electron being promoted to a higher energy state. The electron then falls back to a ground state by losing energy and emits a photon. If the electron falls back to a different energy level, the energy loss by the electron is different to that of the initial energy absorption from the photon. In this case the energy of the emitted photon does not match that of the incident photon (inelastic scattering) and gives rise to Raman scattering (Clockler 1930; Larkin 2011). Raman scattering produces vibrational spectral absorptions in units of intensity plotted against wavenumber.

3.1.2 Instrumental analysis

Infrared spectra of chemicals and cotton fabrics were collected using a Perkin Elmer FT-IR Spectrum BX spectrophotometer with diamond ATR attachment. Spectral scanning was performed from 4000 to 600 cm^{-1}. The data presented an average of 32 scans. The recorded spectra were expressed in percentage of transmittance versus wavenumber. The resolution was 4 cm^{-1} and the interval of scanning was 2 cm^{-1}.

Raman spectra were collected using a Renishaw inVia Raman microscope using Renishaw WIRE software and a laser excitation of 785 nm. The scattered radiation from the samples was collected in the range of 1700 to 100 cm^{-1}.

3.2 Scanning Electron Microscopy (SEM)

3.2.1 Principles of SEM

Scanning electron microscopy (SEM) is a ‘’visualisation’’ analysis technique that acquires image topography information of material surfaces down to the nanoscale.

Typically, in an SEM an electron beam passes through pairs of scanning coils or deflector plates to the objective lens and onto the sample. The deflector plates control the beam position on the sample surface and allow horizontal and vertical scanning of the sample in a rectangular raster (Joshi, Bhattacharyya and Ali 2008). The electron beam interacts with sample material and gives rise to backscattered electrons (BSE), secondary electrons (SE), photons (X-rays) and visible light (cathodoluminescence), Figure 3.2. Typically, SE are considered the most important electrons as they provide detailed topography information, while BSE can be used to differentiate between different material components and X-rays can provide information on elemental composition of the sample (Akhtar et al, 2018).

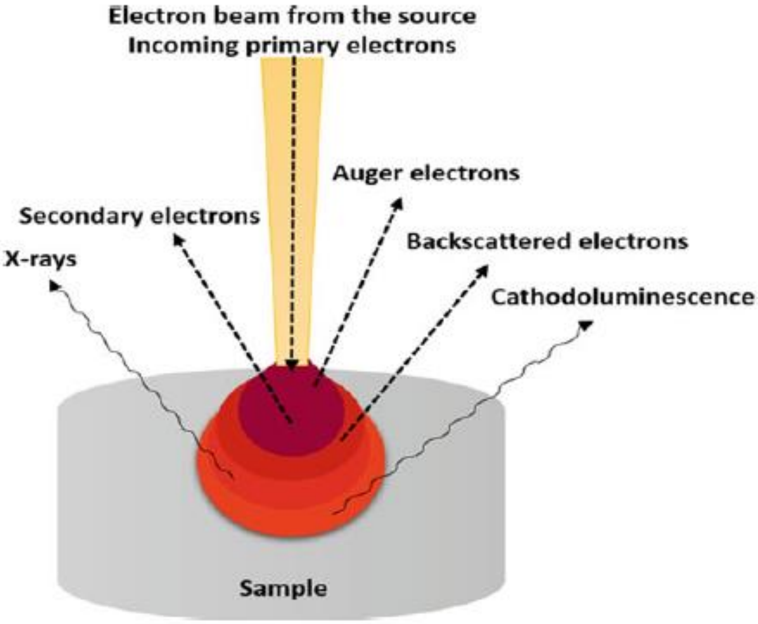


Figure 3.2 Principle of SEM electron-sample interaction (Akhtar et al, 2018)

Usually textile fibres are organic in nature and will become electrostatically charged in the electron beam. Therefore, samples are coated with a conducting layer prior to SEM analysis to prevent charge build-up, extreme brightness and poor imaging.

Coating of the sample may also reduce microscope beam damage, increase thermal conduction, improve secondary electron emission, reduce beam penetration with improved edge resolution and protect beam sensitive specimens. Sputter-coating is used to apply an ultra-thin coating (2-20 nm) of electrically conducting metal (gold, platinum, iridium, etc.) onto the non-conducting sample (Höflinger 2013; Akhtar et al, 2018).

X-rays generated during SEM analysis can provide elemental identification and semi-quantitative compositional analysis using Energy Dispersive X-ray (EDX) analysis. Figure 3.3 shows how x-rays are generated in SEM analysis. The atom of each element consists of a nucleus which in turn comprises neutrons and protons, surrounded by an electron cloud. Every atom has a unique number of electrons that are located in different orbital shells which each have different energies. The shell closest to the nucleus is known as the K shell, followed by the L, M, N, O, P and Q shells. EDX analysis generally focuses on electrons in the inner shells (K, L and M) (Thermo Fisher Scientific 2018).

X-ray generation happens in two steps (Joshi, Bhattacharyya and Ali 2008). Firstly, when the electron beam hits the sample it may result in the ejection of an inner shell electron (1). This leaves the atomic nuclei unstable with a vacancy in the electron shell. This vacancy can be filled by an electron from an outer shell which emits an X-ray photon and the atom regains stability (2). The electron transitions between electron shells produce characteristic X-rays: the energy needed to remove an electron from its position is specific to each electron of each element. These X-rays can then be detected by the EDX analysis system, which measures the energy of the incoming X-ray photons (3). The data generated by the EDX analysis is visualised in the form of spectra with signals corresponding to each element detected in the sample (Goldstein et al, 1981; Thermo Fisher Scientific 2018).

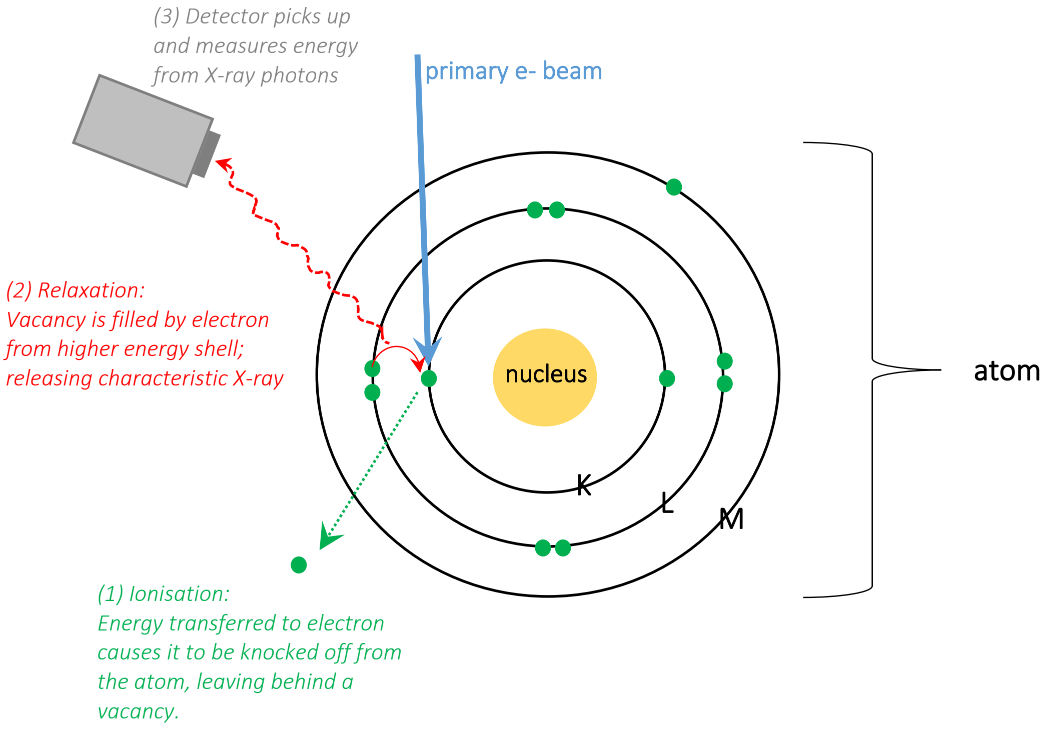


Figure 3.3 X-ray generation process in EDX analysis in SEM (ThermoFischer Scientific 2018)

3.2.2 Instrumental Analysis

SEM analysis was used throughout this study to characterise material topography and composition. However, two different equipment systems were used for SEM analysis due to limited instrumental availability.

Coloured and coloured/stripped cotton fabrics:

Samples were coated with a 30 nm gold layer using an Emitech K550X coating instrument. The images were captured using a Jeol JSM-6610LV SEM operating at an accelerating voltage of 5 kV, with a Backscattered Electron detector. The magnification ranged from x100 to x1000. Elemental analysis was made by the

Oxford Instruments INCA X-Max 80 EDS detector system.

Pigment, cotton fabric, polyamidoamine epichlorohydrin films:
Samples were coated with a 4 nm iridium layer using a Cressington 208HR sputter coater. The images were captured using a FEI Nova NanoSEM 450 FEG-SEM operating at an accelerating voltage of 2, 3 and 18 kV, with an Everhart-Thornley detector, a Through-the-Lens detector and a Circular Backscatter detector. The magnification ranged from x50 to x50,000. Elemental analysis was made by EDAX (AMTEK) at 18 kV.

3.3 Colour Fastness Assessment

3.3.1 Effect of Multicycle Laundering

The colour fastness of the printed and padded cotton substrates to laundering was assessed by subjecting the fabrics to washing conditions based on the standard *BS EN ISO 105-C09:2003* Annex A (British Standards Institution 2003). Specimens were laundered under specified conditions (temperature, alkalinity and bleach concentration) to reflect the effect of a multicycle machine washing. The method is intended to determine the consumer relevant shade change of coloured textiles. The Annex A procedure includes the use of ECE 1998 non-phosphate reference detergent (without optical brightener), sodium perborate tetrahydrate and the low temperature bleach activator, tetra-acetylethylenediamine (TAED). The equipment used was an 8-pot model GyroWash colour fastness to washing tester (James Heal) compliant with AATCC and ISO standards. Specimens were laundered under specific conditions of temperature, alkalinity and bleach concentration such that a fading result, which correlates with a multi-cycle machine washing, was obtained in a conveniently short time. The change in colour of the specimen was assessed instrumentally with reference to the original coloured fabric and the original white cotton fabric using a Datacolor spectrophotometer (details below).

The wash liquor was prepared by dissolving 10 g of the ECE 1998 non-phosphate reference detergent base powder (without optical brightener), 1.8 g of the bleach activator TAED and 12 g of sodium perborate tetrahydrate in 1 L water and stirring the mixture at 25±5°C for 10 minutes. The ratio of washing liquor to fabric (50 x 100 mm) was 100:1. The initial temperature of the solution at addition of the specimen to the liquor was 25±5°C. After commencing, the temperature was raised at a rate of 15±0.5°C per minute to the required temperature of 60±2°C. The test was run at this temperature for another 30±1 minutes. Subsequently, the specimen was rinsed in a beaker filled with 2 L distilled water whilst gently agitating for 1 minute. The beaker was then placed under a cold running tap for 10 minutes. The test specimen was then squeezed by hand to remove excess water and subsequently air dried at ambient conditions.

3.3.2 Effect of Wet and Dry Rubbing

The colour fastness of the printed cotton fabrics was additionally subjected to wet and dry rubbing tests according to the *BS EN ISO 105-X12:2016* standard using a James Heal CrockMaster motorised rub fastness tester (British Standards Institution 2016). Specimens of the coloured cotton fabric, measuring 25 x 100 ± 2 mm were fastened onto the testing equipment by means of clamping. A wet or dry cotton rubbing cloth (desized, bleached, without finish), measuring 50 ± 2 mm was clamped onto the rubbing finger and used to rub onto the test specimen in a straight line for 20 times, 10 times to and 10 times fro, along the long length, with a downward force of 9 ± 0.2 N. Any staining of the colour onto the rubbing cloths was visually assessed with reference to the original rubbing cloth under suitable illumination conditions (D65) and rated using a grey scale.

3.3.3 Colour Measurement

When light is reflected by the surface of an object or transmitted through a medium and reaches the eye of the observer, a series of processes between the eye and the brain results in visual imaging coupled to colour perception. This perception of the colour of an object is dependent on the wavelength distribution of the light source, the degree of reflection or transmission of each wavelength of the incident light by the object and on the visual response of the observer's eye to the wavelengths of light entering the eye (Broadbent 2001). Colour can be objectively described through colour measurement under standardised circumstances.

Instrumental colour measurement was performed using a Datacolor spectrophotometer Spectraflash SF600 Plus-CT equipped with Color Tools software. Taking into consideration any irregularities in levelness of colour application, the aperture for measurement was 20 mm in order to enable colour measurement of a relatively large area as an accurate representation of the sample as a whole. The fabric was folded once prior to measurements and the colour measurement was the average of 3 measurements over the 400 to 700 nm spectral range. Specular reflectance and UV radiation were excluded. In this study, the measured colorimetric parameters to describe the cotton fabrics were colour strength *K/S*, colour difference *ΔE* and lightness *L**.

Colour strength

The coloured fabrics were selected to be described using colour strength K/S , which according to the Kubelka-Munk theory defines the relationship between spectral absorption (*K*) and scattering (*S*) at a specific wavelength with R being the reflectance value of the coloured sample at λ_{max}, Equation 3.1 (Becerir 2017). The fabrics were compared based on K/S obtained at the same specific λ_{max} wavelength where the highest value K/S was obtained.

$$\frac{K}{S} = \frac{(1-R)^2}{2R}$$

Equation 3.1 Kubelka-Munk colour strength (Becerir 2017)

Colour difference

The difference in colour between the cotton fabrics was selected to be described using CIE ΔE, which takes into consideration lightness values from L* 0 = black to L* 100 = white, and colour values a* from green to red and b* from blue to yellow for each measured sample (Habekost 2013). The values for ΔE were calculated by the Datacolor software according to the CIE76 algorithm, Equation 3.2. An optimum result with minimum colour difference would be a value nearing ΔE = 0.

$$\Delta \boldsymbol{E}^{*}_{\boldsymbol{76}} = \sqrt{(\boldsymbol{L_2} + \boldsymbol{L_1})^2 + (\boldsymbol{a_2} + \boldsymbol{a_1})^2 + (\boldsymbol{b_2} + \boldsymbol{b_1})^2}$$

Equation 3.2 CIE76 Colour difference (Habekost 2013; Vega Gutierrez et al, 2018)

Lightness

Alongside colour difference, CIE lightness L* metric was selected to be used to describe the colour of fabrics, more specifically to describe and compare the stripped cotton fabrics to the untreated cotton fabric. L* is expressed in a range of L* values 0 to 100, from the darkest black to the brightest white respectively (Becerir 2017). Values for L* were provided by the Datacolor software.

3.4 Objective Measurement of Fabric Handle using the Kawabata Evaluation System for Fabrics

3.4.1 Principles of Fabric Analysis Using KES-F

The assessment of the handle of fabrics was traditionally carried out by manually manipulating the fabrics and from thereon arrive to a conclusion. This subjective assessment is influenced by the relative experience and personal preferences of the assessors, the choice of description for the fabric handle properties, the assessment conditions, assessment techniques, analysis of results, etc. The Kawabata Evaluation System for Fabrics (KES-F) was developed by Professor Kawabata and his co-workers for the objective measurement of fabric properties and to use these measurements in order to correlate with the subjective assessment of handle (Kawabata and Niwa 1989; Saville 1999). Firstly, important expressions of fabric handle were selected and standardised together with their definition through subjective assessment by experts. These expressions were termed the ‘primary hand’ of fabrics and included stiffness, smoothness, fullness and softness, crispness, anti-drape stiffness, scrooping feeling, flexibility with soft feeling, and soft touch. These terms demonstrate the complexity of describing fabric handle and the overlap of some of the terms used. The primary hand values are rated on a ten point scale and the values considered as satisfactory differed per fabric category, such as women’s thin dress fabrics. The over-all fabric handle is given by combining the primary hand values and is called the ‘total hand’ value. Secondly, a set of instruments was produced with which appropriate fabric properties could be measured which could be correlated to the subjective assessment of handle.

The properties of a fabric that affect its handle are dependent on its behaviour at low loads and extensions. Thus, in the objective assessment using KES-F, fabrics are not subjected to loads and extensions that would result in fabric failure. The KES-F system consists of four specialised instruments: FB1 tensile and shearing, FB2 bending, FB3 compression and FB4 surface friction and variation. These instruments allow the measurement the parameters listed in Table 3.1, intended to mimic fabric deformations which would occur in use.

Table 3.1 Tensile, shearing and bending parameters measured using the KES-F system (Kawabata and Niwa 1989; Ly 1989; Saville 1999)

	Property	Symbol	Unit	Definition
Tensile	Tensile linearity	LT	_	Linearity of the load/extension curve
	Tensile energy	WT	gf cm/cm^2	_
	Tensile resilience	RT	%	_
	Extensibility	EMT	%	Percentage of extension at the maximum applied load of 500 gf/cm specimen width
Shear	Shear stiffness	G	gf/(cm.degree)	Slope of the shear force-shear strain curve
	Shear stress at 0.5°	2HG	gf /cm	Hysteresis width of curve at shear angle of 0.5°
	Shear stress at 5°	2HG5	gf /cm	Hysteresis width of curve at shear angle of 5°
Bending	Bending rigidity	B	gf .cm^2/cm	Slope of the bending moment – curvature curve
	Bending hysteresis	2HB	gf .cm/cm	Energy loss during unloading of bending stresses measured at curvature (*K)* = 0.5 cm^{-1}
Compression	Compression linearity	LC	_	Linearity of compression thickness curve
	Compressional energy	WC	gf.cm/cm2	_
	Compressional resilience	RC	%	_
Surface/constructi	Fabric thickness	T	mm	Fabric thickness at 0.5 gf/cm2 pressure
	Coefficient of friction	MIU	_	Mean value of coefficient of friction
	Mean deviation of friction	MMD	_	Mean deviation of coefficient of friction

	Mean deviation of roughness	SMD	µm	–
	Fabric weight	W	mg/cm^3	Weight per unit area

3.4.2 Methodology

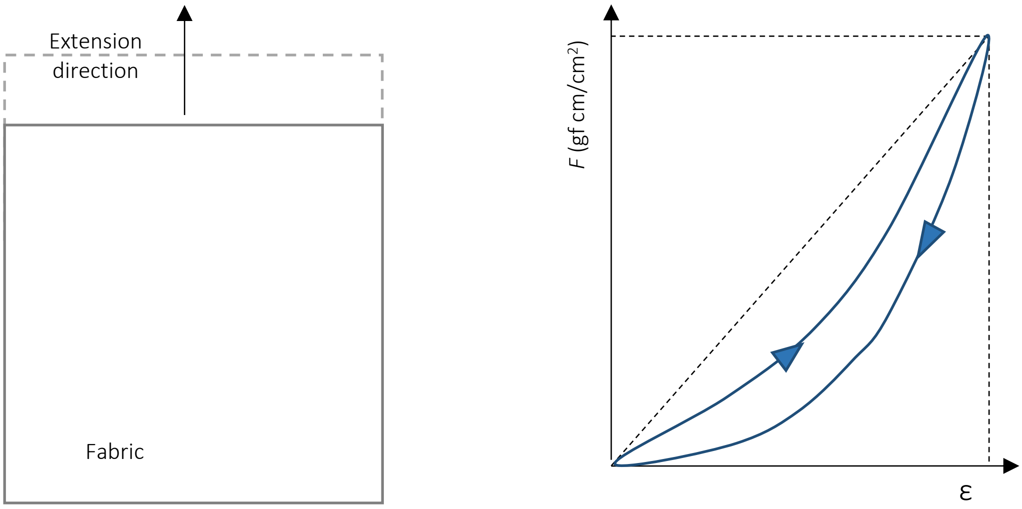
With the application of a binder formulation onto textiles, the fibres are covered with an extra layer of material. Depending on the properties and behaviour of the added material as well as the relative amount added, this may result in providing the fabric with an increased stiffness, decreased ability to be deformed or decreased drapeability. Thus, the application of the binder formulation may result in making the fabric less comfortable when worn on the body. The aim of the thesis research was to apply colour onto cotton fabrics, without the colour formulation components, specifically the binder material, significantly affecting the fabric handle in terms of stiffness/flexibility or drapeability. Shearing and bending properties have been determined to be highly correlated with drape, more so than fabric thickness or weight (Collier 1991). Specifically, Collier identified shear hysteresis at 5° as the most significant measurement for explaining fabric drape. Additionally, measuring the extensibility of the fabrics could provide information on the effect of the treatments on the fabric handle. Extensibility is related to the springiness or crimp per unit area. A high extensibility of a fabric after a treatment could for example indicate a low tensile modulus and suggest a decrease in fabric stiffness (Baig and Carr 2015).

For the thesis research, the untreated and treated cotton fabrics were subjected to assessment using the tensile and shear (FB1) as well as the bending (FB2) system. All specimens were cut into 20x20 cm samples and conditioned at 21°C and 65% relative humidity for a minimum of 24 hours prior to measurement. Tests were carried out along both warp and weft directions. The averaged data for warp and weft was used to compare the tactile properties of the different fabrics.

3.4.2.1 KES-F Tensile properties

The tensile properties were measured by applying extension, ε, along the required direction of the specimen using a load of up to 500 gf.cm/cm^2, using a KES-FB1 tensile and shear tester, Figure 3.4a (Ly 1989; Kawabata & Niwa 1989; Li and Dai 2006). The transverse contraction, which was the reduction or increase in diameter of the specimen in perpendicular to the force applied, was not limited, so the test was a type of biaxial extension. From the data a load-extension hysteresis curve was plotted, which shows the extension and recovery of the sample back to its original length, Figure 3.5b. From the curves, the following parameters were derived:

- *WT* (tensile energy) = area under the load strain curve
- *LT* (linearity) = $\frac{WT}{area\ triangle\ OAB}$
- *RT* (tensile resilience) = $\frac{area\ under\ load\ decreasing\ curve}{WT} \times 100\ \%$
- *EMT* (extensibility) = strain at 500 gf/cm of tensile load



a) Specimen extension

b) Load-extension curve

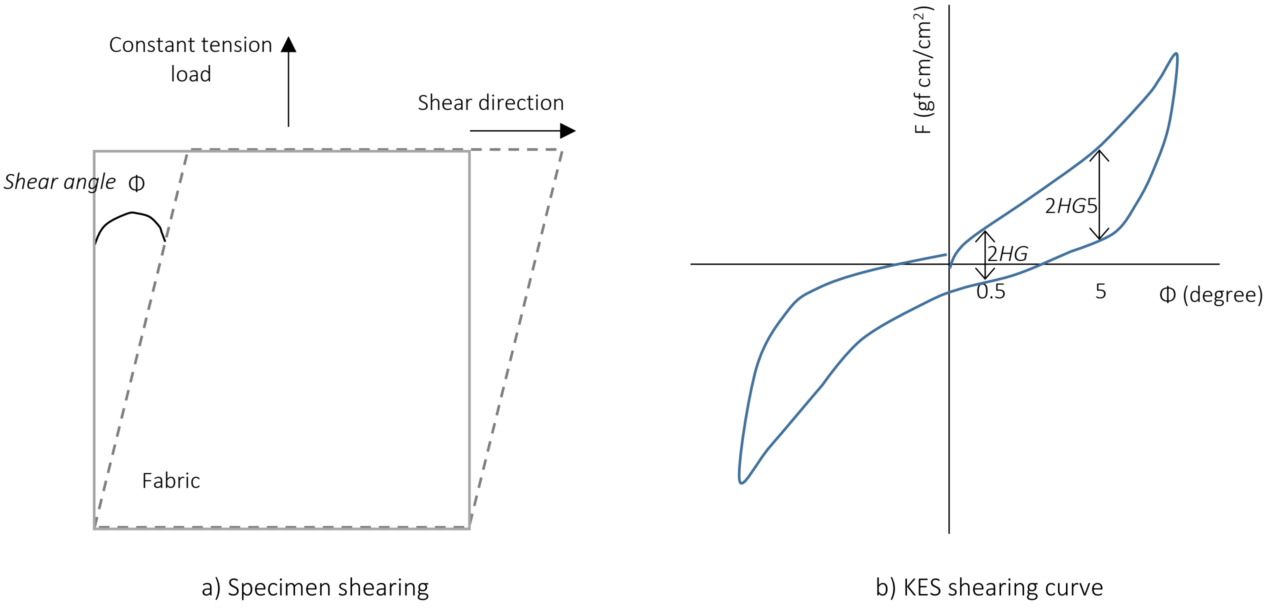
Figure 3.4 KES-FB1 Tensile test and resultant data curve (Li and Dai 2006)

The effect of a binder on the tensile properties is uncertain as it could increase the tensile strength by dividing the load over the surface of the whole fabric or it could negatively affect the mechanical property by making the fibrous material more rigid depending on the nature of the binder and on the concentration applied (Attia et al, 2017). For the thesis research extensibility (EMT) was selected as the most relevant property of the tensile properties to be measured using using KES-FB1 as it would provide the most accurate representation of the effect of the treatments on the tensile properties of the fabrics. EMT is defined as the percentage of extension at the maximum load applied.

3.4.2.2 KES-F Shear properties

KES-FB1 Shearing tests were performed by applying shear strain with a rate of *Fs* (8.34×10^{-3}/sec) to the specimen under a constant tension load (10 gf/cm), up to a maximum shear angle of 8°, Figure 3.5a (Saville 1999; Li and Dai 2006). The data was presented in the form of a shear-force/shear-angle hysteresis curve from which the following parameters were measured, Figure 3.6b:

- *G* (shear stiffness) = slope of shear force-shear strain curve
- *2HG* (force hysteresis at shear angle of 0.5°) = hysteresis width of curve at 0.5°
- *2HG5* (force hysteresis at shear angle of 5°) = hysteresis width of curve at 5°



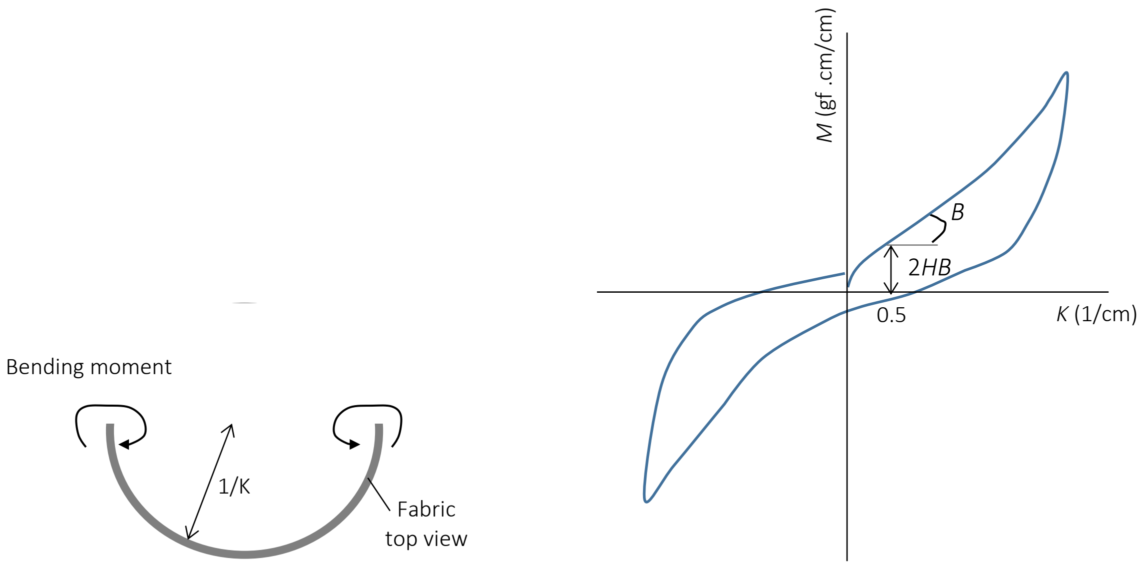
a) Specimen shearing b) KES shearing curve

Figure 3.5 KES-FB1 Shear test and resultant data curve (Li and Dai 2006)

3.4.2.3 KES-F Bending properties

The bending test was carried out using a KES-FB2 bending tester. A specimen was deformed due to the applied bending moment, *M*. This deformation was measured as the curvature *K* of the fabric. Bending occurs between the curvatures -2.5 and 2.5 cm^{-1} , with the radius of bending being 1/*K* as shown in Figure 3.7a (Saville 1999; Li and Dai 2006). The resulting data was presented in the form of a bending curve, from which the following parameters were measured, Figure 3.7b:

- *B* (bending rigidity) = slope of the bending moment – curvature curve
- *2HB* (Moment of hysteresis) = hysteresis width of the curve measured at *K*= 0.5 cm^{-1}



a) Specimen bending

b) KES bending curve

Figure 3.6 KES-FB2 Bending test and resultant data curve (Li and Dai 2006)

Chapter 4 – Bunte Salt Polymers as Potential Binder Materials for the Colouration of Cotton

From an environmental perspective, it is desirable to develop a colouration and colour removal system where minimal impact on the environment is achieved. This includes the selection of the materials to function as a potential binder and the selection of the method for application of the pigment-binder mixture onto the cotton fabric. The work described in this chapter involves the initial study into using a bio-based material and a commercial alternative as resources to produce Bunte Salt-terminated polymers to function as potential binder materials.

4.1 Materials

Remazol Brilliant Blue R (Dystar), *Invadine O* (Huntsman), Antimussol (Clariant) ammonium sulphate (Sigma Aldrich, >99%), acetic acid (Fisher Scientific), 2,4,7,9–Tetramethyl –5–Decyne–4,7–Diol-ethoxylate (Sigma Aldrich), ammonium hydroxide (Fisher Scientific), hydrochloric acid (≥ 37%, Fisher Scientific), sodium bisulphite (Fisher Scientific), sodium hydroxide (≥98%, Fisher Scientific), propylene glycol (Sigma Aldrich), ethylene glycol (Sigma Aldrich), glycerol (Fisher Scientific), Pigment Green B (C.I. Pigment Green 8) (Albion Colours), sodium carbonate (Fisher Scientific), tetraacetylethylenediamine (SDC Enterprises), were used as received. All reagents were of analytical grade. All solutions were prepared with the use of distilled water. 56’s wool top (Bulmer & Lumb) was used for preparation of the binder material. Plain woven cotton fabric (100%, bleached only, no optical brightening agent, 142.8 g/m^2) was supplied by Phoenix Calico Limited, Denby Dale, UK was used throughout this study.

4.2 Preparation of the Bunte Salt-Terminated Polymers from Wool

4.2.1 Wool Dyeing

Bunte Salt-terminated wool protein derivatives (WBS) were produced by oxidative sulphitolysis. Prior to the protein derivatisation, the wool top was dyed with Remazol Brilliant Blue R (C.I. Reactive Blue 19). Being a vinylsulphone-based reactive dye, the expected dyeing mechanism was a Michael addition reaction between the nucleophilic reactive groups of the fibre and the reactive vinylsulphone groups of the dye, forming a covalent bond (Lewis 1982). C.I. Reactive Blue 19 reacts with amino groups in wool, Figure 4.1 (Rouette et al, 1971; Rusznak, Frankl and Gombkötő 1985). The pre-bonding of the dye to the wool fibre suggests that the interaction between the dye and the cotton substrate will be very limited. This would allow colour fastness testing of the coloured cotton as an indirect assessment of the interaction between the WBS binder material and the cotton.

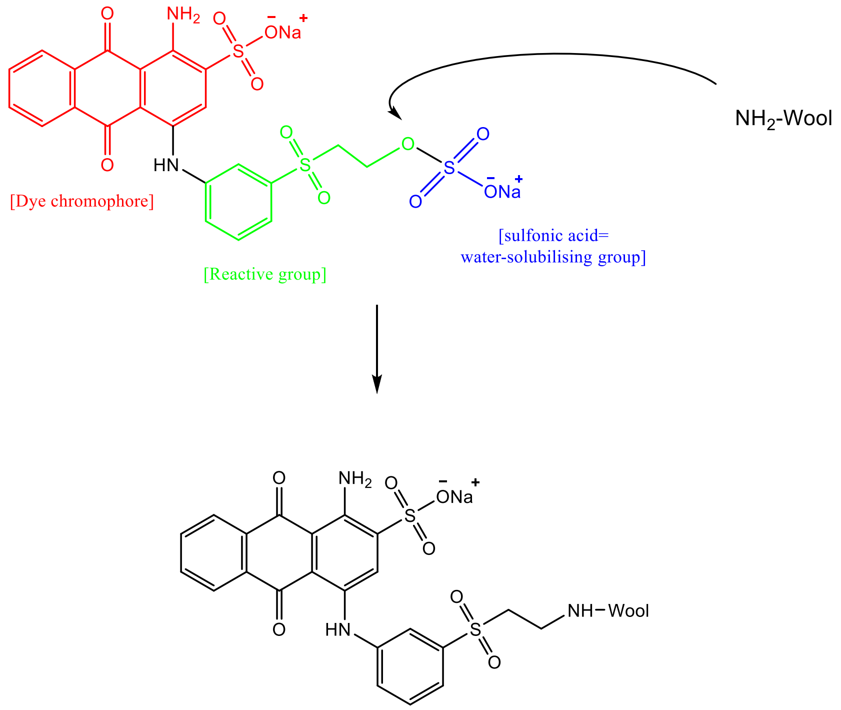


Figure 4.1 The suggested dyeing reaction of wool with C.I. Reactive Blue 19 (RB19) (Rouette et al, 1971; Rusznak, Frankl and Gombkötő 1985)

The wool was pre-treated by soaking 10 g wool in a 1 g/L *Invadine O* aqueous solution (1:10 fibre to liquor ratio) for 20-30 minutes at room temperature. The dyeing solution was prepared by mixing 0.4 g C.I. Reactive Blue 19, 0.8 g ammonium sulphate and 0.4 g acetic acid in 100 ml distilled water, obtaining a 4% depth of shade on dry weight of fibre. It was ensured that the pH of the dyeing solution was around pH 5.5 by gradually adding diluted ammonium hydroxide to the dyeing solution. After the appropriate time in the wetting agent solution, the wool was removed from the solution and squeezed by hand to remove excess of the solution before addition into a dyeing tube together with the dyeing solution (1:10 fibre to liquor ratio). Dyeing was carried out in a Mathis infrared dyeing machine and involved exhaustion at 70°C for 20 minutes followed by fixation at 98°C for 1 hour, Figure 4.2 (Broadbent et al, 2018). Following dyeing, the wool was subjected to an alkaline treatment using a 10 ml ammonium hydroxide solution (1%) in order to remove any unfixed and hydrolysed dye. This solution was added to the tube containing the wool and dyeing solution and the mixture was left to run at 80°C for 15-20 minutes. Finally, the dyed wool was rinsed thoroughly under a cold running tap.

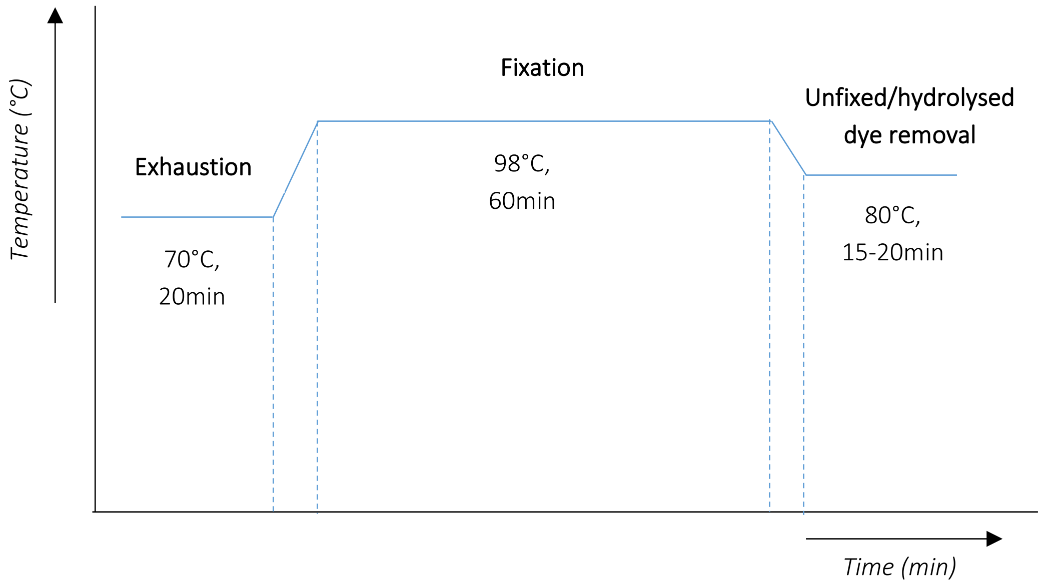
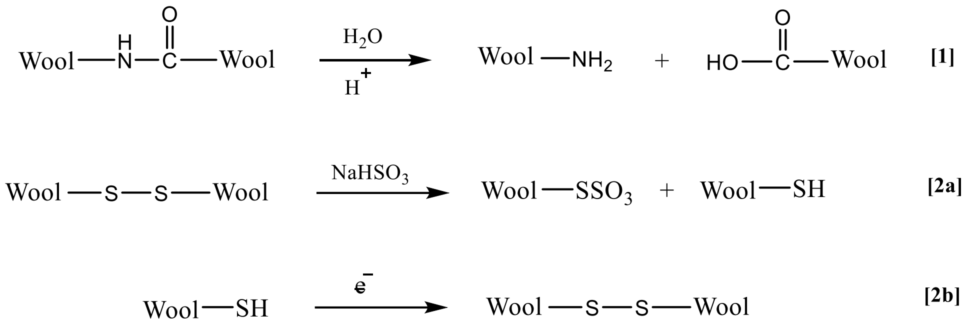


Figure 4.2 Schematic diagram of the wool dyeing process with RB19

4.2.2 Acid Sensitisation

The aim of acid sensitisation of the wool was to break some of the amide linkages present in the wool protein, to facilitate later cleaving of the accessible disulphide linkages, Scheme 4.1 (Belot 2005). According to the study carried out by Belot, increase of the sensitisation temperature up to boiling (100°C) resulted in rapid solubilisation of the wool and most likely the production of low molecular weight polypeptides, whereas sensitisation at 60-70°C was found to produce one fraction of solubilised proteins and one fraction of undissolved partially hydrolysed proteins. It is undesirable for all the wool to be solubilised as the current aim is to obtain a high concentration of the cystine disulphide linkages to allow later chain scission by oxidative sulphitolysis, for the formation of the Bunte salts, Scheme 4.1. Therefore, temperatures of 60°C and 80°C were selected as appropriate temperatures for sensitisation.



Scheme 4.1 Preparation of WBS by [1] acid hydrolysis and [2a] oxidative sulphitolysis yielding cysteine-S-sulphonate and cysteine and [2b] reformation of the disulphide bond by oxidation of cysteine (Belot 2005)

Based on the procedure carried out by Belot (Belot 2005), ~20 g dyed wool was added to a conical flask containing heated hydrochloric acid solution (6M) in such amount to thoroughly wet the bulky wool with a fibre to liquor ratio of 1:10. The flask was placed in a waterbath and gently shaken for 1 hour. After sensitisation the resulting product was comprised of solids (undissolved wool) and a liquid (solubilised wool). The whole mixture, without neutralisation, was treated with sodium bisulphite in order to oxidatively sulphitolyse the wool protein and produce the WBS.

4.2.3 Oxidative Sulphitolysis

After sensitisation, the wool was oxidatively sulphitolysed with the reducing agent sodium bisulphite ($NaHSO_3$) for cleaving of the disulphide bonds in the wool fragments and the resulting formation of the $-SSO_3$ and unstable cysteine thiol (-SH) groups, Figure 4.3. The bisulphite solution (6% w/v) was prepared by diluting 12 g sodium bisulphite in 200 ml distilled water. A drop of Antimussol was added to the solution, to prevent any excess foaming later in the process. The acid sensitised wool mixture was then added to the bisulphite solution. The pH of the wool and bisulphite mixture was then adjusted to pH 5.5 by gradually adding sodium hydroxide pellets and by pipetting of an aqueous sodium hydroxide solution until the desired pH was obtained. Due to the high acidity of the solution the direct addition of sodium hydroxide pellets was required for the initial neutralisation, which could then be finetuned to the appropriate pH of 5.5 using a dilute sodium hydroxide solution.

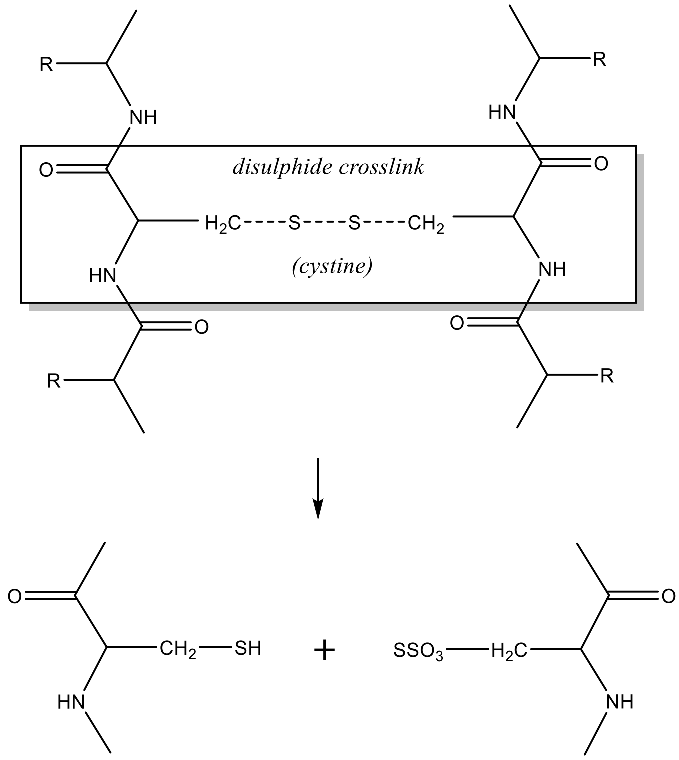


Figure 4.3 Suggested wool disulphide bond reduction

Simultaneous oxidation by bubbling atmospheric oxygen through the mixture for the whole treatment time was to enable continuous disulphide bond reduction and reconverting the oxidation susceptible thiols back to disulphides, scheme 4.1 (Belot 2005). The reaction mixture was left to stir for 24 hours. After oxidative sulphitolysis some of the excess water was evaporated off under vacuum at 40°C until the mixture had reached a viscosity of ≥ 8 centipoise (cP). If necessary, the pH was then re-adjusted to around pH 5.5. Throughout oxidative sulphitolysis and storage it is important that the solution is at the appropriate pH to ensure stability of the Bunte Salt compounds. Lowering or raising of the pH would result in decomposing of the Bunte Salt back to its thiolate ($–S^{-}$) form. Under more acidic conditions, the thiol formed will become protonated to its –SH form, whereas under more alkaline conditions the thiol will gradually reform the disulphide bond (–S–S–). To further prevent polymerisation, the WBS solution was stored in a fridge.

4.3 Bunte Salt-Terminated Polymers from Hercosett™ 617

The potential of PAE to be converted to a Bunte Salt-terminated polymer (PAE-BS) has been previously discussed in published work (Cockett and Lewis 1976). In the current work the commercial PAE resin Hercosett™ 617 was used as an alternative binder precursor to wool, but still incorporated the Bunte salt functional groups. The derivatives were produced by mixing 36 g of the PAE solution and 3.6 g sodium thiosulfate ($Na_2S_2O_3$) (10% w/v). The pH of the mixture was then adjusted to around pH 5.5 and the solution was left to stir for 24 hours. It was expected that Bunte Salts would be formed on reaction with the azetidinium ring (AZR) reactive groups in the polymer, Figure 4.4, and the Bunte Salt groups on the PAE-BS could be exploited in their ability to form disulphide bonds.

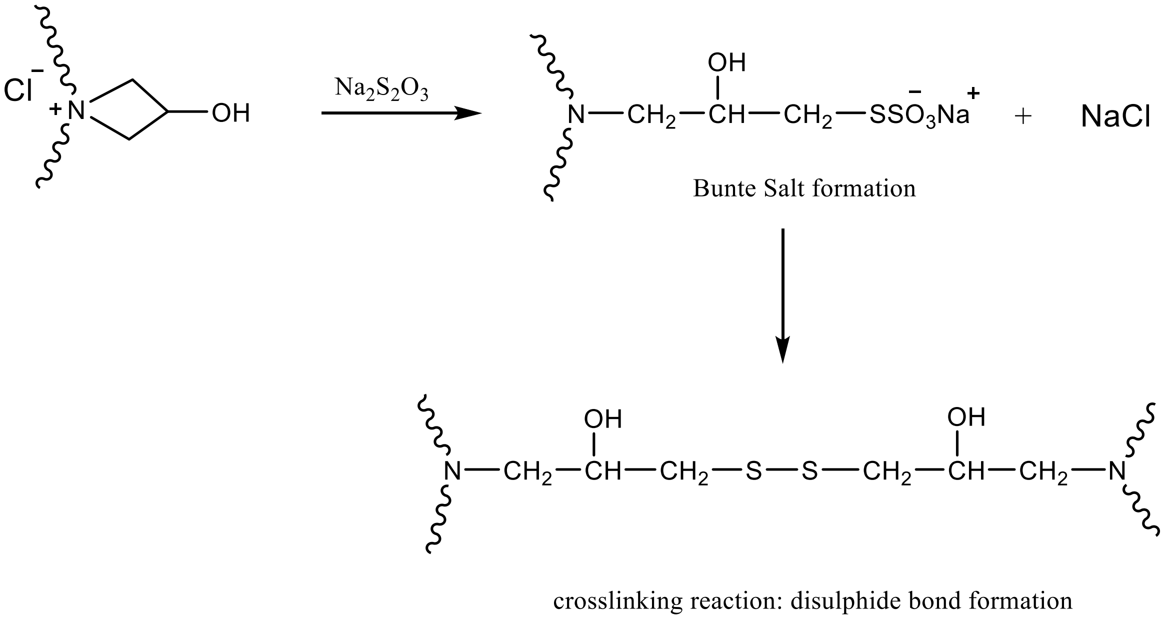


Figure 4.4 Proposed reaction scheme for the formation of Bunte Salts-terminated side chains on the PAE backbone and subsequently disulphide bond formation for crosslinking

4.4 Assessing the Behaviour of Bunte Salt-Terminated Polymers as Potential Binder Materials

4.4.1 Characterisation of the Bunte Salt-Terminated Polymers

To function as an effective binder for the pigment colouration of cotton fabrics, it is a requirement that the material has the ability to form a thin solid matrix around the pigments and adhere as a film onto the textile substrate. The WBS and PAE-BS films were prepared by pipetting 1 ml of the solutions without further dilution onto glass microscope slides, followed by drying in an Equiptex N75 CFD model ventilated oven. It was ensured that no air bubbles were present before placing the slides into the oven. After drying the glass slides were placed in a beaker with distilled water with slight agitation, to rinse off any contaminants, and subsequently dried in a desiccator containing silica. Initial experiments focussed on producing films from the WBS were unsuccessful as the dried ‘’film’’ immediately dissolved in the water during rinsing. Further characterisation of the WBS solution was therefore carried out on the solutions and on the polymer isolated from the solutions.

Table 4.1 identifies the variables at which the PAE-BS films were produced for the current study. Siqueira previously produced PAE films by casting PAE in Teflon plates and left them to form films in an oven at 105°C for 24 hours (Siqueira 2012). In the current study, PAE-BS films were prepared by drying at a temperature of 105°C for a duration of 24 hours and at 150°C for 20 minutes to observe the effect of temperature on the film formation. Supplier recommendations include appropriate pH for crosslinking of the PAE to be between pH 4-9. PAE-BS films were thus also prepared with the addition of sodium carbonate (Na_2CO_3) to observe the effect of the chemical on the film formation. 20 g/L sodium carbonate was thoroughly dispersed in 200 g PAE-BS solution using an OV5 Homogeniser (VELP scientifica) at a speed of 10,000 rpm.

Table 4.1 Film composition and preparation conditions for PAE-BS film formation

Components	PAE-BS	PAE-BS & Na_2CO_3	PAE-BS	PAE-BS & Na_2CO_3
Temperature	105°C	105°C	150°C	150°C
Time	24 hours	24 hours	20 min	20 min

4.4.2 Colouration of Cotton with Bunte Salt-Terminated Polymers

4.4.2.1 Inkjet Printing of Cotton Using a WBS Ink

Colouration of cotton using the WBS was carried out by Drop-on-Demand inkjet printing using a FUJIFILM Dimatix Materials Printer DMP-2850. The printer used a micro-electro-mechanical systems (MEMS)-based cartridge style printhead which allows manual refilling, Figure 4.5. The fluid reservoir had a capacity of approximately 1.5 ml. The jetting module comprised 16 nozzles linearly spaced at 254 µm (Fujifilm n.d.). The printing ink was prepared according to a standard ink formulation, Table 4.2 (Zhmud and Tiberg 2003; Hou et al 2019). The ink was comprised of 2 ml propylene glycol (20% v/v), 1 ml ethylene glycol (10% v/v), 0.5 ml glycerol (5% v/v), approximately 0.1 g of the surfactant 2,4,7,9– Tetramethyl –5–Decyne–4,7–Diol-ethoxylate (1% w/v) and 6.4 ml of the WBS solution (64% v/v) to make a 10 ml solution. Glycols such as propylene glycol and ethylene glycol and glycerol typically serve as humectants, to slow down the evaporation rate, preventing the ink from drying in the printing nozzles and to adjust the ink viscosity (Fox and Hudd 2012; Hou et al 2019), whereas the surfactant allows reducing of the surface tension of the ink to allow wetting of the substrate during printing (Zhmud and Tiberg 2003).

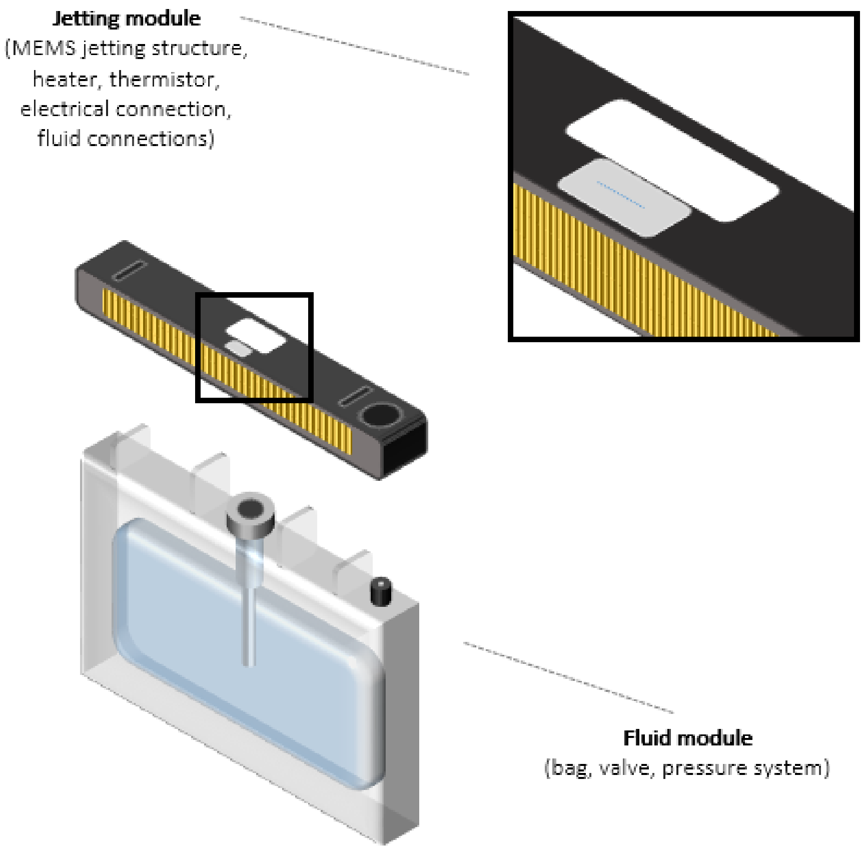


Figure 4.5 Schematic diagram of a Dimatix printer cartridge

Table 4.2 WBS ink composition

Component	Concentration
Propylene glycol	20%
Ethylene glycol	10%
Glycerol	5%
Surfactant	0-1%
WBS	To 100%

Table 4.3 Inkjet printing specifications

Pattern & Dimensions	Rectangle 29x20 cm
Drop spacing	40 µm (635 dpi)
Layers	8
Cleaning	Spit Purge Spit
Jetting Frequency	2.0 kHz
Jetting Voltage	25.00 (for all nozzles)
Cartridge Temperature	35°C
Meniscus Vacuum	4.0 inches of H_2O
Number of Jets Used	16
Cartridge Print Height	1 mm
Cleaning	Start of printing: purge 2.0 seconds During printing: purge 0.3 seconds

Printing of the WBS ink onto cotton was carried out without the addition of pigment, as the initial aim was to assess the behaviour of the polymer in terms of fixation onto the cotton fabric. The assessment of this fixation by means of colour fastness testing was expected to be possible due to the dyeing of the wool prior to the protein derivatisation allowing printing of a blue ink. The standard printing specifications are shown in Table 4.3. It was selected to print 8 layers in order to obtain an opaque print on the cotton fabric. The printed fabric was then baked for 3 minutes at 150 °C using a Werner Mathis laboratory baker-steamer unit.

4.4.2.2 PAE-BS as a Binder Material for Pigment Padding of Cotton

The Bunte-salt terminated polymer derived from the commercial PAE Hercosett™ 617 was applied to cotton fabrics by pad-dry-baking. Pigment Green B (C.I. Pigment Green 8) was selected as a readily available pigment for pigment dyeing of cotton fabrics, Figure 4.6. The pad liquor was prepared by dispersing 0.5 g C.I. Pigment

Green 8 (10 g/L) and 1 g sodium carbonate (20 g/L) in 50 g of the PAE-BS solution for 20 minutes using an OV5 Homogeniser (VELP scientifica) at a speed of 10,000 rpm. The pad liquor was used immediately following dispersion of the pigment. The fabric was immersed in the pad liquor, excess liquor was squeezed out by hand and the fabrics were then passed through the padding-mangle nip at a padding speed of 2 m/min with a pressure set to obtain a wet pick-up of ~100 %. The padded fabric was dried at 80°C for 3 minutes, then baked for 3 minutes at 150°C using a Werner Mathis laboratory baker-steamer unit.

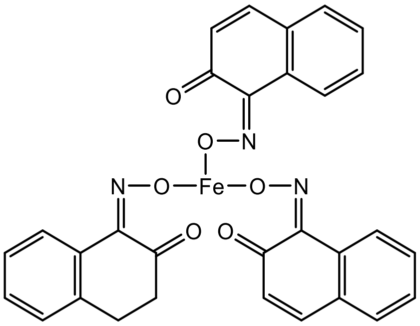


Figure 4.6 Structure of Pigment Green 8 (Alfa Chemistry, n.d.)

4.4.3 Fixation of the Bunte Salt-Terminated Polymers on Cotton

Fixation of the BS polymers applied to the cotton fabrics was indirectly assessed by subjecting the coloured cotton to wet and dry rubbing according to the *BS EN ISO 105-X12:2016* standard (British Standards Institution 2016) and to laundering according to the *BS EN ISO-105-C09:2003* standard (British Standards Institution 2003). The rubbing tests involved rubbing the coloured cotton with a dry and wetted standard test fabric, which is then assessed and rated according to a grey scale assessment. The laundering test involved using a non-phosphate reference detergent incorporating a low temperature bleach activator. The effect of laundering was assessed by comparing the colour strength K/S and lightness L* of the fabrics before and after washing. In comparison to other washing standards, the C09 version is regarded as a ʻʻharshʼʼ assessment, designed to simulate multiple domestic/commercial laundering processes as would be the case of a garment going through a lifetime of laundering. It is therefore suggested to be the most appropriate method for testing the colour fastness of the pigment-dyed cotton fabrics. Please refer to chapter section 3.3 for a detailed description of the methods and materials.

4.5 Results & Discussion

4.5.1 Bunte Salt-Terminated Wool Protein Derivatives

4.5.1.1 Preparation and Characterisation of the Polymer

Initial experiments included the preparation of the WBS with varying temperatures of sensitisation (60°C and 80°C). In accordance with literature, the product derived from the oxidative sulphitolysis of wool was a cloudy solution which upon standing overnight changed to an evident two-phase mixture (Cockett and Lewis 1976). The upper layer was clear with a pH of ~7 and the bottom layer comprised of solids and appeared to be approximately one-third of the mixture total volume. It was observed that when the above two layers were shaken, they became miscible before separating into two phases once more upon standing over time.

During the process it was found that a number of factors needed to be optimised when preparing the WBS. Cutting the wool top into smaller pieces before addition to the hydrochloric acid solution resulted in increased solubilisation of the wool. This could be explained by the fact that the decrease of the size of the textile material facilitates better agitation, which may influence the diffusion of the reagents to the fibre, in turn promoting the breaking of the amide bonds in the peptide chain.

It was attempted to produce films from the Bunte salt solutions for characterisation of the polymer and establish its potential for self-crosslinking. The oven-dried blue WBS ʻʻfilmʼʼ was rinsed in water after removal from the oven. However, the dried material almost immediately dissolved, suggesting that little or no crosslinking had occurred. Further analysis was carried out on the WBS solutions. FT-IR analysis was run on substances isolated from the liquid phase and on substances isolated from the solid phase. Substances were isolated from the solutions by pipetting acetone into the solutions and letting the mixture stand for evaporation of the liquid at room temperature. FT-IR analysis of the powder isolated from the WBS-60 liquid phase showed weak signals around 1022 cm^{-1} and 1194 cm^{-1} , possibly correlating to the S-O vibration for the cysteine-S-sulphonate groups, Figure 4.7 (Douthwaite and Lewis 1994). However, FT-IR of the dried solids did not obtain any significant signals. Additionally, reproduction of the obtained signals for the Bunte salt using the 60°C sensitisation methods was not successful as the FTIR spectra of the two repetition samples did not show any signals correlating to the Bunte salt groups. Upon addition of acetone to the WBS-80 liquid phase, a powder as well as a sticky waxy gel was produced as previously reported by Cockett and Lewis (Cockett and Lewis, 1976). The precipitated powder could be explained by oxidation of excess bisulfite to sulfate salts (Belot, 2005). Figure 4.8 shows an FT-IR spectrum for WBS-80. The strong signals around 1025 cm^{-1} and 1200 cm^{-1} can be assigned to the Bunte salt groups and in this case, reproduction was successful with two repetition samples producing similar signals correlating to the Bunte salt groups. Furthermore, for the WBS-80 solutions the presence of the Bunte salts were observed in both the isolated liquid as well as in the dried solids from the mixture. This suggests that perhaps the increase in temperature from 60°C to 80°C is beneficial for the Bunte salt formation.

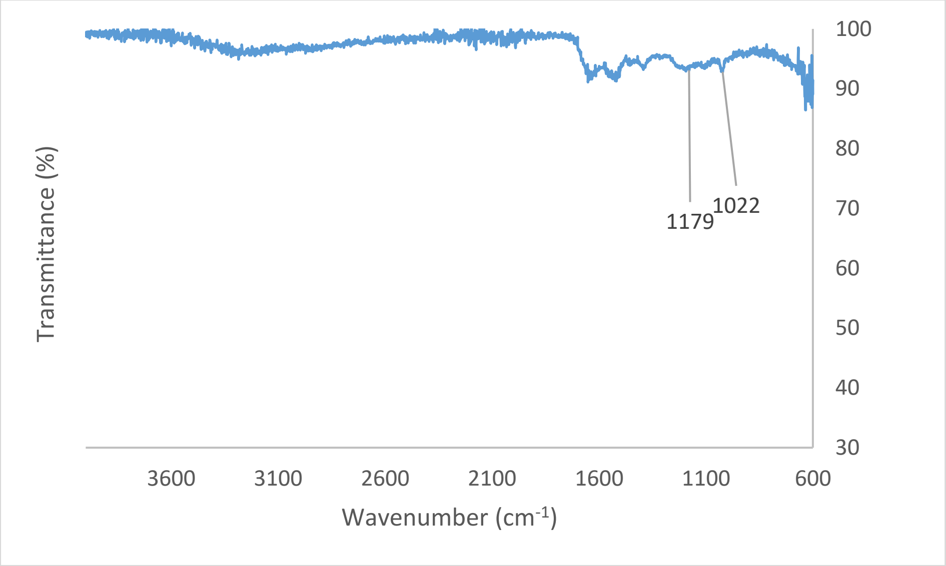


Figure 4.7 FT-IR spectrum of WBS-60 isolated from WBS liquid phase

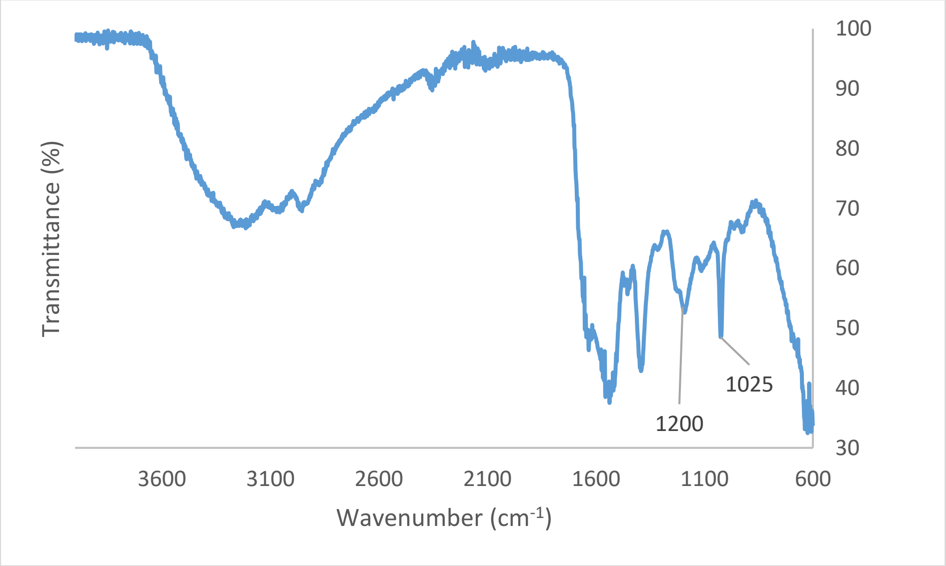


Figure 4.8 FT-IR spectrum of WBS-80 isolated from WBS liquid phase

4.5.1.2 Fixation of the WBS Polymer Printed on Cotton

Printing of the coloured WBS onto cotton was carried out using the ink prepared from the WBS-60 solution. Additional printing of repetition samples and printing of the WBS-80 polymer solution was unfortunately inhibited as it was found that the ink had prematurely polymerised due to unsuitable pH storage conditions. This limited the amount of printed cotton substrate available for subsequent characterisation. This point was taken into consideration with the analysis of the results as a representation for the degree of fixation of the wool protein derivative layer on cotton. The results described below are to be seen as initial results, to show the progress of the work carried out.

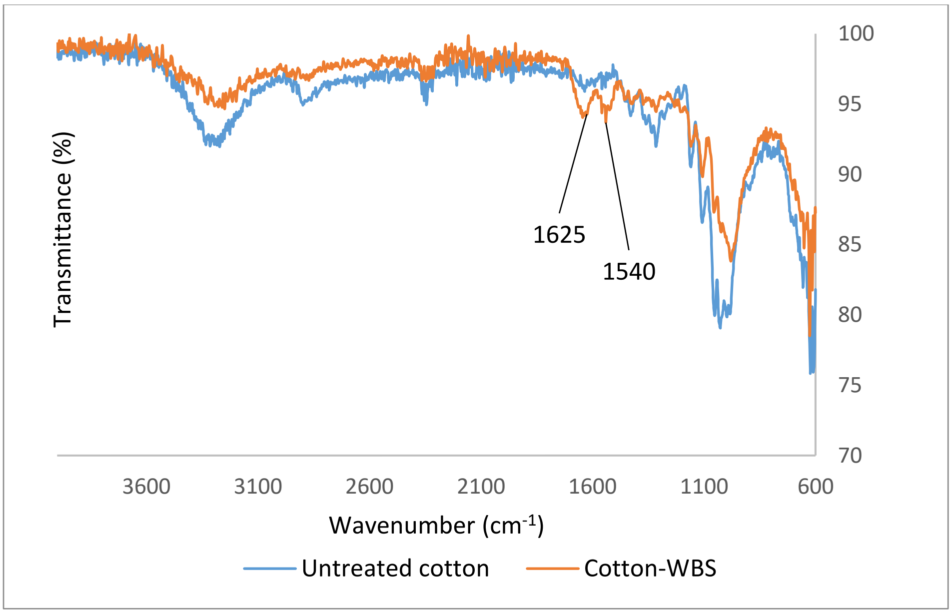


Figure 4.9 FT-IR spectra of untreated cotton and cotton printed with the blue WBS ink

Printing of the coloured WBS onto cotton

The FT-IR spectrum of untreated cotton in Figure 4.9 showed typical signals around 3270 cm^{-1} for O-H stretching (intermolecular hydrogen bonds) vibrations, around 2890 cm^{-1} and 1430 cm^{-1} for CH_2 asymmetric stretching and symmetric deformation or scissoring, around 1315 cm^{-1} for C-H bending, around 1155 cm^{-1} for antisymmetric bridge C-O-C stretching, around 1110 cm^{-1} for asymmetric ring stretching mode and around 1020 cm^{-1} for C-O and/or C-C stretching (Abidi et al, 2008). The printed cotton fabric showed increased signals around 1540 cm^{-1} and around 1625 cm^{-1} correlating to the wool protein.

Figure 4.10 and Figure 4.11 show SEM images of untreated cotton and of the printed cotton, respectively. The SEM images of untreated cotton shows clean characteristic images of non-mercerised cotton fibres identified by their flat ribbon structure exhibiting periodic convolutions. The images of printed cotton show an obvious layer covering mostly the top fibres of the fabric, representing the coloured WBS layer. The printed layer is observed connecting adjacent fibres which is typical of a textile binder. The surface of this layer is observed to be rougher than a typical textile binder.

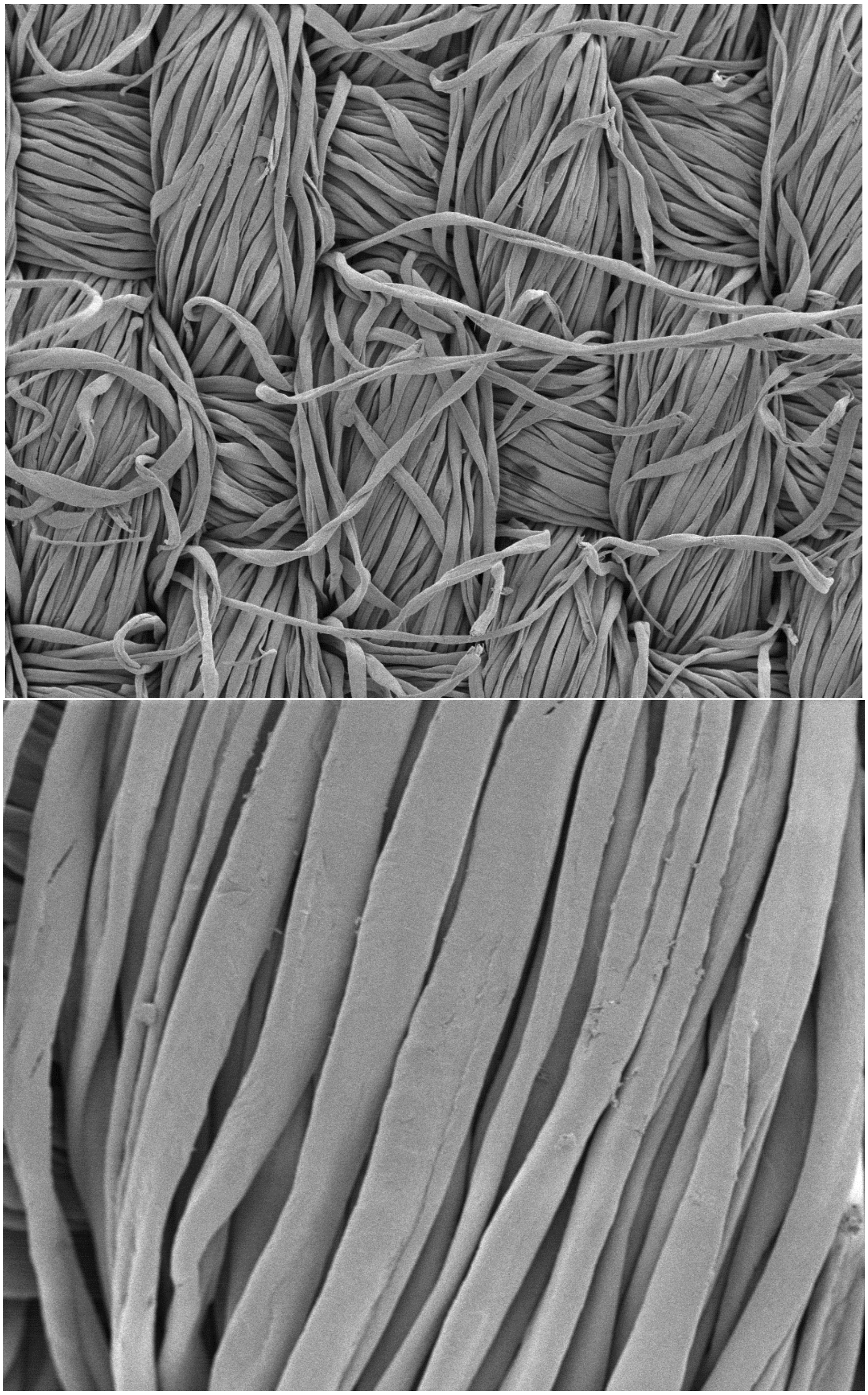


Figure 4.10 SEM images of untreated cotton, with mag x100 (top) and mag x500 (bottom)

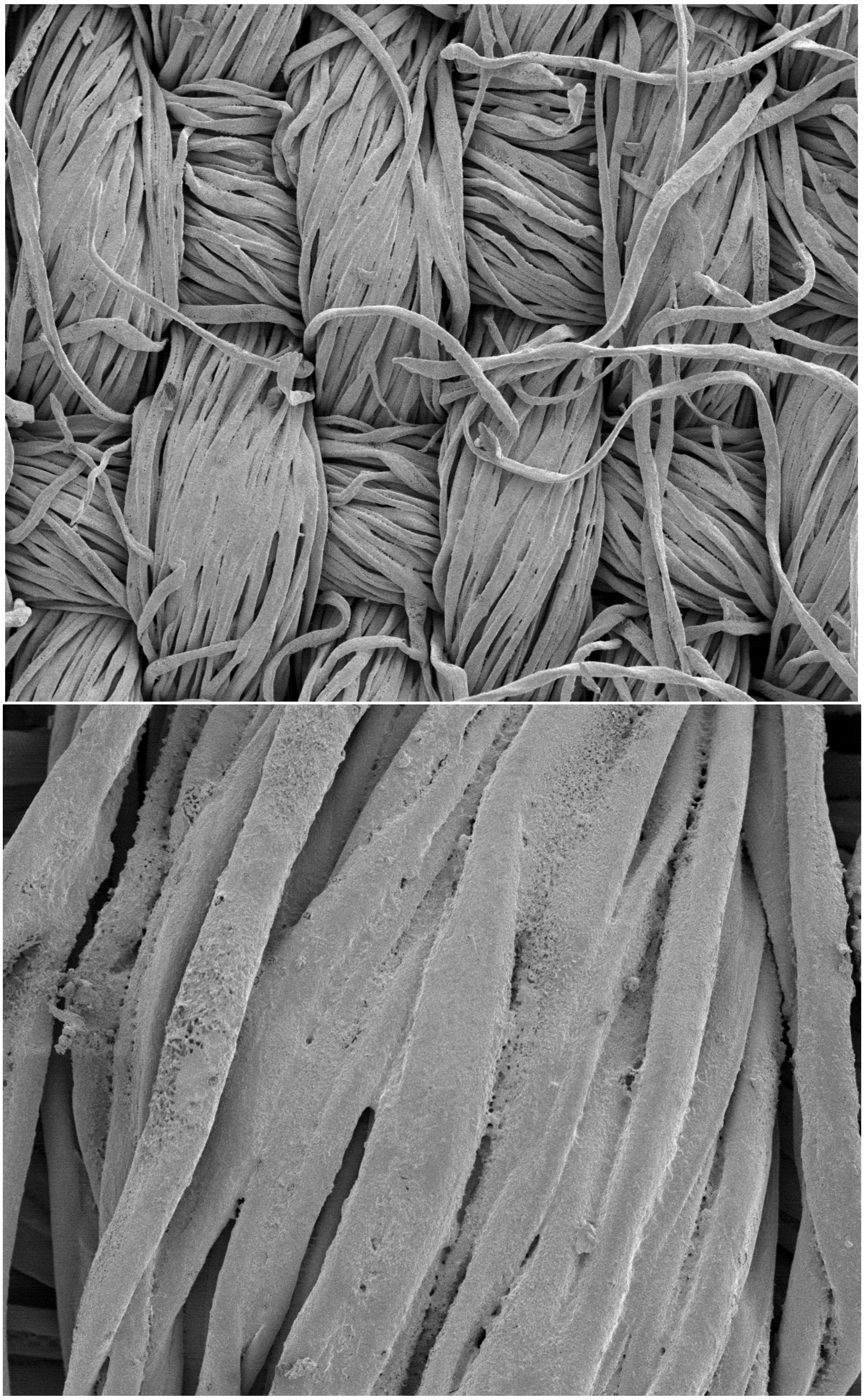


Figure 4.11 SEM images of printed cotton, with mag x100 (top) and mag x450 (bottom)

Colour assessment: Colour fastness to rubbing ISO 105-X12

The colour fastness of the printed WBS to rubbing was assessed according to the ISO 105-X12 standard as described in chapter section 3.3. The coloured fabric was subjected to both dry and wet rubbing. The staining on the cotton rubbing cloths was assessed with a Grey Scale under suitable illumination according to the standard. Rubbing with a dry cotton cloth did not appear to have any effect as there was no noticeable staining on the rubbing cloth. However, wet rubbing did have a significant effect, Table 4.4. The coloured layer immediately appeared to rub off in contact with the wetted rubbing cloth. It appeared that the coloured WBS was water-soluble as the colour started to dissolve and migrate when in contact with the wetted rubbing cloth creating a typical halo effect, Figure 4.12. This suggests that there was no or limited fixation of the functional polymer onto the cotton surface, indicating that no or limited crosslinking had occurred, in turn suggesting the insufficient or even unsuccessful production of Bunte salts from the wool protein.

Table 4.4 Staining assessment after rub fastness testing of cotton printed with the blue WBS ink

Test	Grey Scale assessment
Dry rubbing	5
Wet rubbing	2

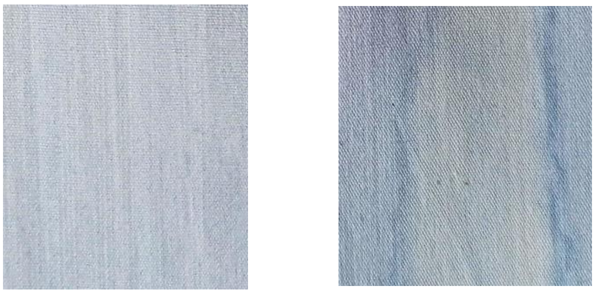


Figure 4.12 Visual appearance of cotton printed with blue WBS ink, after dry rubbing (left) and with a halo effect after wet rubbing test (right)

Colour assessment: Colour fastness to laundering ISO 105-C09

The colour fastness of the printed cotton fabrics was assessed according to the ISO 105 C09 standard as described in chapter section 3.3. After washing of the printed cotton, it appeared all of the colour had been removed, leaving a white substrate. Similar to the results after the wet rub fastness test, this suggests that there was limited or no fixation of the WBS polymer on the cotton substrate or the dye colorant was lost from the WBS. However, the latter is unlikely as a reactive dye has formed a covalent bond with the wool before wool derivatisation. Thus, like with the colour fastness to rubbing, the most likely explanation for the poor colour fastness to laundering could be a result of a lack of Bunte salts produced in the first place. The highest value of colour strength K/S λ_{max} was obtained at 580 nm correlating to the colour blue (Radovic et al, 2014). After washing K/S λ_{max} had reduced from 0.39 to 0.01, Table 4.5. After washing, lightness had increased from L* 76.9 to L* 95.2, indicating that the washed cotton had lost most, if not all colour provided by the printed WBS layer.

Table 4.5 Colorimetric data for blue WBS-printed cotton fabrics before and after washing

	Before washing	After washing
K/S	0.39	0.01
L*	76.9	95.2

SEM images of the cotton fabric printed with the blue WBS ink captured after the ISO 105 C09 test showed slight signs of fibrillation, Figure 4.13. Additionally, in contrast to the fabric printed with the blue WBS ink before washing, here the WBS appears to be no longer present. These results are supported by FT-IR analysis, where the earlier observed signals correlating to the protein amides (around 1550 cm^{-1} and 1650 cm^{-1}), were no longer obviously present after the laundering of the fabric, Figure 4.14, with the characteristic ′′fingerprint′′ of cotton being more strongly present once again.

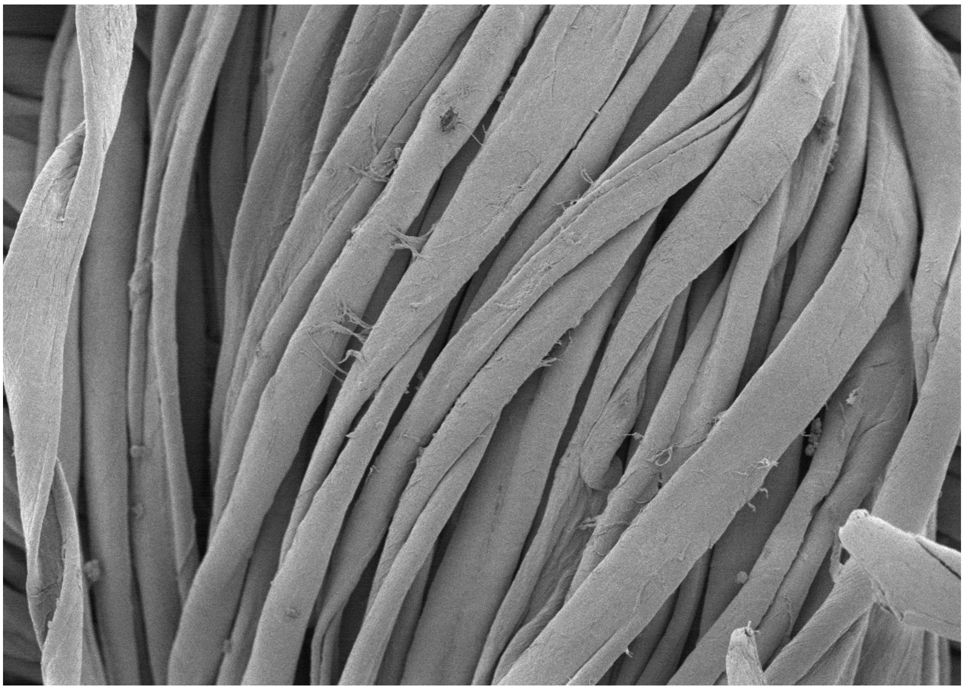


Figure 4.13 SEM image of cotton fibres after printing with the blue WBS ink and after washing (mag x500)

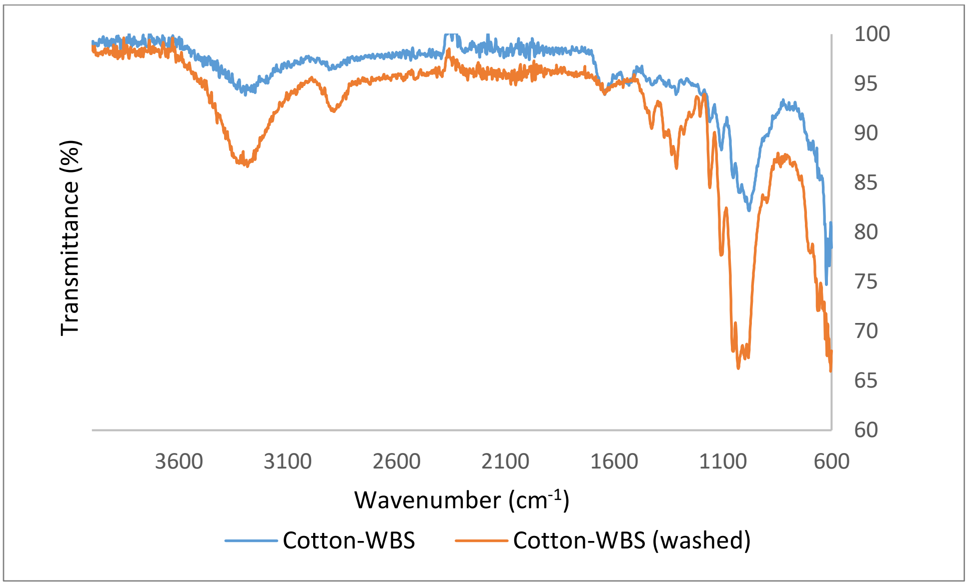


Figure 4.14 FT-IR spectra of cotton printed with the blue WBS ink before (top) and after (bottom) washing

It could be argued that the extensive colour removal after washing could be a result of the aggressive nature of the test due to the incorporation of the bleach activator tetraacetylethylenediamine (TAED). TAED is an oxygen-releasing material. TAED is widely used in bleaching systems for detergent, textile and paper-making industries. Using an oxygen activator such as TAED in addition to a bleaching agent, facilitates a bleaching reaction at low temperatures (Çelik, Türkün, and Yapar 2008). In aqueous washing liquors, the combination of these two will lead to oxidation of a stained substrate. This oxidation reaction could possibly have affected the protein layer by reducing the number of disulphide bonds which were supposedly formed after baking of the printed cotton, possibly resulting in the potential removal of the layer. However, a more likely explanation is the lack of disulphide formation from the Bunte salt functional groups upon heating of the printed fabric. It is proposed that the cause of poor fixation of the protein layer onto the cotton substrate may be related to the pH of the protein solution. Initial experiments did not include ensuring suitable pH storage conditions of the Bunte Salt solution and of the ink formulation after preparation. As discussed before, the Bunte Salts are most stable at ~pH 5.5. At lower pH the -SSO_3 will become protonated to its –SH form, whereas under more alkaline conditions the thiol will gradually reform the disulphide bond. It is possible that upon printing of the ink formulation no or limited Bunte salts were present in the ink, but that thiol groups or disulphide bonds were prematurely formed, resulting in the lack of crosslinking on the fabric after printing and curing. In addition, the ink instability and formation of thiol groups or disulphide bonds could explain the difficulties found during printing as the printhead nozzles required frequent cleaning due to continuous blocking of the nozzles. Fixation was not achieved, as assessed by rubbing and washing fastness tests. Furthermore, a following attempt to produce another printed cotton substrate was not possible as the ink did not allow take up by a syringe through a Millipore filter. This suggests that at that point (after the ink had been stored under possibly too high alkaline pH conditions) a polymerisation reaction had already occurred *in situ*, reforming the disulphide bonds in the solution. Therefore, crosslinking of Bunte salts after printing onto cotton fabrics and after baking was limited, with limited (or no) available Bunte salt groups. Furthermore, it must be noted that after acid sensitisation of the wool, the HCl/wool mixture was neutralised by addition of NaOH pellets. As the mixture was initially highly acidic, a large quantity of alkali was needed to obtain an increase in pH. This neutralisation caused an acid-base reaction leading to the formation of large quantity of inorganic salts. These salts may have also affected the stability of the WBS solution and thus also the stability of the WBS ink contributing to clogging of the printing nozzles. Another possible explanation of the apparent limited production of Bunte salt groups could be related to the direct addition of NaOH pellets. The direct addition of this concentrated alkali, in contrast to the addition of a dilute solution, could have led to the initial localised alkalisation upon addition to the acid sensitised wool solution. This may have affected the sensitised wool fractions and with that also the subsequent attempt to produce the Bunte salt groups.

It was found that with using inkjet printing as an eco-friendly method for the colouration of cotton, many challenges came up as there are various different parameters which need to be taken into consideration for the successful printing of an ink onto a substrate, mainly related to the ink formulation in terms of stability, rheology and printability. For this reason, it was decided that further experiments would be carried out using a commercial alternative material from which Bunte salts could be obtained more easily, using a simple pad/dry/bake method for colour application onto cotton.

4.5.2 Bunte Salt-Terminated Derivatives from Hercosett™ 617

4.5.2.1 Preparation of the PAE-BS Polymers

Bunte salt polymers were prepared from Hercosett™ 617 by reaction with sodium thiosulphate. In accordance with literature and similar to previous reports, the product was a cloudy solution which upon standing overnight changed to an evident two-phase mixture (Cockett and Lewis 1976). The upper layer was clear with a pH of ~7 and the bottom layer comprised of solids and appeared to be approximately one-third of the mixture total volume. It was observed that when the abovementioned two layers were shaken, they became miscible before separating into two phases once more upon standing over time. FT-IR spectra of the unmodified PAE polymer isolated from the original Hercosett solution and of the PAE-BS polymer are shown in Figure 4.15. The isolated unmodified PAE shows signals around 3300 cm^{-1} for the secondary amide stretching vibration, residue water or potentially correlating to the carboxylic acid O-H stretching vibration. The signals observed around 1620 cm^{-1} and 1540 cm^{-1} correlate to the secondary amide C=O stretching vibration. The PAE-BS showed increased signals around 1190 cm^{-1} and 1022 cm^{-1} correlating with the Bunte salt groups and the reduction of transmittance around 1092 cm^{-1} might be assigned to the modification of the AZR functionality. It was expected that Bunte salts would be formed on reaction with AZR rings.

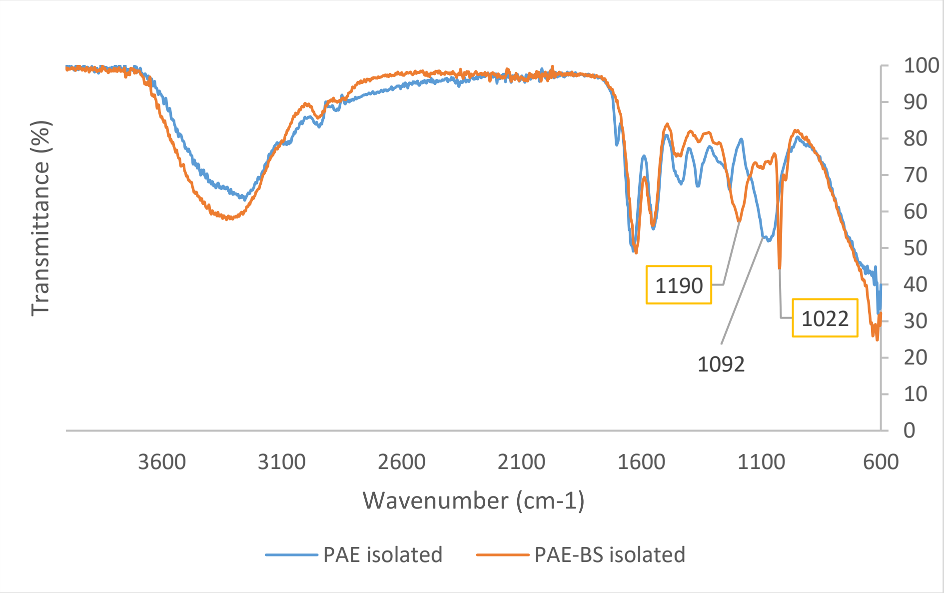


Figure 4.15 FT-IR spectra of the PAE polymer isolated from Hercosett™ 617 and the isolated PAE-BS polymer

4.5.2.2 Film Formation

Films were produced from the PAE-BS solution at 150°C for a drying time of 20 minutes and at 105°C for 24 hours, with and without the addition of sodium carbonate. After rinsing in water, the films remained intact, suggesting that crosslinking had occurred. Due to the thinness or brittleness, the films were ‘’impossible’’ to remove from the glass slides without causing damage, therefore the samples were prepared for SEM analysis by simply breaking off a piece of the slide containing the film.

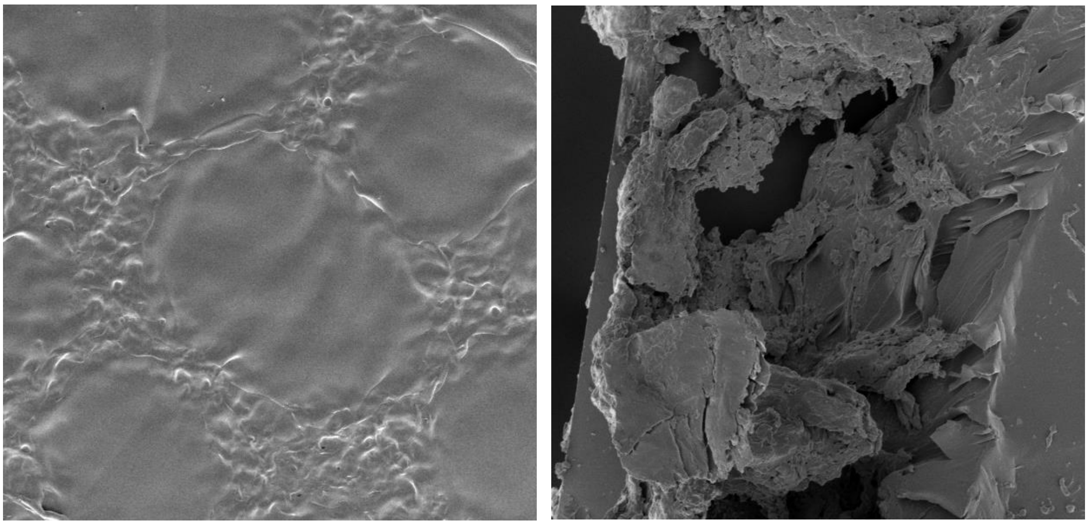


Figure 4.16 SEM images of PAE-BS film, dried at 150°C, with the film top surface (left, mag x50) and the film edge (right, mag x1,000)

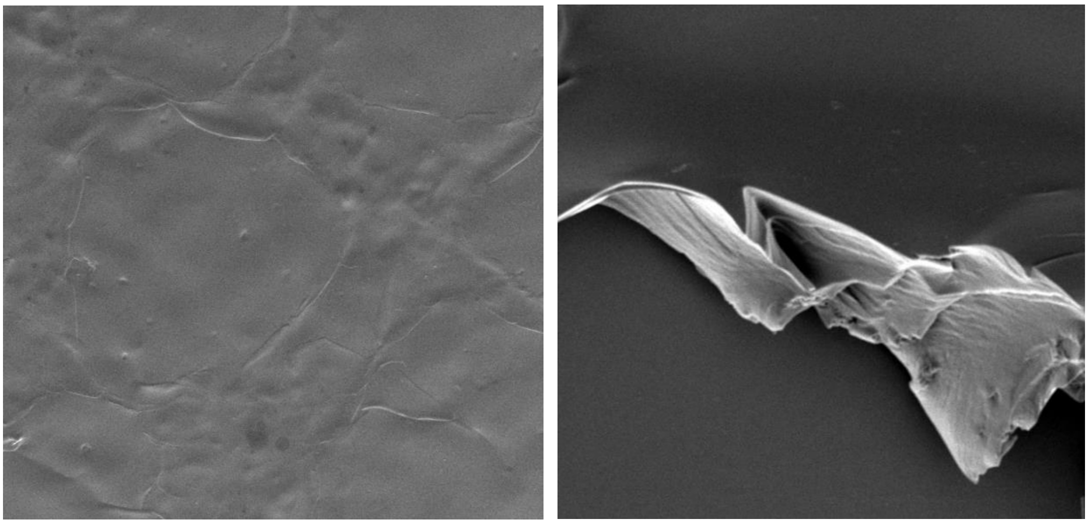


Figure 4.17 SEM images of PAE-BS film, dried at 105°C, with the film top surface (left, mag x50) and the film edge (right, mag x1,000)

The films produced without addition of sodium carbonate show a smooth film surface with some circle shaped wrinkles, most evident in the film produced at 150°C and most likely a result of rapid contraction and drying of the polymer upon moisture evaporation, Figure 4.16 and Figure 4.17. The edge of the PAE-BS film dried at 150°C exhibited some damage, potentially caused during breaking of the glass slide, Figure

4.16. The edge of the film dried at 105°C shows a smooth and dense film throughout thickness, Figure 4.17. Both films appear to exhibit a compact structure.

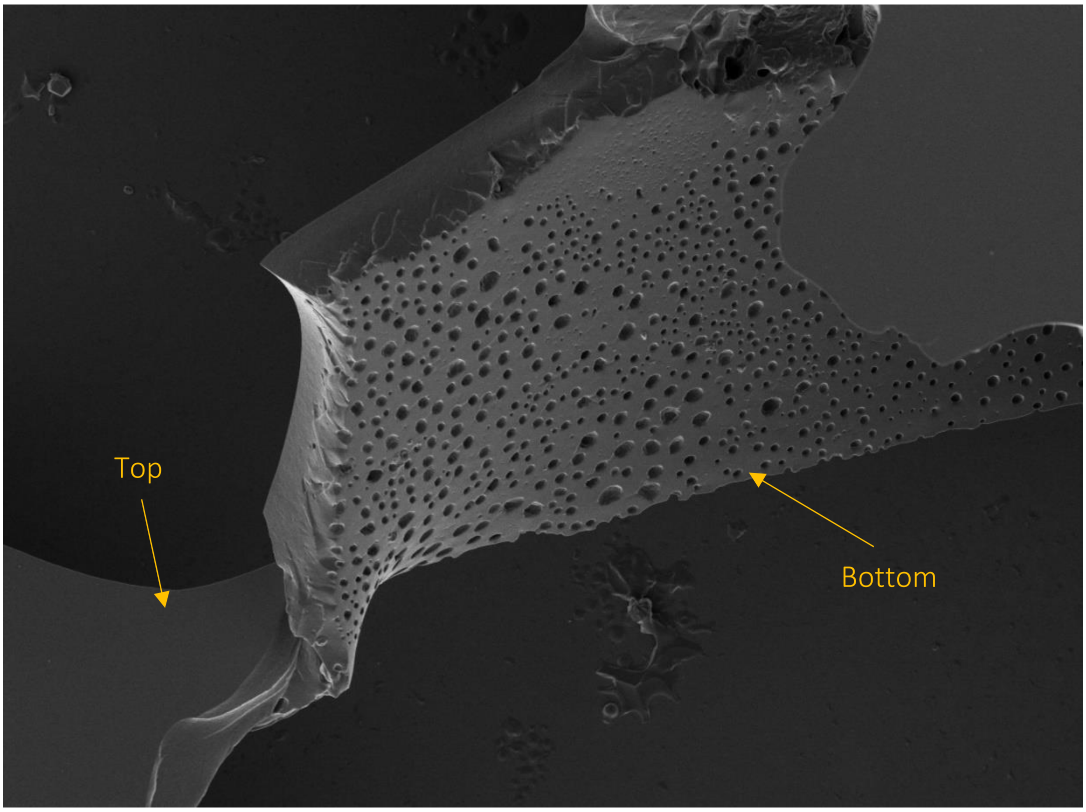


Figure 4.18 SEM image of PAE-BS film with added sodium carbonate, dried at 150°C (mag x500)

Drying of the PAE-BS solution prepared with the addition of sodium carbonate produced more brittle films with smooth top surfaces and rough bottom surfaces. The holes observed on the bottom surface of the PAE-BS prepared with sodium carbonate and dried at 150°C can potentially be explained as air pockets created due to rapid evaporation of the moisture content, Figure 4.18. Similar to the PAE-BS film produced without the addition of sodium carbonate, the film prepared with the addition of sodium carbonate and dried at 105°C shows a more compact film formation in comparison to the film prepared at a higher temperature, Figure 4.19.

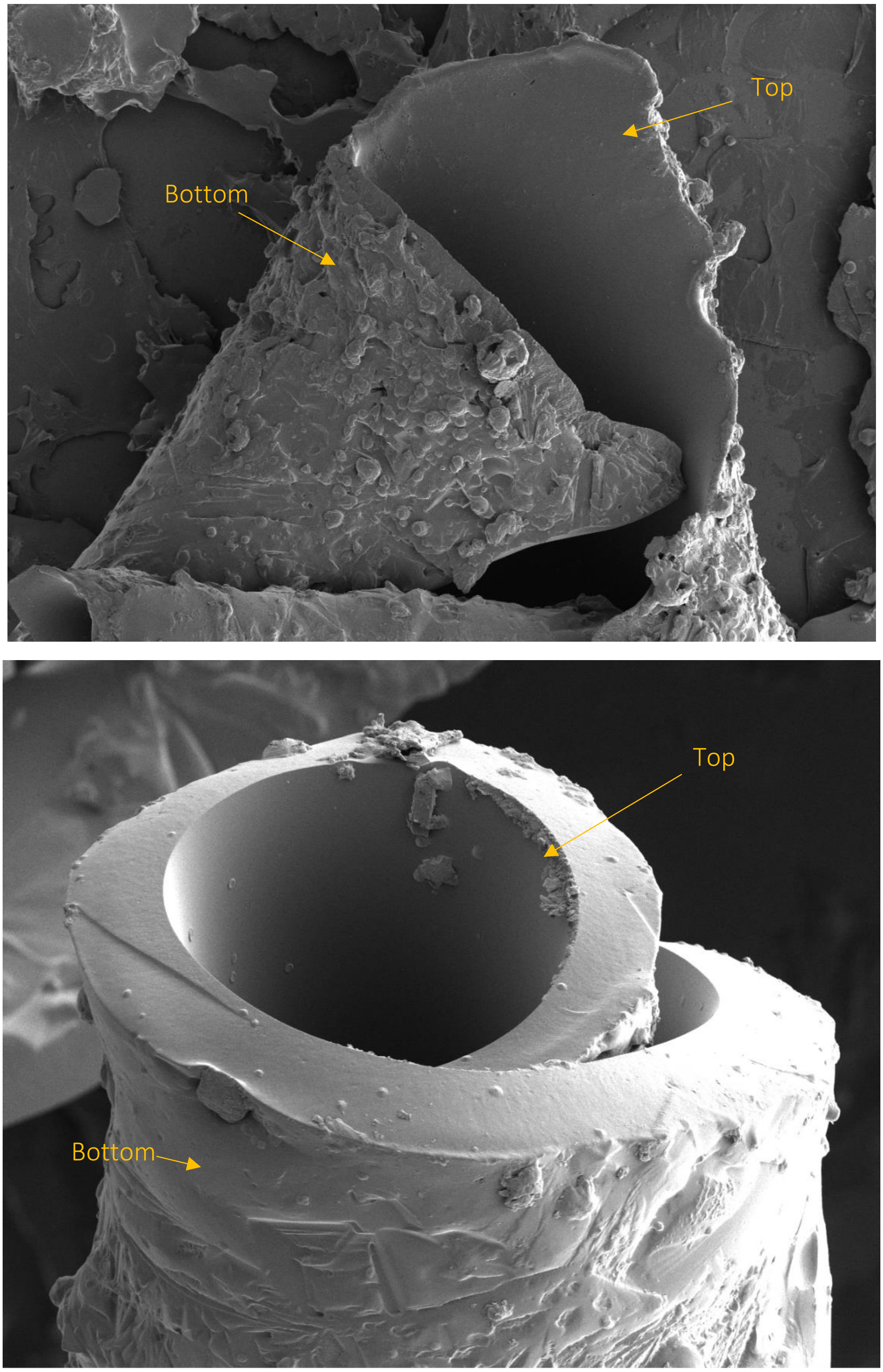


Figure 4.19 SEM images of PAE-BS film with added sodium carbonate, dried at 105°C. (Mag x100 (top) and Mag x500 (bottom))

Additional elemental analysis in the form of Energy Dispersive X-ray (EDX) analysis was carried out on the films in order to further assess the chemical composition of the polymer. All films showed a strong signal for sulphur, carbon, nitrogen and oxygen.

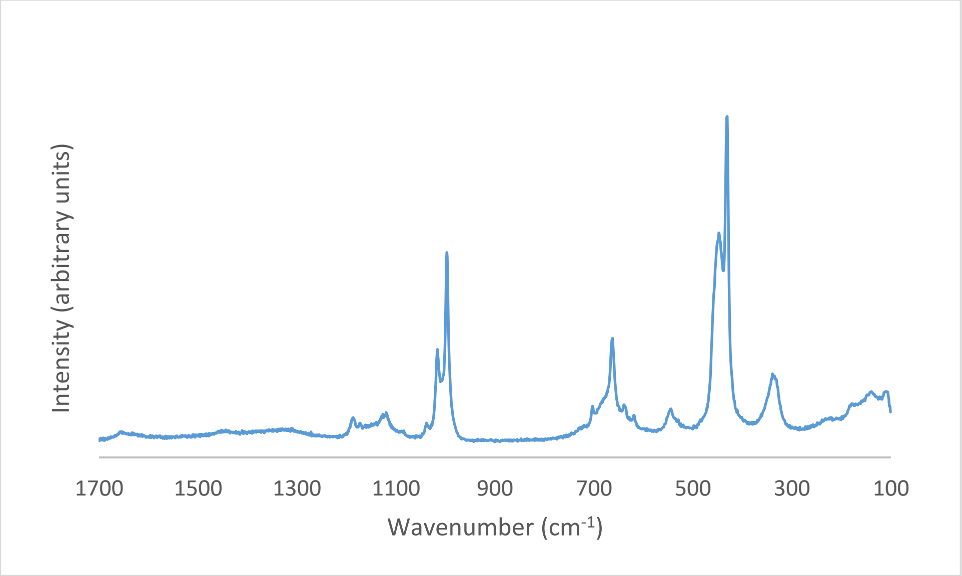


Figure 4.20 Raman spectrum of heat dried PAE-BS polymer

Examination of the Raman spectrum of the PAE-BS solution heated to the boil to evaporate the moisture content showed the presence of the Bunte Salt vibrational signal and was similarly observed in the IR spectrum (Church and Evans 2008). Raman spectroscopy was expected to be particularly useful for the confirmation of the disulphide formation. Strong Raman lines were observed around 998 cm^{-1}, 660 cm^{-1} and around 430 cm^{-1} potentially correlating to symmetrical -SO_3, C-S and S-SO_3 stretching vibrations of the S-sulphonate groups, respectively, Figure 4.20. Unfortunately, no Raman line was obtained for the S-S stretching vibrations, which would be expected at 500 cm^{-1}. This suggests that no disulphide bonds were formed upon heating and evaporation of the liquid from solution, indicating the insufficient

Bunte salt formation in the first place. Although no Raman line was observed for the disulphide bonds, the successful formation of films from the modified PAE solutions does indicate that some form of crosslinking is occurring. It is proposed that the films could have been formed as a result of a crosslinking reaction of unreacted AZR groups. It must be noted that due to limited availability of the Raman equipment, it was not possible to perform repetition analysis tests as well as to perform Raman analysis on the films and that future research should include Raman analysis on the polymer films.

4.5.2.3 Fixation of the PAE-BS on Cotton Fabrics

Padding of the PAE-BS on cotton

The FTIR spectra of the untreated cotton fabric and of the cotton fabric padded with the PAE-BS/pigment are shown in Figure 4.21. It was observed that vibrational signals had appeared in the FTIR spectrum of the padded fabric around 1634 cm^{-1} and around 1558 cm^{-1} correlating to the amide I and amide II stretching vibration.

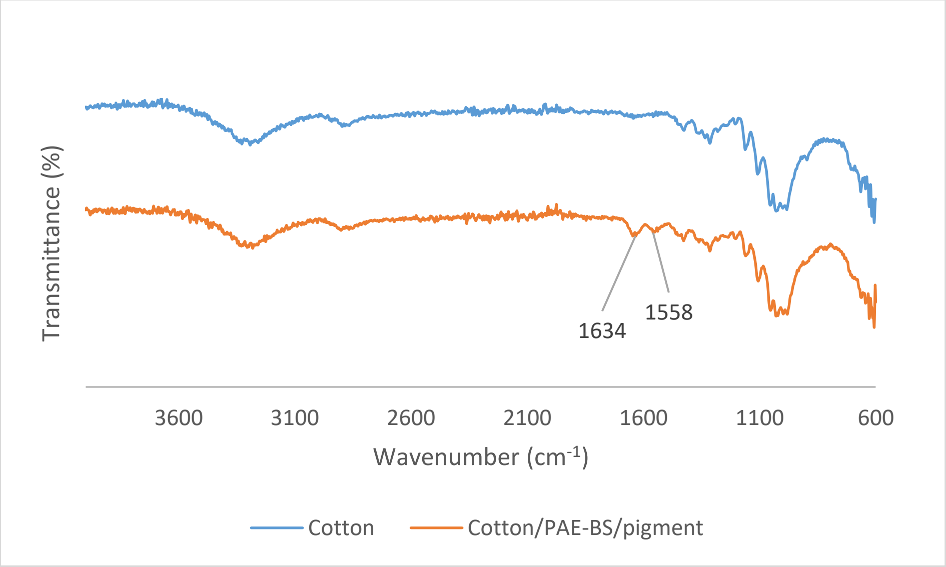


Figure 4.21 FT-IR spectra of untreated cotton and cotton padded with the PAE-BS/pigment

It could be observed from the SEM images in Figure 4.22 that the PAE-BS acted as a binder material, covering and connecting the fibres. Additionally, large particle agglomerations were found on the padded cotton fabric, which were identified as the pigment by EDX analysis showing a signal correlating to the iron compound of the pigment and by additional SEM of the solid pigment.

Colour assessment: Colour fastness to rubbing ISO 105-X12

The fixation of the pigments with the PAE-BS as a binder material was assessed through rub fastness testing. Various samples were tested to assess the effect of baking following drying and to assess the effect of adding sodium carbonate to the padding liquor, Table 4.6. Dry rubbing of the padded fabrics all showed excellent results, with little or no staining of the colour on the white rubbing standard testing cloths. Wet rubbing of the cotton padded with the pigment/binder mixture with the addition of sodium carbonate followed by drying and baking, obtained staining of the testing cloth. This goes against the expectations of the specific method to produce the best colour fastness results with sodium carbonate potentially aiding crosslinking reactions. It must be noted that upon assessment of the coloured cotton fabrics after rubbing tests, no significant colour change was observed in any of the fabrics. This could potentially be explained by poor dispersion of the padding liquor, obtaining pigment agglomerates on the fabric surface.

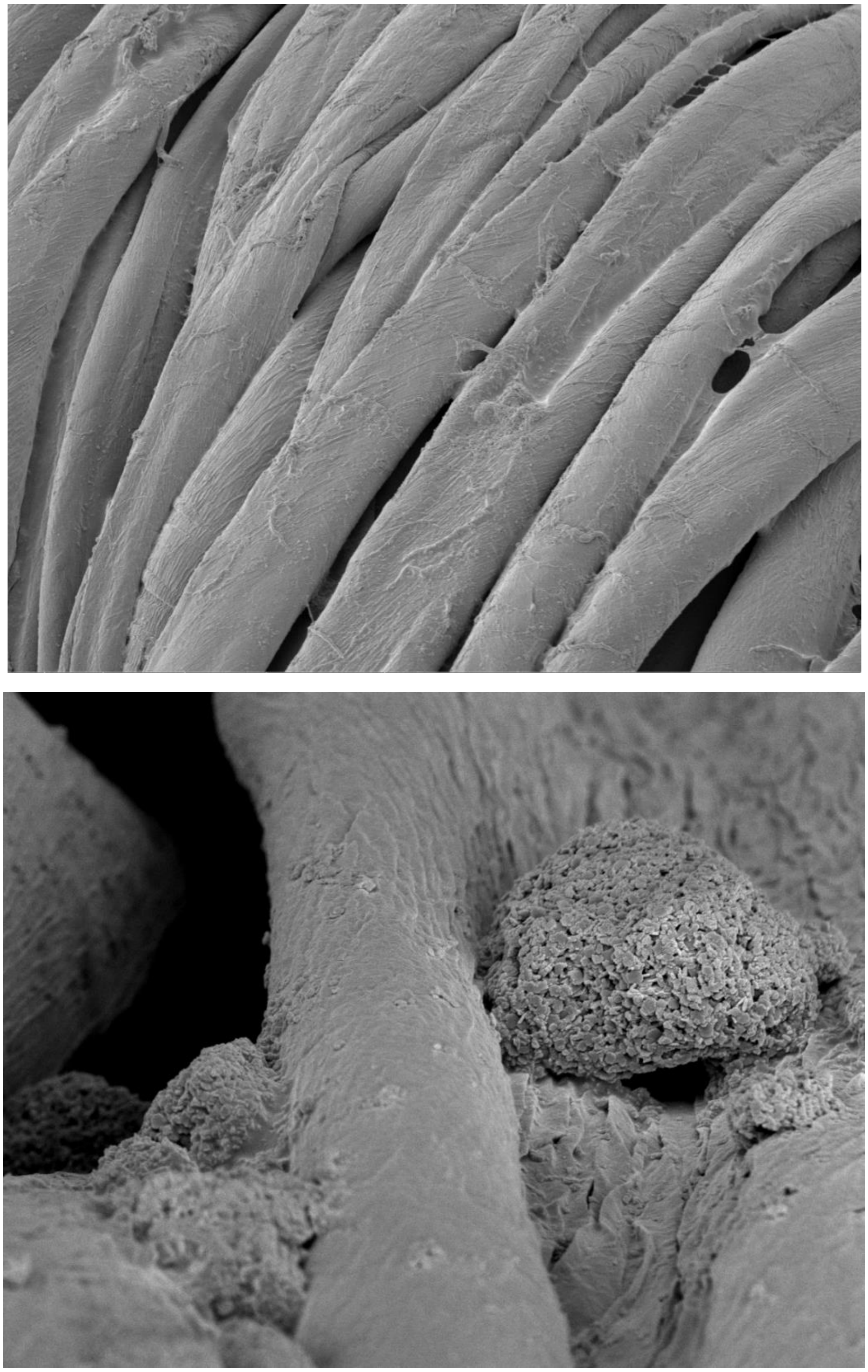


Figure 4.22 SEM images of cotton padded with PAE-BS as a binder for Pigment Green 8 (mag x100 (top) and mag x5,000 (bottom))

Table 4.6 Staining assessment after rub fastness testing of cotton fabrics padded with PAE-BS/pigment

	PAE-BS/pigment/Na_2CO_3 - dried 80°C	PAE-BS/pigment/Na_2CO_3 - dried 80°C - baked 150°C	PAE-BS/pigment - dried 80°C - baked 150°C
Dry rubbing	4/5	4/5	4/5
Wet rubbing	4/5	3	4/5

Colour assessment: Colour fastness to laundering ISO 105-C09

The colour fastness of the green padded fabrics was also assessed by subjecting the fabrics to laundering tests according to ISO 105-C09, Figure 4.23. A colour difference was already visually observed after preparation of the green fabrics according to various parameters. The green padded cotton fabric that was prepared without the addition of sodium carbonate was of a darker green colour in comparison to the fabrics padded with the sodium carbonate-containing liquor. It was observed that during the preparation of the padding liquor, the addition of sodium carbonate immediately resulted in the dispersion of the pigments. Thus, it could be concluded that without adding sodium carbonate, the pigment particles retained their strong forces towards each other which is shown as a darker green colour of the padding liquor and as a darker green colour of the padded fabric due to the pigment agglomeration.

After washing of the green padded cotton fabrics, which were only subjected to a drying step (80°C) following padding, it was observed that the green colour was almost completely removed. Additional baking of the padded fabric at 150°C following drying, obtained a superior colour fastness, with no obvious colour change after washing. Washing of the green padded fabric without addition of sodium carbonate showed a colour loss after washing but had a colour appearance similar to that of the fabric padded with sodium carbonate followed by drying and baking.

Considering the difficulty of cleaning the padding equipment when using the padding liquor without sodium carbonate, the pad/dry/bake colouration method with added sodium carbonate was deemed most appropriate.

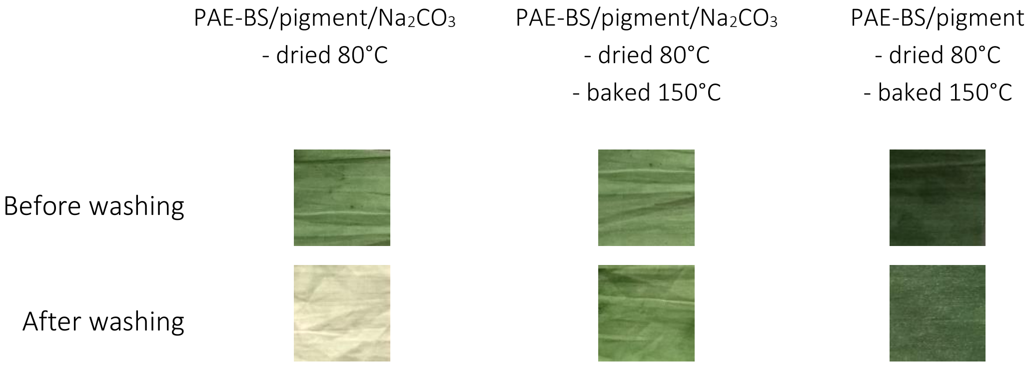


Figure 4.23 Visual appearance of cotton fabrics padded according to various methods, before and after ISO 105 C09 washing

Figure 4.24 shows an SEM image of the PAE-BS/pigment padded cotton fabric which had been subjected to an ISO 105-C09 washing test. The PAE-BS binder was still found to be present on the fibres. The large pigment agglomerations earlier observed on the fabric before washing was no longer present. Thus, it could be concluded that the agglomerations were excess and unfixed particles which were removed by the laundering process.

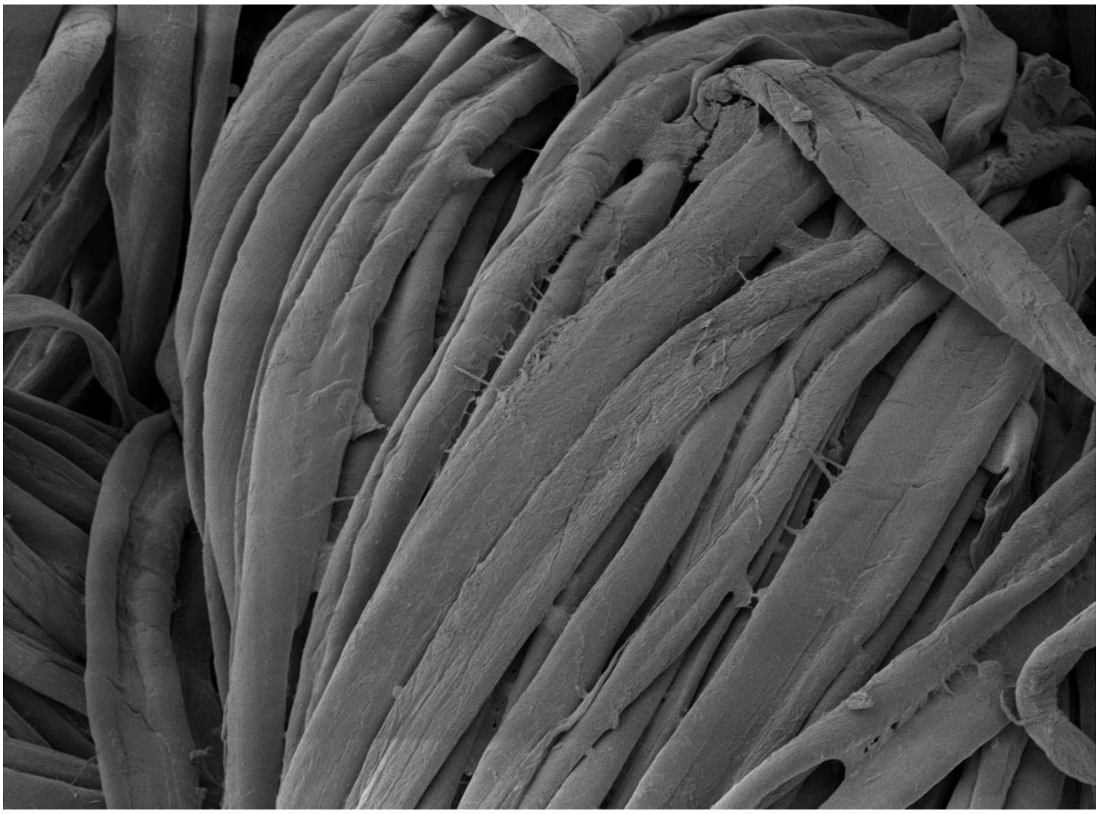


Figure 4.24 SEM image of the cotton fabric padded with PAE-BS/pigment (dried 80°C, baked 150°C) after ISO 105 C09 washing (mag x500)

4.6 Conclusions

The aim of the work described in this chapter was to develop a novel colouration method using potential binder materials based on Bunte salt chemistry, which could also possibly offer the ability for subsequent removal. The expected mechanism would rely on the production of Bunte Salt functional groups (R-SSO_3) with the potential to crosslink into disulphide bonds, which upon recycling of the coloured material could be chemically degraded. Wool was initially used as a bio-based material to produce Bunte salt-terminated protein derivatives. FT-IR analysis of the WBS solutions showed that Bunte salt groups were more efficiently produced with an increase in wool sensitisation temperature from 60°C to 80°C. An attempt to film formation by drying of the WBS solution was however not successful as the dried

’’film’’ immediately dissolved in water during rinsing. Inkjet printing was selected as an eco-friendly colour application method for the blue dyed wool-derived Bunte salt (WBS) ink. The WBS solution prepared with a sensitisation temperature of 60°C was successfully printed onto cotton in multiple layers. However, the print showed poor colour fastness to wet rubbing and poor colour fastness to laundering. Furthermore, printing of the ink showed great difficulty as the print cartridge required regular cleaning due to clogging of the nozzles. A number of variables could be the cause, potentially related to the stability of the ink as a result of ink formulation and storage at inappropriate conditions. It is suggested that future studies should thoroughly ensure appropriate conditions for ink formulation and storage (pH, storage temperature) as well as investigate the higher temperature (80°C) acid sensitisation method as a potentially more efficient production method of Bunte salt-terminated wool derivatives for application as a binder material for the colouration of textiles such as cotton fabrics.

An alternative and less time-consuming process of producing Bunte salt-terminated polymers involved the reaction of Hercosett™ 617, a commercial polyamide epichlorohydrin (PAE), with sodium thiosulphate. FT-IR of the isolated of the Bunte salt-terminated PAE derivative (PAE-BS) showed the presence of the Bunte salt groups. Drying of the PAE-BS solutions successfully obtained water-insoluble films. The films prepared with the addition of sodium carbonate appeared more brittle and fragmented. It was observed that at a temperature of 105°C films were produced with a relatively more uniform appearance in contrast to those produced at 150°C. The non-uniformity in the films produced at the higher temperature is suggested to be a result of rapid moisture evaporation and contraction of the polymer. A PAE-BS polymer solution was heated to the boil to quickly produce the dried polymer for assessment using Raman spectroscopy. Surprisingly, no Raman lines associated with the S-S stretching vibration were observed, which indicated that no significant disulphide bond formation had occurred. After padding/drying/baking of cotton fabrics with the PAE-BS/pigment/sodium carbonate padding liquor SEM and EDX analysis indicated the presence of pigment agglomerations on the fabric, which were subsequently removed by laundering. Padding cotton fabrics followed by drying at 80°C and an additional baking step at 150°C showed satisfactory colour fastness to washing, suggesting the potential of the PAE-BS as a binder for pigment colouration of cotton fabrics as well as ensuring stability of the Bunte salt polymer solutions during storage.

The work described in this chapter shows the potential of Bunte salt polymers to function as binder materials for pigment colouration of textiles such as cotton fabrics. Based on published works as well as the initial results obtained by the thesis research described in this chapter, Bunte salt chemistry is shown to be promising for the development of a colouration and targeted colour removal method. The chemistry could allow fixation of the binder material onto fabrics by a crosslinking mechanism as well as allow targeted degradation when removal of the colour formulation is required. Future work is suggested to finetune the production and characterisation of Bunte salt polymers from the starting materials such as wool or polyamidoamine epichlorohydrin, as well as investigate the polymer crosslinking mechanism and fixation onto textiles such as cotton fabrics. Specifically, the use of Bunte salt polymers produced from wool would be of key interest in terms of the development of a ‘’sustainable’’ method of colouration, as it would provide a platform for using renewable or waste resources in a colouration-colour removal system.

Chapter 5 – PAE as a Potential Binder for Pigment Dyeing of Cotton

The work described in this chapter was the initial investigation into the potential of PAE as a binder material. This includes investigating the fixation of the polymer onto cotton fabrics to assess its potential to function as a binder for pigment colouration. Furthermore, initial attempts of colour stripping through degradation of the binder material were carried out using the oxidising agents potassium persulphate and Kybreak™.

5.1 Materials

Hercosett™ 617(12-25% total solids in solution) and Kybreak™ 500 were kindly supplied by Solenis and Pigment Green B (C.I. Pigment Green 8) was provided by Albion Colours. Sodium carbonate anhydrous (Riedel-de Haën), tetra-acetylethylene diamine (SDC Enterprises), sodium perborate tetrahydrate (Honeywell), ECE non-phosphate reference detergent base powder without optical brightener (SDC Enterprises), potassium persulphate (Fluorochem), sodium hydroxide (≥ 98%, Sigma Aldrich) and hydrochloric acid (≥ 37%, Sigma Aldrich) were used as supplied. All reagents were of analytical grade. All solutions were prepared with the use of distilled water. Plain woven cotton fabric (100%, bleached only, no optical brightening agent, 142.8 g/m^2) was supplied by Phoenix Calico Limited, Denby Dale, UK was used throughout this study.

5.2 Assessing the Behaviour of PAE as a Potential Binder Material

The expected crosslinking mechanism of PAE is related to the reactive AZR ring groups on the polymer backbone. The main crosslinking of the potential binder material is expected in the formation or 2-propanol bridges, with potential secondary crosslinking in the form of ester bond formation (Siqueira 2012).

5.2.1 Film Formation

To function as an effective binder for pigment dyeing of cotton fabrics, it is a requirement that the material has the ability to form a thin solid film around the pigments and adhere onto the substrate. Hercosett™ 617 PAE films were prepared according to the same method as described for the Bunte salt-terminated film formation in chapter 4. Table 5.1 shows an overview of the variables at which the films were produced. One batch of the PAE solution was used as supplied and another batch was prepared by mixing 200 g PAE solution with 20 g/L sodium carbonate using a OV5 Homogeniser (VELP scientifica) at a speed of 10,000 rpm. The films were prepared by pipetting 1 ml of PAE solutions onto glass slides and drying in an Equiptex N75 CFD model ventilated oven. It was ensured that no air bubbles were present before placing the slides into the oven. After film formation the glass slides were placed in a beaker with distilled water with slight agitation, to rinse off any contaminants, and subsequently dried in a desiccator containing silica.

Table 5.1 Sample variables for PAE film formation

Film Composition and Preparation Conditions				
Composition	PAE	PAE & Na_2CO_3	PAE	PAE & Na_2CO_3
Temperature	105°C	105°C	150°C	150°C
Time	24 hours	24 hours	20 minutes	20 minutes

5.2.2 Pigment Dyeing of Cotton Fabric

Similar to the method described in Chapter 4 for the colouration of cotton using the Bunte salt-terminated polymer derived from Hercosett, here the pigment dyeing of cotton was also carried out by the pad-dry-bake method. C.I. Pigment Green 8 was selected as a readily available pigment for pigment dyeing of cotton fabrics. The chemical structure of the pigment is shown in Figure 4.6. The pad liquors were prepared by dispersing 10 g/L of the pigment using a homogeniser, as per described in the preparation of the films, in 400 g of the PAE solution, without further dilution for a minimum of 10 minutes. The pad liquor was used immediately following dispersion of the pigment. The padding liquors were prepared with and without the addition of 20 g/L sodium carbonate to assess the effect of the component on the fixation behaviour of the polymer. The cotton fabrics were immersed in the liquor, excess liquor was squeezed out by hand and the fabrics were then passed through the padding-mangle nip of a Werner Mathis laboratory padder, at a padding speed of 2 m/min with a pressure set to obtain a wet pick-up of ~100% on mass of fabric. The padded fabrics were then dried at 80°C for 3 minutes, followed by baking at 150 °C for 3 minutes using a Werner Mathis laboratory baker-steamer unit.

5.2.3 Wash Fastness of the Pigment-Dyed Fabric

Fixation of the PAE onto the pigment-dyed cotton fabrics was indirectly assessed by subjecting the PAE/pigment-padded cotton to laundering tests according to BS EN ISO 105-C09:2003 standard (British Standards Institution 2003). The test involved using a non-phosphate reference detergent incorporating a low temperature bleach activator. The effect of laundering was assessed by comparing the colorimetric values K/S, ΔE and L* of the fabrics before and after washing. In comparison to other washing standards, the C09 version is regarded as a ‘’harsh’’ assessment, designed to simulate multiple domestic/commercial laundering processes as would be the case of a garment going through a lifetime of laundering. It is therefore suggested to be the most appropriate method for testing the colour fastness of the pigment-dyed cotton fabrics. Please refer to chapter section 3.3 for a detailed description of the ISO 105 C09 method and materials.

5.3 Stripping of the PAE/Pigment Formulation from Cotton Fabric

After establishing a method for pigment dyeing of cotton using the PAE/pigment formulation giving satisfactory colour fastness results, work was done looking into the subsequent removal of PAE/pigment from the cotton fabrics. The fabrics used for these experiments were pigment-dyed using the padding-dry-cure method and subsequently washed according to ISO 105 C09 washing standard as described in chapter section 3.3. This was done to assess the durability of the binder on the fabric as well as to simulate the state of a garment at the end of its life having been subjected to multiple washing cycles. The removal of the PAE/pigment formulation from these fabrics would in turn simulate the removal of colour content from cotton garments in order to recover white cotton fibres. Removal of the PAE/pigment formulation from the cotton fabrics involved using potassium persulphate or Kybreak™ 500 as the ‘‘stripping’’ agent.

5.3.1 Effect of Potassium Persulphate as a ‘‘Stripping Agent ‘‘

The use of persulphate salts such as potassium persulphate has shown to be effective in the degradation of PAE resins in wet-strength paper as reported in published literature. The mechanism of the PAE chain scission caused by potassium persulphate is shown in Figure 5.1 (Siqueira 2012). It was proposed that the addition of the oxidant potassium persulphate salt produces free radicals. Oxidation of the N-substituted primary amides on the PAE backbone occurs as a free radical attack, activated by the electron pair on the nitrogen atom, on the α-carbon (with respect to the amide nitrogen). For example, 1 mol persulfate can produce three free radicals: 2 $SO_4^{-\cdot}$ and $^{\cdot}OH$. The subsequent degradative reaction is N-C scission, producing an unsubstituted primary amide and an aldehyde through dealkylation.

The 70 ml (fabric to liquor ratio 1:100) stripping solution was prepared by dissolving 1.925 g (2.75% (w/v) potassium persulphate per 0.07 g (0.01% w/v) PAE/pigment present on the sample, in distilled water based on work from Siqueira (Siqueira, 2012). The content of PAE/pigment in the samples was estimated prior to preparation of the stripping liquor, by weighing untreated cotton (*C*) and the PAE/pigment-padded cotton (C_p) fabrics of identical surface area and conditioned at room temperature and a relative humidity of 65%. The difference in weight was calculated according to Equation 5.1.

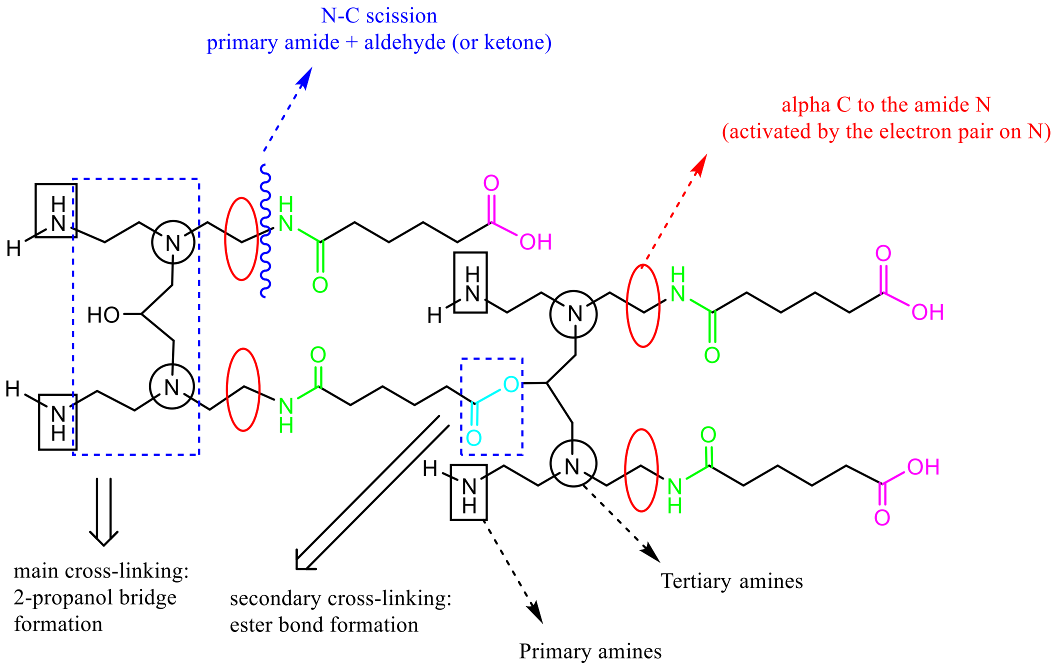


Figure 5.1 Schematic representation of the suggested main mechanism of degradation of PAE using potassium persulphate (Siqueira 2012)

$$\%\ PAE/pigment\ content = C_p - C$$

Equation 5.1

The pH of the solution at room temperature was recorded to be pH < 7. The solution was then heated to 80°C and the fabric was immersed in the solution with gentle agitation. The fabrics underwent stripping treatments according to three different methods, Table 5.2. The *first method* was a one-step pH method where the sample was subjected to a stripping treatment for 30 minutes without adjustment of the pH of the stripping liquor so that the treatment was performed in acidic pH conditions. The *second method* was a 2-step pH stripping treatment where the fabric was subjected to the treatment for 60 minutes under the before mentioned acidic conditions. This ‘’acidic stripping’’ step was followed by the gradual addition of an aqueous NaOH solution to adjust the stripping liquor pH to pH 10-11. The fabric was then left for the for another 60 with gentle agitation for the ‘’alkaline stripping’’ step. The *third method* involved treating the sample under the stated acidic and alkaline persulphate conditions, followed by a washing treatment for 30min according to the ISO 105 C09 standard. For all methods, after the stripping treatment all fabrics were rinsed under a cold running tap for 5 minutes and left to airdry at room temperature with a relative humidity of 65%.

Table 5.2 Method variables for stripping using potassium persulphate solution

Stripping method	Treatment
1-step pH	30 min pH <7
2-step pH	60 min pH <7 → 60 min pH >10
2-step pH + C09	60 min pH <7 → 60 min pH >10 → C09 washed

5.3.2 Effect of Kybreak™ 500 as a ‘’Stripping Agent’’

Kybreak™ 500 is an oxidising product specifically formulated for re-pulping of paper and paperboard that have been treated with wet strength resins such as Kymene™ or Hercosett™. The re-pulping aid comprises a potassium persulphate mixture, Table 5.3, with the main component being pentapotassium bis(peroxymonosulphate) bis(sulphate), Figure 5.2.

The degradation solution was prepared by heating 70 ml distilled water (fabric to liquor ratio 1:100) up to 70°C. Following the recommendations of the supplier, after reaching the appropriate temperature, the pH of the water was adjusted to pH 10-11 prior to dissolving 2.1 g (3% w/v) Kybreak™ 500.

Table 5.3 Kybreak™ 500 hazardous components

Chemical Components	CAS Number	Concentration (%)
Pentapotassium bis(peroxymonosulphate) bis(sulphate)	70693-62-8	>= 80 - <90
Dipotassium peroxodisulphate; potassium persulphate	7727-21-1	>= 3 - <5
Tetra[carbonato(2-)]dihydroxypentamagnesium	7760-50-1	>= 1 - < 2.5

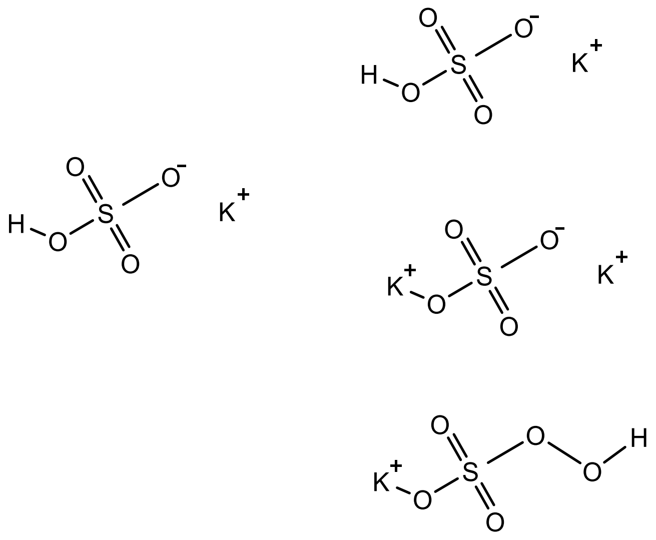


Figure 5.2 Kybreak™ 500 main component: pentapotassium bis(peroxymonosulphate) bis(sulphate) (National Centre for Biotechnology Information n.d.)

Based on the weight difference of cotton fabrics before and after padding, calculated as described before and using Equation 5.1, the padded fabrics contained approximately 6% omf PAEP. Kybreak is designed for commercial purpose as a cellulose re-pulping aid, with a recommended concentration by the supplier of 1-3% w/v. In this recommendation no reference was made towards the quantity of wet-strength resin in the pulp material. A range of PAE dosages have been proposed in a number of published works (Stratton 1991; Andreasson, Forsström and Wågberg 2005; Obokata and Isogai 2007; Siqueira 2012). In the current work calculations of the amount of Kybreak added to the stripping solutions were based on the work carried out by Siqueira, with a PAE addition of ≤ 1% omf. Therefore, the context of this work was based on the assumption that the 1-3% omf Kybreak suggested by the supplier is applied to fabrics containing a 1% PAE based on dry fibre weight. Furthermore, it needs to be taken into consideration that the application of Kybreak on cellulose pulp has an increased accessibility of the chemical to the fibrous material in comparison to application of Kybreak onto fabric material. With the prepared fabric in the current work containing approximately six times more of PAE content and considering that the oxidising agent is applied to woven fabrics, it was assumed that a minimum of 18% omf Kybreak is required to successfully remove the PAE/pigment from the cotton fabrics. Trials started with a high stripping liquor concentration, to establish a starting point from whereon reductions could be made to find the appropriate concentration required. The experiments started with using 318% omf of Kybreak as a stripping agent, which was calculated to be equal to 30 g/L. The ratio of fabric to solution was kept similar as with the trials using potassium persulphate as a stripping agent: ~1:100. The fabrics were treated for 30, 60 and 120 minutes, followed by rinsing in distilled water and washing according to ISO 105 C09 laundering standard, Table 5.4.

Table 5.4 Method variables for stripping using Kybreak™ 500 solution

Stripping method
70°C, 30 minutes → C09 washed
70°C, 60 minutes → C09 washed
70°C, 120 minutes → C09 washed

5.4 Results & Discussion

5.4.1 PAE Film Formation

After heating the PAE solution on the slides, the dried PAE films were removed from the oven. The resulting films were then rinsed with slight agitation in distilled water. It was observed that the films prepared without the addition of Na_2CO_3 broke apart during rinsing. However, the fragments remained insoluble in the rinsing water, suggesting that crosslinking has successfully occurred. Further analysis was carried out on the films prepared with the addition of Na_2CO_3, Figure 5.3.

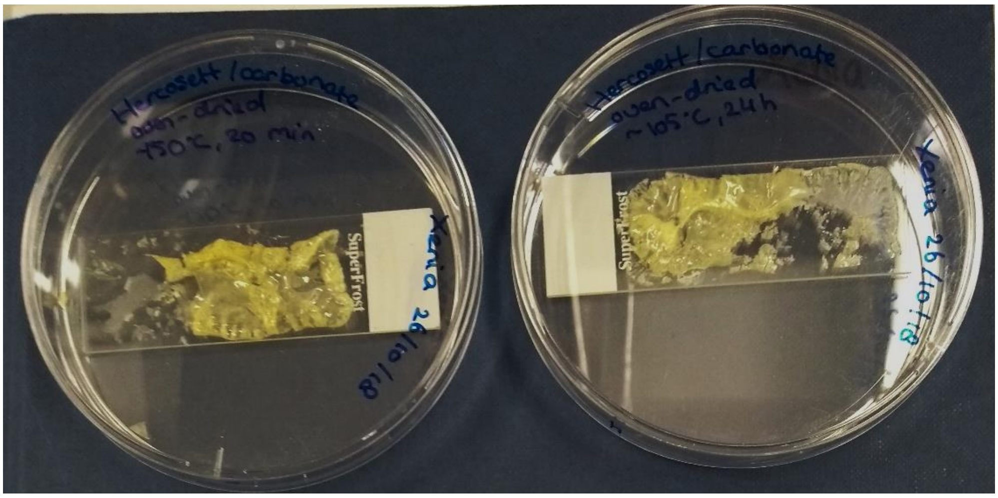


Figure 5.3 Visual appearance of PAE films after rinsing, with film dried at 150°C for 20 minutes (left) and film dried at 105°C for 24 hours (right), prepared with the addition of Na_2CO_3

Figure 5.4 shows the SEM images of PAE film samples prepared with the addition of Na_2CO_3 at temperatures of 150°C and 105°C, respectively. The images were captured prior to degradation experiments. For both films the surface initially appears smooth, apart from slight indentation possibly from air bubbles created from evaporation of water during film formation in the oven. At higher magnification a pattern becomes visible of what appears to be ruptures in the surface of the films. SEM images of the edges of the films show that these holes appear to be present throughout the thickness of the film. The PAE film prepared at 150°C for a duration of 20 minutes additionally shows rod-shaped structures, potentially suggesting the formation of initial crystallites.

Figure 5.5 shows SEM images of film ruptures of differing dimensions but it can be discounted that they are a result from washing out of sodium carbonate particles, as the measured dimensions of the ruptures vary from 0.2 - 7µm, whereas the particle size for sodium carbonate generally falls within the range of 90-120 µm (light sodium carbonate) or 250-400 µm (dense sodium carbonate) (HERA 2005). Size measurements were not taken of all the ruptures in the films, but these few measurements are suggested to be an appropriate indication of the range of dimensions. A possible explanation could be that the ruptures are a result of drying of the film in the ventilated oven or from placement of the films in a vacuum environment for SEM analysis. In these situations, water is rapidly evaporated off, causing contraction of the polymer, causing ruptures in the film and potentially in the form of these odd shapes.

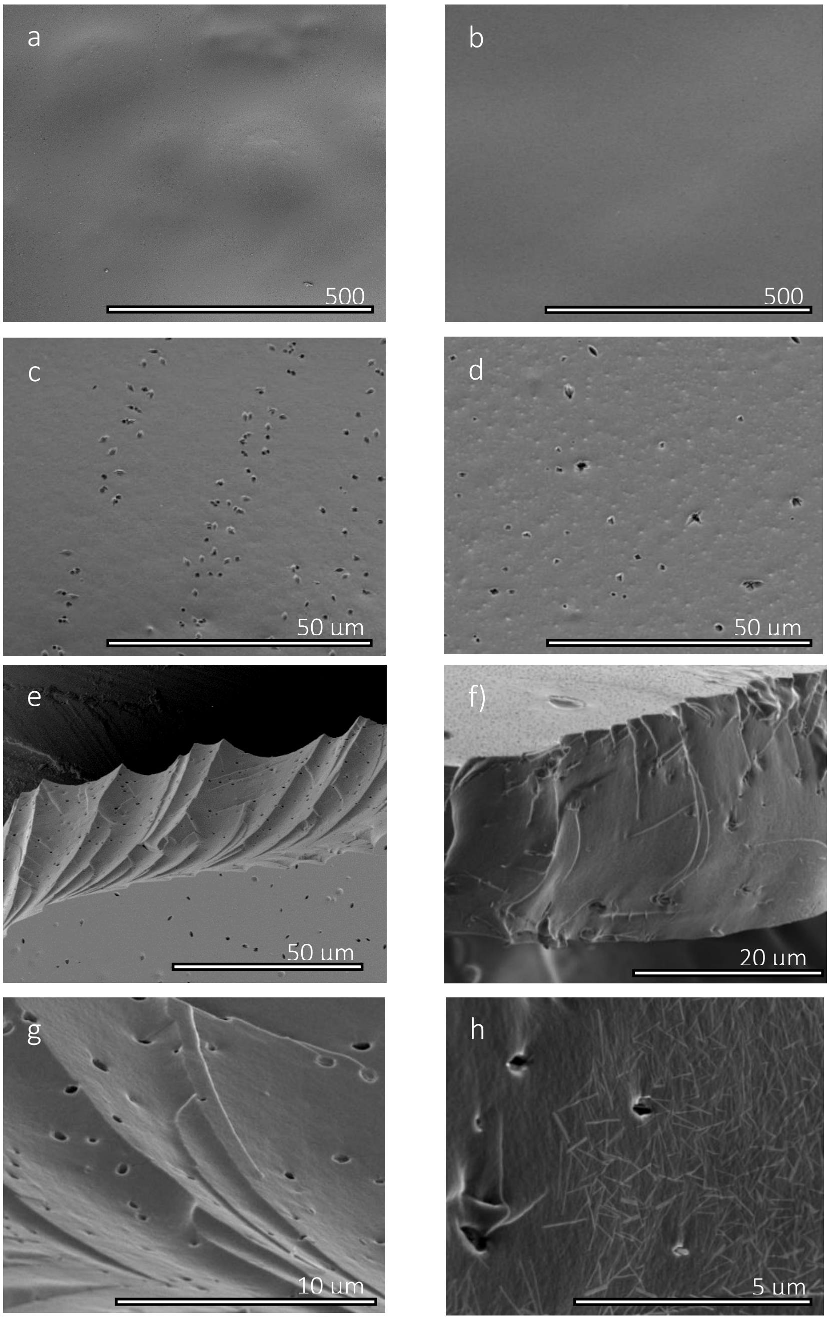


Figure 5.4 SEM images of film samples 150°C (left column) and 105°C (right column) with: a) mag x100, b) mag x100, c) mag x1,000, d) mag x1,000, e) mag x1,000, f) mag x2,000, g) mag x 5,000 and h) mag x10,000

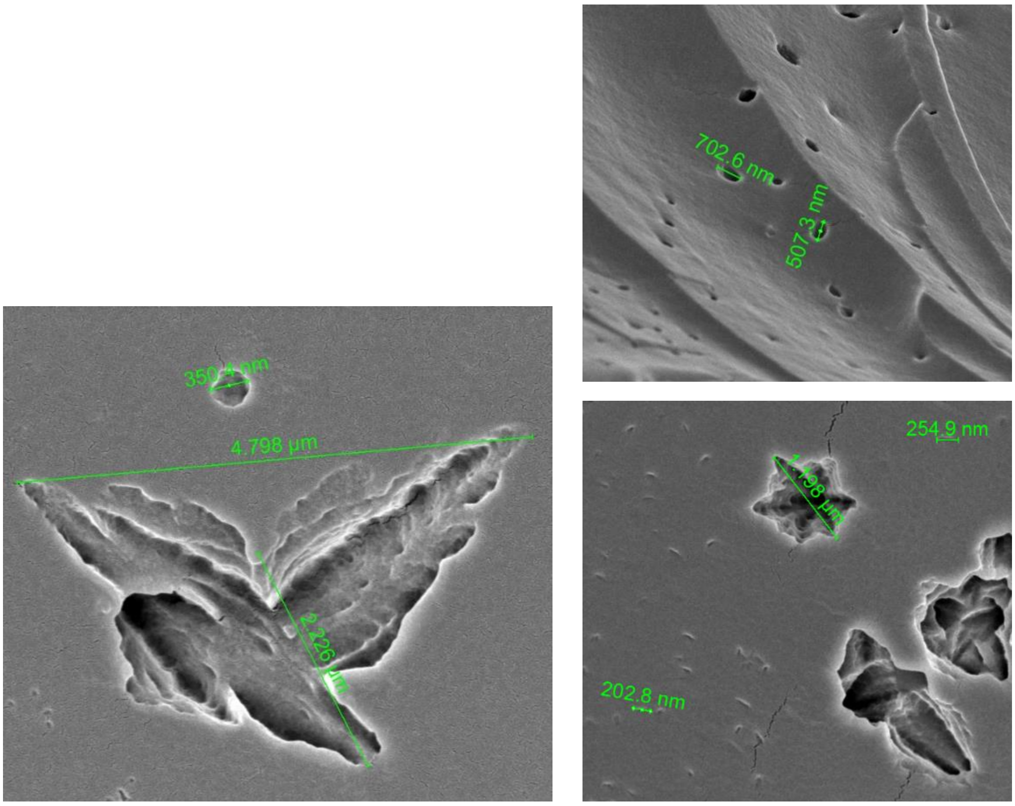


Figure 5.5 SEM size measurement of ruptures observed in various PAE films

The FT-IR spectra for the polymer isolated from the PAE solution and for the heated PAE film are shown in Figure 5.6 and Figure 5.7, respectively. The broad peak around 3100-3500 cm^{-1} for the polymer film could be assigned to the secondary amide N-H stretch vibration. This could be potentially be overlapped by the -OH stretch in the isolated polymer for the presence of water, as the isolated polymer may not have been completely dry. Additionally, the strong broad signal could correlate to the carboxylic acid O-H stretch vibration. The signals found at ~1640 cm^{-1}, and ~1552 cm^{-1} for the isolated polymer and ~1634 cm^{-1}, ~1532 cm^{-1} for the polymer film, correlate to the secondary amide C=O stretching vibration. In accordance with findings by Siqueira, heating of the PAE resulted in an increase of transmittance around 1240 cm^{-1} (amide III Band) correlating to C–N stretching vibrations of tertiary amine groups and C–O stretching vibrations of secondary alcohols (2-propanol bridges) (Siqueira, 2012). This suggests the confirmation of the expected main crosslinking reaction of 2-propanol bridge formation. Additionally, a slight reduction of transmittance around 1060 cm^{-1} might may be due to the AZR functionality.

The formation of ester bonds between the carboxyl end groups on the polymer chain and AZR groups has been discussed before with an association with bands around 1730 cm^{-1} for CO stretching vibrations of the ester groups (Obokata and Isogai 2007; Siqueira 2012). In the current work, the FTIR spectrum for unheated isolated PAE shows a transmittance peak around 1702 cm^{-1}. This peak is only present in the form of a weak signal observed around 1740 cm^{-1}. Therefore, FT-IR was not useful for the confirmation of the secondary crosslinking reaction in the form of ester bond formation.

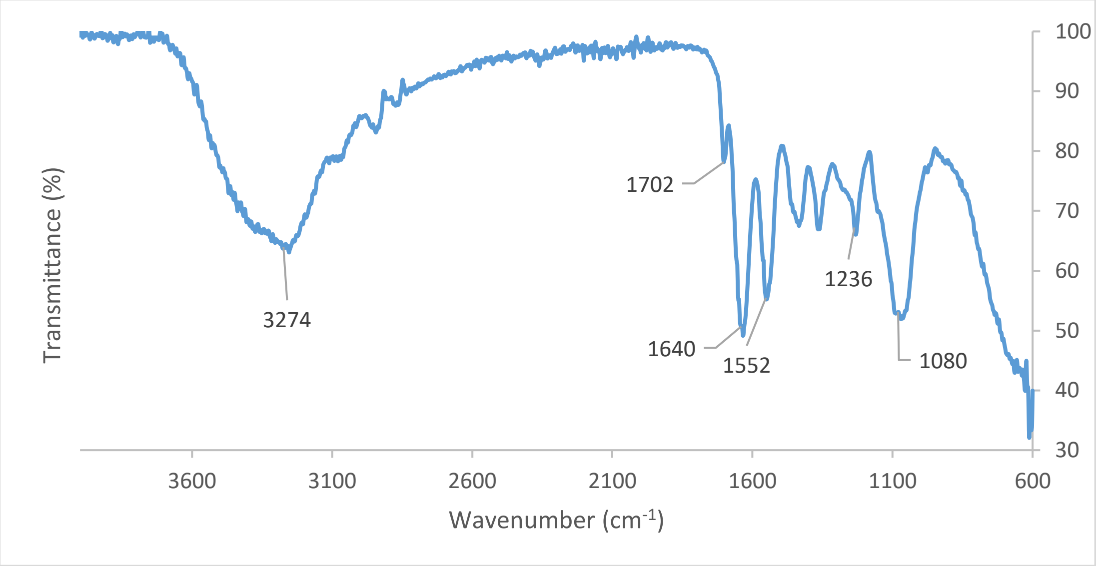


Figure 5.6 FT-IR spectrum of the polymer isolated from Hercosett™ 617 solution

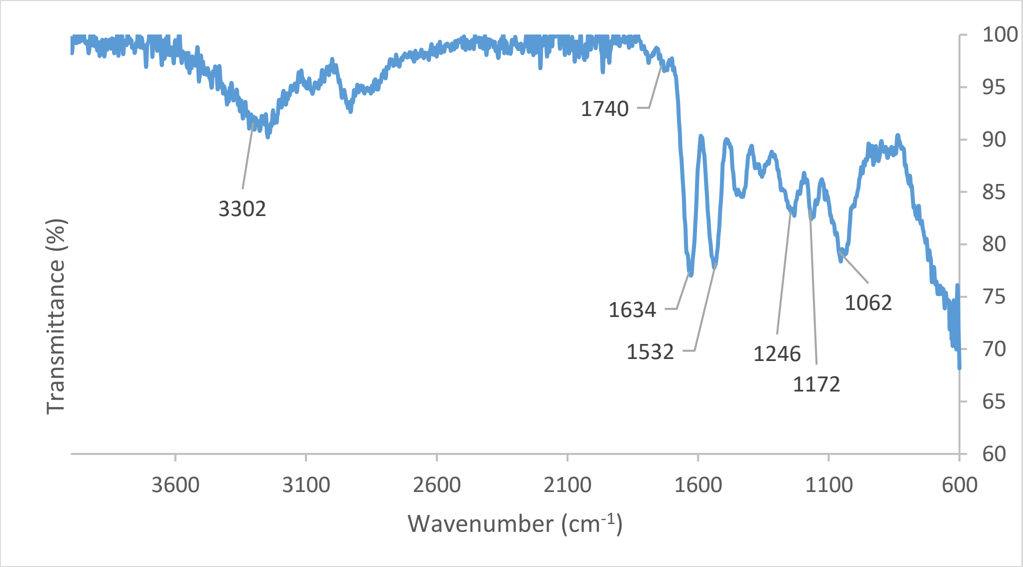


Figure 5.7 FT-IR spectrum of the Hercosett™ 617 polymer film prepared at 105°C

5.4.2 Fixation of the PAE/Pigment Formulation on Cotton Fabric

During the preparation of the cotton fabrics, the two-step drying and curing method ensured evaporation of the water content in the wet fabric to facilitate crosslinking of the PAE and minimising the migration of water-soluble species. It is expected that the polymer would act as a binder for pigment colouration, by enveloping the pigments and facilitate the fixation of the coloured particles by conformal coating of the fibre surface. The fixation of the pigments therefore relies on the binder properties. In order to assess the expected PAE crosslinking and fixation of the PAE/pigment formulation on cotton, the PAE/pigment-padded cotton fabrics were subjected to wash fastness tests as described in chapter section 3.3. Only a slight increase in lightness L* from 55.5 to 56.0 and decrease of K/S at λ_{max} (400nm) from 2.54 to 2.37 was observed, suggesting that little to no colour removal occurred after ISO 105 C09 washing (Figure 5.8).

The slight change in colour strength and lightness are most likely a result of washing off of a small portion of PAE/pigment from the fabric surface which was not fixed.

These results suggest that the PAE is suitable as a binder as it facilitated fixation of the coloured pigments onto cotton fabrics to obtain excellent colour fastness to washing.

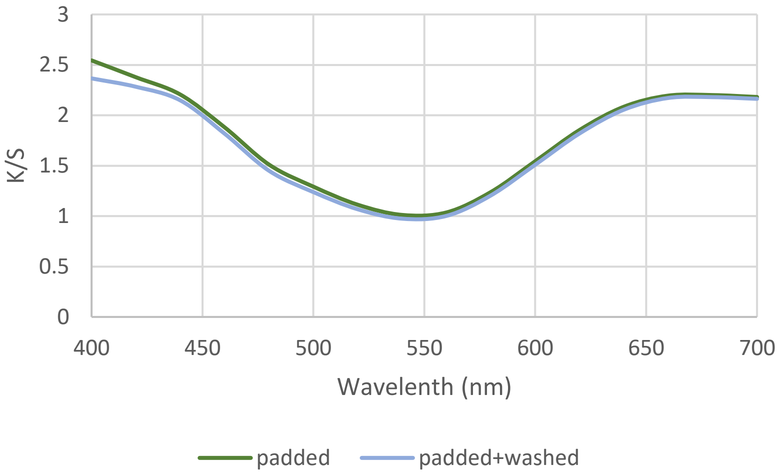


Figure 5.8 Colour strength K/S of PAE/pigment-padded cotton fabrics before and after ISO 105 C09 washing

It was not possible to obtain an FT-IR spectrum of the green PAE/pigment-padded cotton, probably due to the absorption of the pigment on the surface. For this reason, further FT-IR analyses were limited to cotton fabric padded with only the PAE and 20 g/L sodium carbonate. Figure 5.9 shows the FT-IR spectra of untreated cotton and PAE/pigment-padded cotton before and after washing, respectively. For untreated cotton typical signals are found at ~3306 cm^{-1} for O-H stretching (intermolecular hydrogen bonds) vibrations, at ~2886 cm^{-1} and ~1436 cm^{-1} for CH_2 asymmetric stretching and symmetric deformation or scissoring, ~1324 cm^{-1} for C-H bending, at ~1152 cm^{-1} for antisymmetric bridge C-O-C stretching, at ~1112 cm^{-1} for asymmetric ring stretching mode and finally at ~1020 cm^{-1} for C-O and/or C-C stretching (Abidi et al, 2008). It was observed that for the PAE-padded cotton fabric additional signals were present at ~1640 cm^{-1} and ~1540 cm^{-1}, Figure 5.9. These signals were not clearly present in the spectrum of the untreated cotton, suggesting that they correlate to the secondary amide, earlier observed in the FT-IR spectra of PAE. The same signals are observed in the FT-IR spectra of both PAE-padded cotton and PAE/pigment-padded cotton fabric, Figure 5.10, after washing, suggesting that the PAE remains present on the cotton fabric even after multiple laundering cycles.

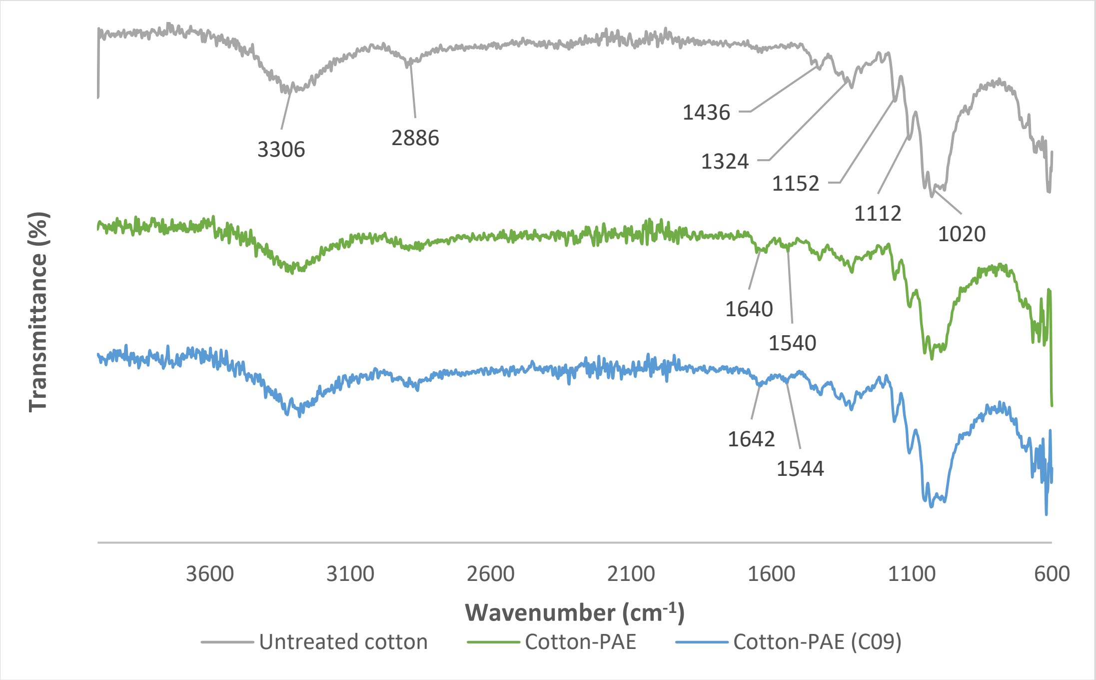


Figure 5.9 FT-IR spectra of untreated cotton fabric (top), cotton-PAE before (middle) and after ISO 105 C09 washing (bottom)

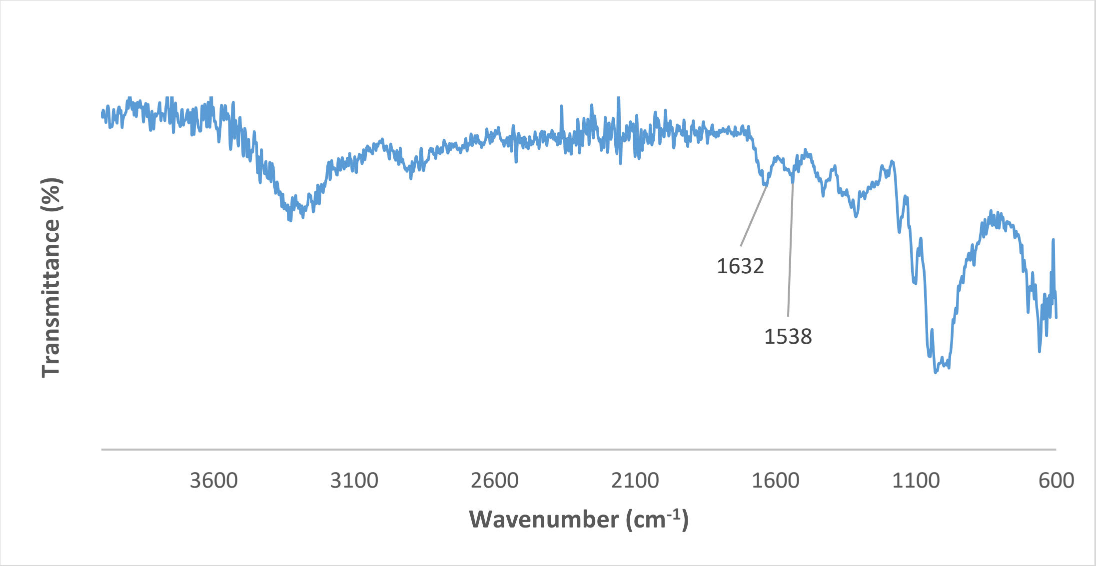


Figure 5.10 FT-IR spectrum of PAE/pigment-padded cotton after ISO 105 C09 washing

5.4.3 Stripping of the PAE/Pigment Formulation from Cotton Fabric

5.4.3.1 Effect of Potassium Persulphate

Table 5.5 shows the results of initial tests with potassium persulphate as a potential stripping agent to remove the PAE/pigment formulation from cotton fabrics. The stripped samples have all been treated with a 2.75% w/v potassium persulphate solution. One sample was subjected to a 1-step alkali treatment for 30 minutes without adjustment of the pH (pH 5-6). Another sample was treated for 60 minutes without adjustment of the pH (pH 5-6), then NaOH was added for a subsequent treatment stage at alkaline pH (pH >12) for 60 minutes. A third sample was treated with the same 2-step pH treatment followed by a washing treatment for 30min according to ISO 105-C09 standard. Colour strength K/S was calculated using the maximum spectral absorbance of K/S λ_{max} at 400 nm. Colour difference ΔE was calculated by the Datacolor software with white cotton as a standard.

Table 5.5 The effect of potassium persulphate on PAE/pigment-padded cotton fabric colour (ΔE relative to white cotton fabric)

Treatment		K/S	ΔE	L*
PAE/pigment-padded cotton, ISO 105 C09 washed		1.3	31.6	65.2
1-step pH		3.7	46.1	47.6
2-step pH		0.4	16.0	82.2
2-step pH + C09		0.2	11.5	87.8

The 1-step persulphate treatment in acidic conditions appears to have darkened the colour of the fabric. This could be explained by the treatment conditions affecting the PAE and/or the pigment. It is possible that oxidation of the ferric complex in Pigment Green 8 is modified forming organic complexes or inorganic oxides. The 2-step acid-alkali treatment produced clear fading of the colour with the fabric appearance after stripping showing uneven white and green patches. The 2-step pH treatment followed by a ISO 105 C09-based washing cycle showed that the added washing was effective as more colour appeared to have been removed. After washing, K/S was reduced from 0.4 to 0.2, ΔE was reduced from 16.0 to 11.5 and L* had increased from 82.2 to 87.8.

5.4.3.2 Effect of Kybreak

Table 5.6 shows the cotton fabrics before and after stripping treatment at various processing times with Kybreak™ 500 as a stripping agent. In contrast to using potassium persulphate, Kybreak allowed a more efficient colour removal, after only 30 minutes of the stripping treatment. Increasing the treatment time resulted in further decrease in colour difference and an increase in the lightness of the fabrics. This method of stripping showed excellent potential and appears to be more efficient as method for the removal of PAE/pigment formulation from cotton fabrics in comparison to using potassium persulphate as a stripping agent. The pH of the stripping liquor recorded at the end of the treatment cycle was pH <2 in all cases, therefore it was assumed that the degradation treatment was mostly run under acidic conditions It is suggested that the efficiency of stripping could be contributed to the high concentration of the oxidising agent in the stripping liquor and Kybreak being specifically formulated for the degradation of PAE as well as the acidic pH conditions. PAE is a neutral/alkaline curing resin which is most stable at acidic conditions. Thus, it could be proposed that degradation of PAE was mainly facilitated by the pH of the Kybreak solution as well as the oxidising agent, aided by appropriate elevated temperature, agitation and time for the oxidising agent to diffuse towards the coated fibre surface, for the degradation of PAE to occur.

Table 5.6 The effect of Kybreak™ 500 on PAE/pigment-padded cotton fabric colour (ΔE relative to white cotton fabric)

Treatment time		K/S	ΔE	L*
PAE/pigment cotton, ISO 105 C09 washed		1.3	31.6	65.2
30 mins		0.1	3.3	91.0
60 mins		0.1	3.2	91.1
120 mins		0.1	2.5	91.8

5.5 Conclusions

Heat drying of the PAE solution on glass slides resulted in film formation. The films prepared with the addition of sodium carbonate appeared more mechanically robust and remained intact after gentle rinsing in distilled water, suggesting that the addition of sodium carbonate facilitated a more efficient crosslinking of the polymer. SEM analysis supported the successful formation of the films. Rupture patterns were observed in the films, which could be due to rapid evaporation of the water content and rapid contraction of the solid substance during film formation in the oven.

Fixation of the green pigmented PAE formulation on cotton fabrics was successful and showed by excellent colour fastness to ISO 105-C09 laundering. Additionally, the

FT-IR spectrum of the washed PAE/pigment-padded cotton showed signals correlating to the PAE on the fabric.

Kybreak™ 500 showed excellent potential as a stripping agent for the removal of PAE/pigment from cotton fabrics as the treatment allowed the recovery of white fabrics. The Kybreak treatment used a high concentration of the stripping agent in the stripping liquor but reflects the relatively high add-on of the PAE/pigment formulation. Further investigation into the efficiency of the stripping agent at lower concentration is required from an economical and environmental perspective in order to apply this method at an industrial scale. Additionally, the method involved an aftertreatment comprising a washing procedure based on ISO 105 C09 which includes the use of the low-temperature bleaching agent TAED. Due to the presence of TAED, the PAE/pigment removal and the resulting white fabric cannot be fully attributed to the Kybreak treatment. The ISO 105 C09 laundering cycle is also not a viable treatment, when considering the method to be applied at an industrial scale and much simpler after-washing procedures can be employed. Further investigation is required to assess the recovery of white cotton fibres with alternative aftertreatment methods following the stripping treatment.

Chapter 6 – Investigation into the Effectiveness and Action of Kybreak™ on Pigment Stripping from Cotton Fabric

The work described in this chapter is a more in-depth investigation into the ‘’stripping’’ of the polyamide epichlorohydrin (PAE)/pigment formulation from cotton fabrics using Kybreak™, following the work described in chapter 5. In particular studying the effect of the process factors such as liquor pH, -concentration and aftertreatments on the stripping efficiency.

6.1 Materials

Hercosett™ 617 and Kybreak™ 500 were kindly supplied by Solenis and Pigment Green B (C.I. Pigment Green 8) was provided by Albion Colours, Leeds UK. Sodium carbonate anhydrous (Riedel-de Haën), tetra-acetylethylenediamine (SDC Enterprises), sodium perborate tetrahydrate (Honeywell), ECE non-phosphate reference detergent base powder without optical brightener (SDC Enterprises), Hostapal NIN (Clariant), Uniperol Bleach IT (BASF), commercial cationic fabric softener (Easy), sodium hydroxide (≥ 98%, Sigma Aldrich) and hydrochloric acid (≥ 37%, Sigma Aldrich) were used as supplied. All reagents were of analytical grade. All solutions were prepared with the use of distilled water. Plain woven cotton fabric (100%, bleached only, no optical brightening agent, 142.8 g/m^2) was supplied by Phoenix Calico Limited, Denby Dale, UK was used throughout this study.

6.2 Optimisation of the Process Variables

6.2.1 pH of the ‘’Stripping’’ Liquor

Re-pulping and bleaching efficiency of the stripping agent Kybreak™ 500 is most efficient at a temperature of 60-70°C and pH 10-11 (Solenis 2014a). Initial stripping experiments, as described in chapter 5 were carried out at 70°C, with an initial pH of

10-11 before the addition of the required amount of the stripping agent. The pH of the stripping liquor recorded at the end of the treatment cycle was pH <2 in all cases, therefore it was assumed that the treatment was mostly run under acidic conditions.

Here the effect of an alkaline environment for the stripping treatment was observed by running the treatment as followed: water was heated up to 70°C, followed by addition of Kybreak™. The pH of the solution was then adjusted to 10-11 and run for the required time. The pH was recorded afterwards, confirming that the treatment maintained an alkaline pH throughout. The fabric was then removed from the stripping bath and washed according to the ISO 105 C09 standard before leaving to air-dry at room temperature.

6.2.2 Kybreak™ Concentration and Treatment Time

The aim of the work was not just to establish a method that is effective in the removal of the PAE/pigment formulation from cotton fabric, but to also to aim at achieving this with the lowest possible amount of chemicals and shortest possible treatment time and an appropriate aftertreatment. The aim was to lower the processing time and the stripping liquor concentration where possible and minimise effluent management, effect on cellulose structure and cotton handle, and overall cost.

For re-pulping of paper, the concentration of Kybreak™ 500 in the liquor is generally 1-3% based on dry fibre weight. In this work the initial stripping experiments used a high concentration of the stripping agent (318% omf, 30 g/L) for 120 minutes. Here the aim was to achieve a large reduction in the concentration of the stripping agent in the stripping liquor, as well as looking at the potential of reducing the stripping treatment time to increase cost and time efficiency in the final industrial application. Table 6.1 shows the variables used in optimisation of the stripping liquor concentration.

Table 6.1 Overview of Kybreak™ 500 stripping liquor concentration and treatment times

Kybreak™ Concentration		Processing Time (minutes)	
g/L	% on mass of fabric		
30	~ 318	60	120
10	~ 106	60	120
5	~ 53	60	120
2.5	~ 26	60	120
1.25	~ 13	60	120
0.63	~ 6.6	60	120

6.2.3 Aftertreatment

6.2.3.1 Effect of ISO 105-C09 (no TAED) Treatment on Pre-Kybreak Treated PAE/Pigment-Padded Cotton

Initial tests were carried out followed by ISO 105 C09 laundering including the low temperature bleach activator TAED. In this study same laundering conditions were applied, but without the addition of TAED to the washing liquor. The aftertreatment liquor was prepared by dissolving 12 g/L sodium perborate tetrahydrate and 10 g/L ECE non-phosphate reference detergent (without optical brightening agent) in distilled water with a fibre to liquor ratio of 1:100. The mixture was then heated to the required temperature and added to the washing tubes along with the fabrics. After the aftertreatment cycle, the fabrics were removed from the washing liquor and first rinsed in distilled water, followed by rinsing under a running cold tap. Excess water was squeezed out by hand. The fabrics were sandwiched within paper towels and left to dry at ambient conditions.

6.2.3.2 Effect of Reductive Bleaching Treatment on Pre-Kybreak treated PAE/Pigment Padded Cotton

From an industrial point of view, it needs to be considered that the method of stripping and after-treatment should be easily integrated with existing manufacturing facilities and equipment. Bleaching is one of the stages in the preparation of textiles, used for the decolorisation of the fabrics, fibres and yarns to remove the natural fibre colour and obtain white fibres for further processing. For integration of the colour removal stage, bleaching is therefore seen as a logical alternative after-treatment following stripping of the PAE/pigment formulation. Reductive bleaching using sodium dithionite is known to be efficient in decolorisation processing (Fišerová et al, 2018; Bigambo et al, 2019). A reductive bleaching process was carried out using Uniperol® Bleach IT as the bleaching agent. It is a stabilised formulation, based on sodium dithionite, without optical brightener, and used on wool, silk, polyamide and cellulose. Bleach IT reductively modifies chromophores rendering them colourless and water-soluble. Colour stripping tests were carried out on fabric samples with small surface area (~5x10cm), and large surface area (~20x20cm) dimensions for preparation of the Kawabata analysis. The process for the ʻʻsmallʼʼ fabrics was carried out in a beaker with a hotplate stirrer set-up and using a temperature probe to ensure constant temperature control. Stripping of the larger samples was carried out using appropriate machinery to facilitate agitation. The equipment used was a Mathis IR dyeing machine or a James Heal Gyrowash.

The after-treatment liquor was prepared by heating distilled water (fabric to liquor ratio 1:50) to 70°C, before addition of 3 g/L Bleach IT. For the ʻʻsmallʼʼ samples, the stripped fabric was left to stir in the after-treatment solution for 30 minutes. For the larger samples, after preparation, the after-treatment liquor was added to the tubes followed by the fabrics. The tubes were then placed inside the equipment and left to run for 30 minutes. After the treatment the fabrics were removed and twice over rinsed with distilled water at 60°C for 10 minutes each time, followed by once rinsing under a cold running tap to ensure removal of any PAE/Pigment and chemicals present on the fabrics. Excess water was squeezed out by hand. The fabrics were sandwiched within paper towels to absorb any residual moisture and then left to air-dry at ambient conditions.

6.2.3.3 Effect of Sequential Reductive Bleaching/Soaping Treatment on Kybreak treated PAE/Pigment-Padded Cotton

Additionally, a combination of reductive bleaching and soaping was tested as an alternative after-treatment method. After bleaching, the fabrics were removed from the liquor and rinsed at 60°C for 10 minutes, followed by rinsing under a running tap before immersion into the soaping liquor. The soaping liquor was prepared by dissolving 2 g/L sodium carbonate and 2 g/L Hostapal NIN in distilled water (fabric to liquor ratio 1:100). The solution was then heated to 60°C, followed by addition of the fabric and was stirred for 30 minutes. After the treatment the fabrics were removed and rinsed under a cold running tap. Excess water was squeezed out by hand. The fabrics were sandwiched within paper towels to absorb any residual moisture and then left to dry at room temperature. Table 6.2 shows an overview of the treatments tested following the Kybreak stripping treatment.

Table 6.2 Overview of aftertreatments following Kybreak™ stripping treatment

Aftertreatment	Agents	Temperature	Time
ISO 105 C09 (no TAED)	Sodium perborate + ECE non-phosphate reference detergent without OBA	60°C; 60°C + steel balls; 70°C	30 min
Reductive bleaching	Bleach IT	70°C	30 min
Reductive bleaching + Soaping	Bleach IT → Na_2CO_3 + Hostapal NIN	70°C + 60°C	30 min → 30 min

6.3 Handle Assessment

The Kawabata Evaluation System for Fabrics (KES-F) testing was used to assess the effects of stripping treatments and aftertreatments on the ′′handle′′ of the cotton fabrics. Several fabrics were also prepared with the incorporation of a commercial cationic softener (Easy) into the padding liquor, with the aim to reduce the effect of the binder on the fabric mechanical properties. The stiffness or softness of a binder-treated fabric is determined by the nature of the binder material but can be modified by the incorporation of a softener into the pigment formulation (AATCC 1995). The expected mechanism of the cationic softener is for the positively charged surfactant ions to be drawn towards the negatively charged fibres and stick to them, lubricating the fibres in the yarns and therefor the yarns in the fabric and making the fabric feel softer and more flexible (Juodsnukyte, Gutauskas, Krauledas 2005). The padding liquor was prepared by dispersing 10 g/L of the pigment, 20 g/L sodium carbonate and 0.5 g/L cationic softener using a homogeniser in 400 g of the PAE solution, without further dilution for a minimum of 10 minutes. The pad liquor is used immediately following dispersion of the pigment. Table 6.3 lists the fabric samples tested and a list of their preparation steps. In addition to green PAE/pigment padded cotton fabrics, various untreated cotton fabrics were also subjected to KES-F testing, including: untreated cotton, untreated/C09 washed cotton and blank padded/C09 washed/Kybreak™ treated/Reductive bleached + soaped cotton fabrics. Furthermore, green PAE/pigment cotton fabric samples prepared with a commercial cationic softener was were also tested.

The pre-conditioned fabric samples (20x20cm) were assessed using the FB1 tensile and shearing system and FB2 bending system along both warp and weft direction. For comparison of the tensile, shearing and being properties of the fabrics, the data obtained for warp and weft was averaged per fabric property. Tensile testing involved extension (up to 500 gf.cm/cm^2) along the required direction of the fabric samples, producing a load-extension hysteresis from which a number of parameters could be derived. The most relevant parameter selected from this data was

Table 6.3 Overview of KES-F cotton test fabrics and related process steps

Cotton Fabric Preparation				‘’Stripping’’	Aftertreatment	
Fabric treatment	PAE/pigment padded	Softener	C09 washed	Kybreak™ Application	C09 (no TAED)	Reductive Bleach/Soap
Untreated	X	X	X	X	X	X
Untreated	X	X	√	X	X	X
Untreated	X	X	√	2.5 g/L, 60 mins	X	√
Padded	√	X	X	X	X	X
Padded	√	X	√	X	X	X
Padded	√	X	√	2.5 g/L, 60 mins	X	X
Padded	√	X	√	2.5 g/L, 60 mins	X	√
Padded	√	X	√	2.5 g/L, 60 mins	√	X
Padded	√	X	√	1.25 g/L, 120 mins	X	X
Padded	√	X	√	1.25 g/L, 120 mins	X	√
Padded	√	X	√	1.25 g/L, 120 mins	√	X
Padded	√	√	X	X	X	X
Padded	√	√	√	X	X	X
Padded	√	√	√	2.5 g/L, 60 mins	X	X
Padded	√	√	√	2.5 g/L, 60 mins	X	√

extensibility (EMT), the percentage of extension at the maximum applied load. Using the same equipment, a rate of shear strain (8.34×10^{-3}/sec) was applied to the fabric samples under a constant extension load (10 gf/cm) up to a maximum shear angle of 8°. This produced a shear force/shear angle hysteresis curve from which a number of parameters could be derived. The selected relevant parameters were shear rigidity

(G), hysteresis of shear force or shear stress at a shearing angle of 5° (2HG5). Bending testing involved the deformation of the fabric samples due to applied bending movement between the curvatures of -2.5 and 2.5 cm^{-1}. The resulting data was given in the form of a bending hysteresis curve, from which the parameters bending rigidity (B) and hysteresis of bending moment, measured at a curvature of 0.5 cm^{-1} (2HB) were selected for comparison of the fabrics.

6.4 Results & Discussion

6.4.1 Stripping the PAE/Pigment Formulation from ''Small'' Cotton Fabrics

Figure 6.1 and Figure 6.2 respectively show the images and colorimetric data for PAE/pigment-padded cotton fabrics after padding, after stripping and after ISO 105 C09 washing cycle. Colour strength K/S was calculated at λ_{max} with padded and subsequently washed cotton fabric as a standard with K/S λ_{max} values based on absorption at 400 nm. As the desired result after stripping is the white appearance of untreated cotton, colour difference ΔE was calculated against white cotton as the standard. It was observed that the stripping treatment with 30 g/L Kybreak, affects the colour of the PAE/pigment-padded fabrics. The initial green appearance changes to a darker grey/brown colour after stripping, before removal of the colour through the ISO 105 C09 washing cycle, recovering a white appearance similar to that of the bleached white cotton material. The initial colour change caused by the Kybreak stripping treatment could possibly be explained by the treatment conditions affecting either the fabric, the binder material or the pigment. Reflecting the visual colour change from green to white, both K/S and ΔE also decreased due to the stripping treatment and L* increased.

Padded + C09 washed

Stripped 30 g/L

Stripped + C09 washed

Figure 6.1 Visual appearance of PAE/pigment-padded cotton after padding and ISO 105 C09 washing (left), after stripping (middle) and after sequential stripping/C09 washing (right)

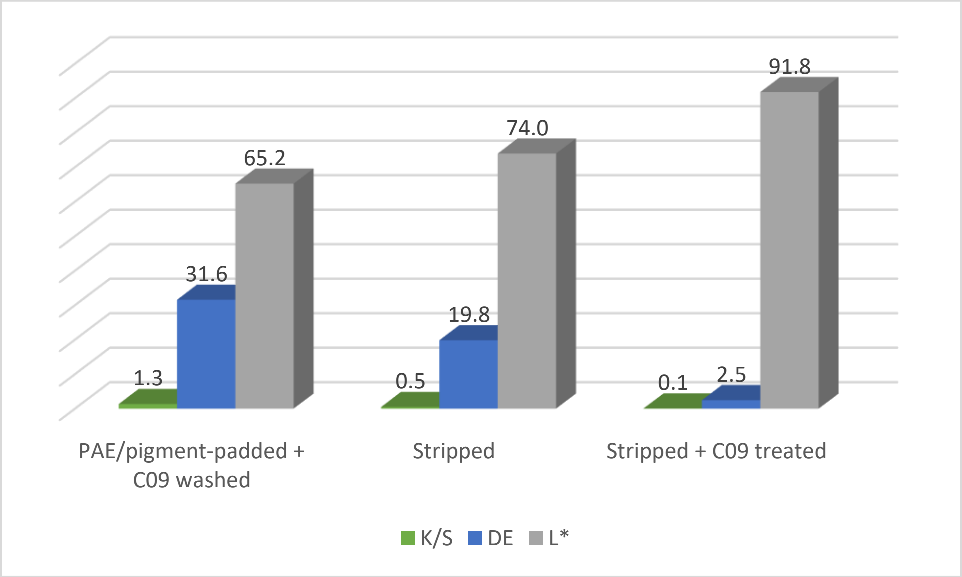


Figure 6.2 Colorimetric data for PAE/pigment-padded cotton fabric after padding and ISO 105 C09 washing, after stripping and after sequential stripping/C09 aftertreatment

In response to these initial stripping tests, the same stripping treatment was carried out on blank padded white cotton fabrics to assess the effect of the treatment on the cotton itself. In comparison to the original white cotton the blank padded and treated fabric showed no yellowing or other colour change. This suggests that the colour change observed after subjecting the green padded cotton fabric to the stripping treatment was a result of the stripping treatment affecting the PAE/pigment present on the fabric.

6.4.1.1 Effect of pH and Kybreak

In Chapter 5 the effect using Kybreak, based on the recommended application conditions, involved stripping of the polymer binder and pigment under acidic conditions. Figure 6.3 shows the effect of the stripping treatment on the colour of the fabrics, carried out in the suggested acidic pH, in alternative alkaline pH and in acidic without the addition of Kybreak.

Cotton-
PAE/pigment
(C09 washed)

Stripped
< pH 3
(with Kybreak)

Stripped
> pH 10
(with Kybreak)

'Stripped'
< pH 3
(no Kybreak)

Figure 6.3 Visual appearance of treated cotton fabrics exhibiting the effect of stripping liquor pH and of ''stripping'' in absence of Kybreak on PAE/pigment-padded cotton

It is clear that the established method involves adjusting of the pH of the water to pH >10 before addition of Kybreak (30 g/L) which then lowers the pH to allow stripping under acidic pH conditions (pH <3). As discussed in Chapter 5, this method results in removal of the green colour and allowing recovery of white cotton fabrics.

An alternative alkaline method involved the dissolution of the stripping agent without prior pH adjustment, resulting in a lowered pH initially (pH 1-2), followed by raising the pH of the aqueous solution (pH 10-11) by addition of diluted NaOH solution. The final pH measured after 120 minutes was pH 9-10. The result of this alkaline stripping treatment, followed by ISO 105 C09 washing treatment, did not result in an efficient removal of the colour. This is shown by the colorimetric values remaining similar to that of the fabric before the alkaline treatment (Figures 6.4-6.6). This suggests that an acidic stripping liquor pH is required for the stripping agent to be effective, supporting the established method of adjusting the pH to alkaline pH prior to addition of the stripping agent.

To observe the effect of the stripping process conditions on PAE/pigment-padded cotton, the padded fabric was additionally subjected to the stripping treatment under the established conditions, but without the addition of the stripping agent. After 120 minutes and subsequent ISO 105 C09 laundering, K/S and ΔE were only slightly reduced and L* was slightly increased. This fading can be a result of the washing process following the stripping treatment which includes a bleach activator. However, the fabric remains green and colorimetric values are not near those of the fabric treated with Kybreak under the same conditions, meaning that treating the PAE/pigment-padded cotton under acidic conditions at 70°C for 120 minutes according to the established method, but without the addition of Kybreak, is not sufficient to remove the PAE/pigment formulation from the fabric.

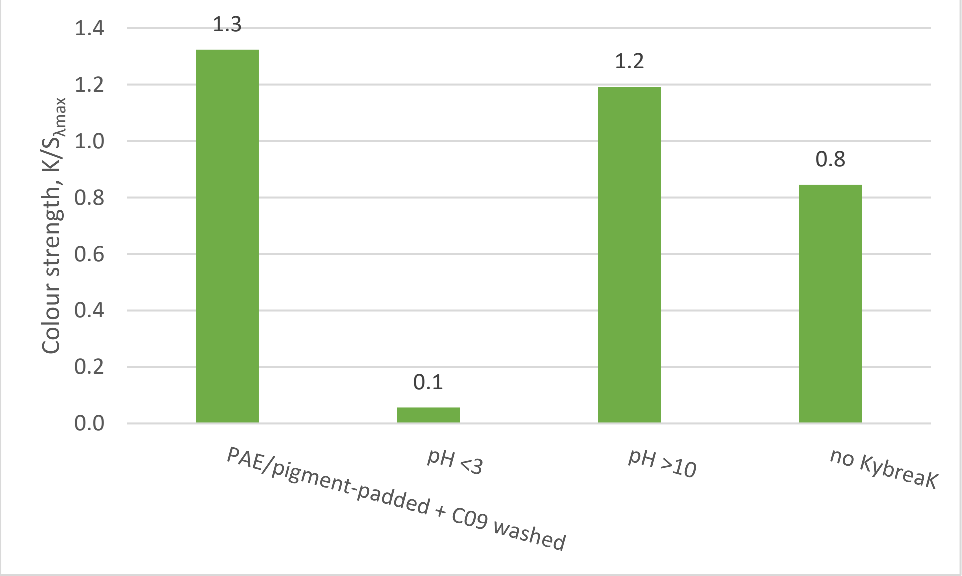


Figure 6.4 K/S values for fabrics treated at different pH or without Kybreak

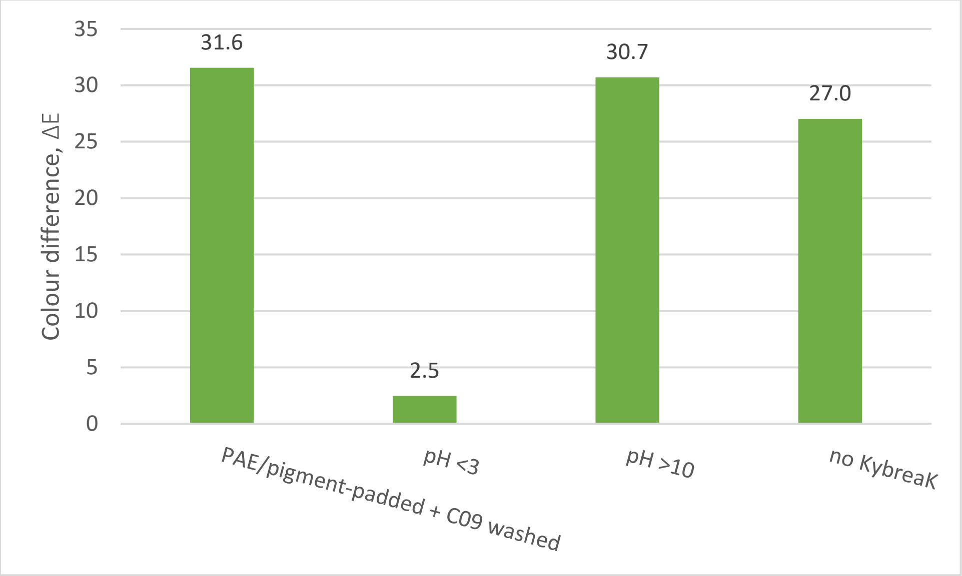


Figure 6.5 ΔE values for fabrics treated at different pH or without Kybreak

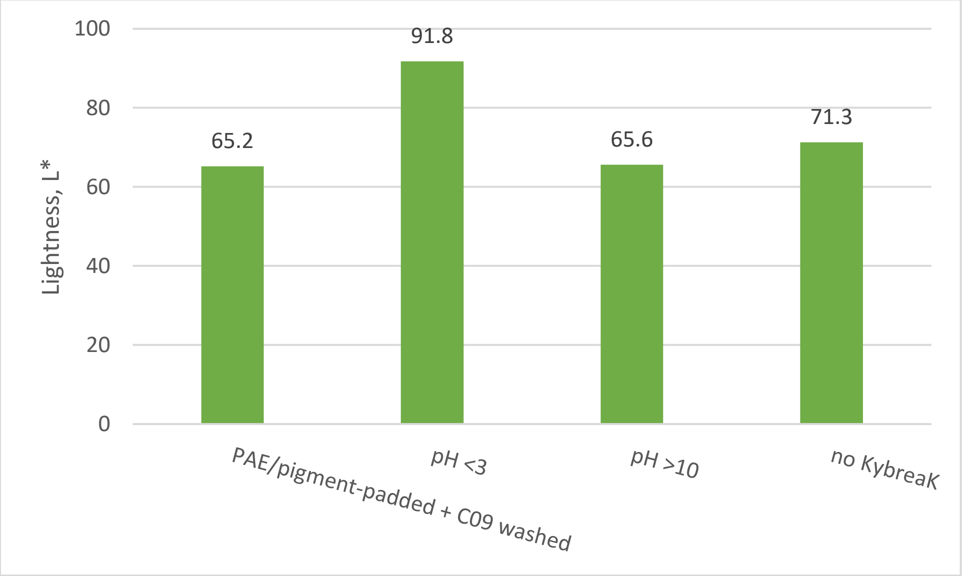


Figure 6.6 L* values for fabrics treated at different pH or without Kybreak

6.4.1.2 Effect of Kybreak Liquor Concentration and Treatment Time on Fabric Colour

The aim of the work was not just to establish a method that is effective in the removal of PAE/pigment from cotton fabric, but to also to aim at achieving this with the lowest possible amount of chemicals and shortest possible treatment time.

Figure 6.7 shows the colour of cotton fabrics treated with varying concentrations of the stripping agent and varying treatment times. Following the stripping treatment, all fabrics were washed according to the ISO 105 C09 standard including steel balls. All fabrics treated with 10 g/L down to 1.25 g/L Kybreak obtained a white appearance similar to that of untreated cotton, suggesting that most of the PAE/pigment has been removed after stripping and the ISO 105 C09 wash aftertreatment. Even using 0.63 g/L Kybreak over 120 minutes obtained a white coloured fabric. In contrast, the fabric removed from the stripping liquor after 60 minutes, followed by the ISO 105 C09 laundering cycle still had a green coloured appearance.

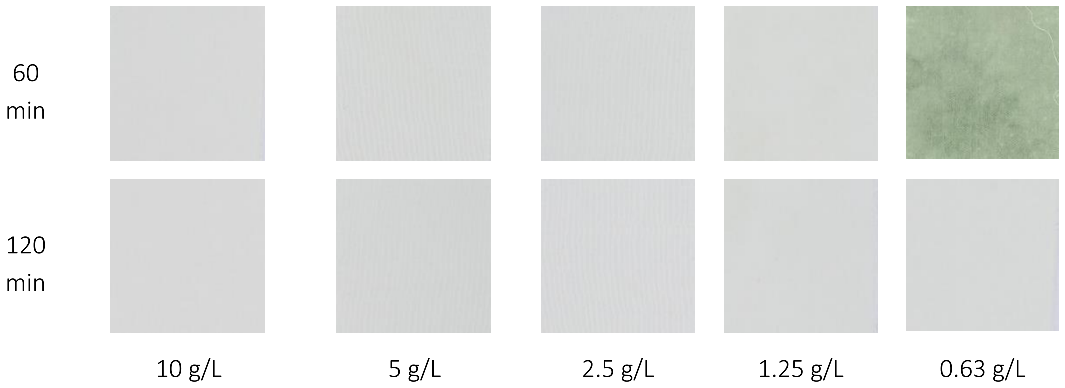


Figure 6.7 Visual appearance of treated cotton fabrics exhibiting the effect of Kybreak concentration in treatment liquor and treatment time on the colour of PAE/pigment-padded cotton fabric. Fabrics were post-treated with ISO 105 C09 washing.

The colorimetric data for the stripped fabrics are shown in Figure 6.8, Figure 6.9 and Figure 6.10. It was expected that with increasing treatment time, both K/S and ΔE would reduce and L* would increase. This was observed in most cases, but some inconsistency was found in the data for the fabrics treated with 2.5 g/L, where colour strength and colour difference was greater for the fabric treated for only 60 minutes. However, the differences were small and within experimental error.

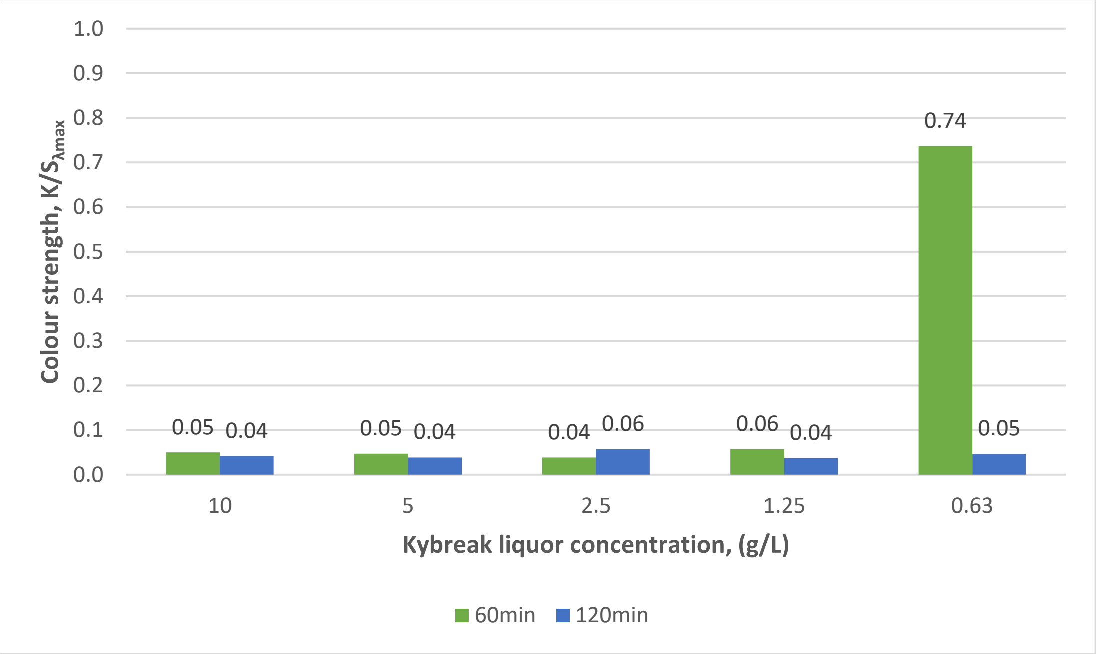


Figure 6.8 K/S values for fabrics treated for 60 or 120 minutes with various Kybreak liquor concentrations. Fabrics were post-treated with ISO 105 C09 washing.

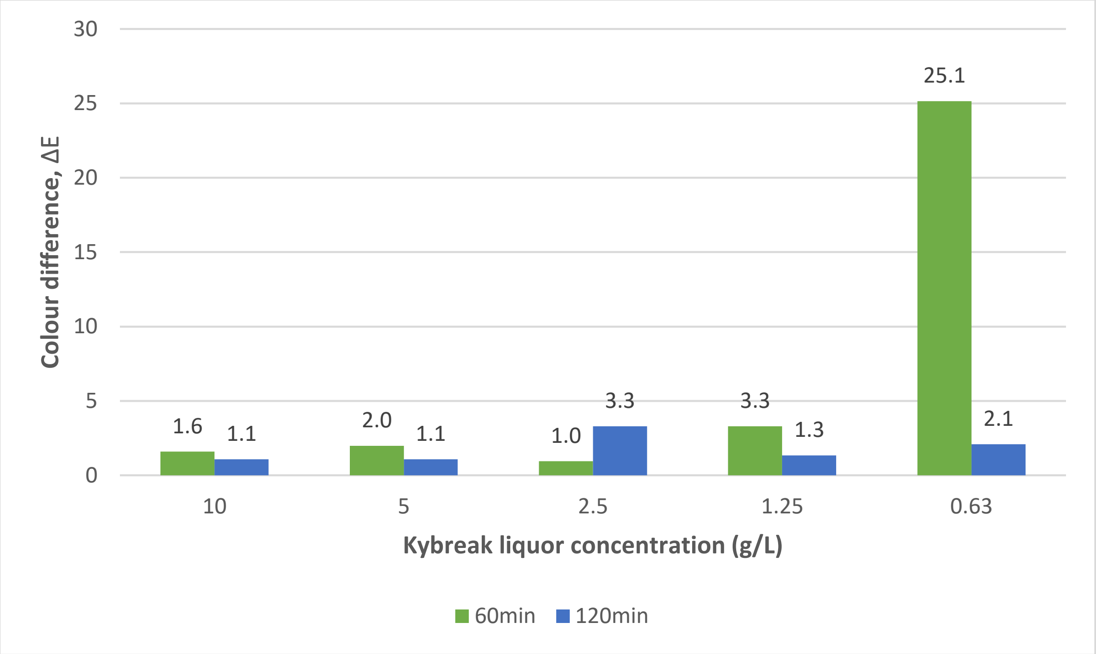


Figure 6.9 ΔE values for fabrics treated for 60 or 120 minutes with various Kybreak liquor concentrations. Fabrics were post-treated with ISO 105 C09 washing.

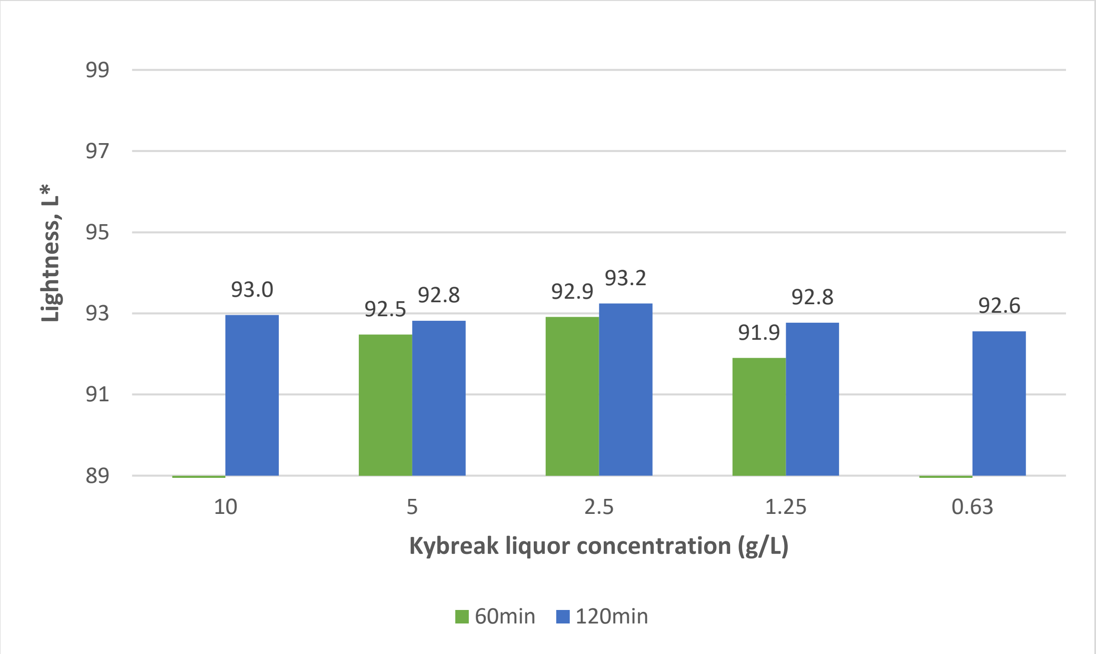


Figure 6.10 L* values for fabrics treated for 60 or 120 minutes with various Kybreak liquor concentrations. Fabrics were post-treated with ISO 105 C09 washing.

Taking into consideration the visual perception of the fabrics and the colorimetric values obtained by the Datacolor software, it could be concluded that when using the Kybreak/C09 stripping sequence, satisfactory results were obtained down to a stripping liquor concentration of 0.63 g/L Kybreak. Only with the Kybreak concentration of 0.63 g/L with a shorter time of 60 minutes was incomplete removal of colour evident.

6.4.1.3 Effect of Aftertreatment on Fabric Colour

ISO 105 C09 laundering

Figure 6.11 shows the fabrics washed according to ISO 105 C09 laundering standard with various modifications. The standard method with a washing temperature of 60°C, with and without the addition of 25 steel balls appears to offer the best effect. The fabric washed at 70°C still had a greenish fade. Visually, the stripped fabric washed at 60°C (no steel balls) appeared less white as the fabric still contained a slight green fade, in contrast to the fabric washed with the addition of steel balls. The latter combination was therefore chosen as the optimum approach to perform future washings. K/S values for all fabrics were near 0.1. The ΔE value for the 70°C method was higher compared to the fabric washed at 60°C with steel balls, but the latter method had obtained the fabric with the highest L* value, Figure 6.12 and Figure 6.13.

60°C

70°C

60°C + steel balls

Figure 6.11 Visual appearance of PAE/pigment-padded cotton stripped with 30g/L Kybreak, followed by various ISO 105 C09-based laundering cycles

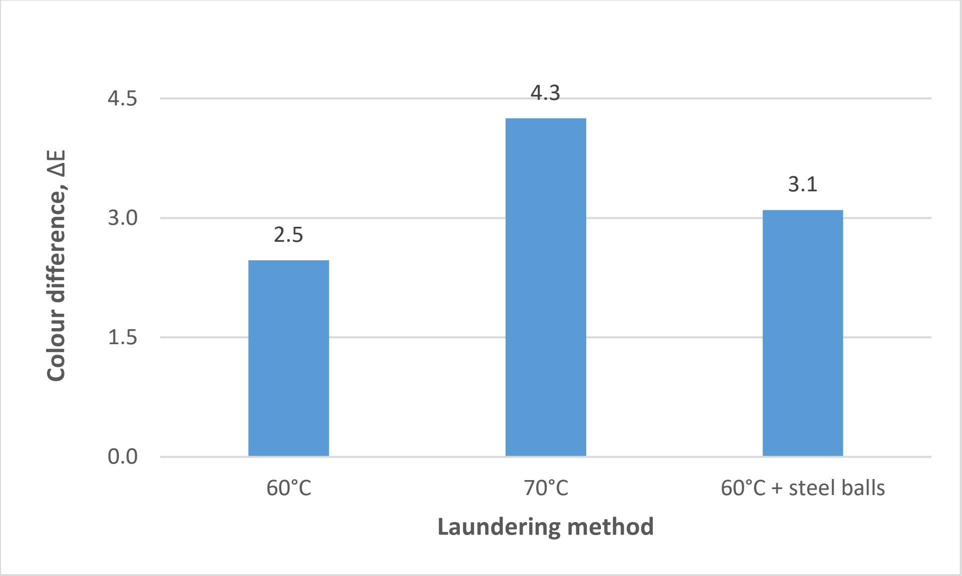


Figure 6.12 ΔE values for fabrics laundered according to modified ISO 105 C09 washing methods after 30 g/L Kybreak stripping

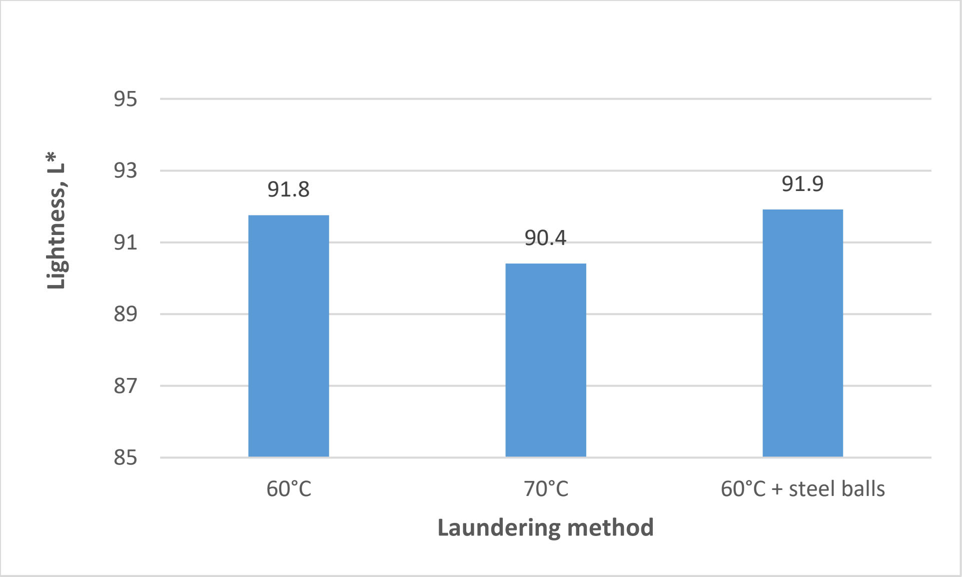


Figure 6.13 L* values for fabrics laundered according to modified ISO 105 C09 washing methods after 30 g/L Kybreak stripping

ISO 105 C09 laundering (no TAED)

Considering the addition of TAED in the ISO 105 C09 laundering method might influence the whiteness result by aiding the oxidative bleaching process, tests were done to observe whether the ISO 105 C09 laundering method would be effective without the addition of TAED. Figure 6.14 shows the fabrics stripped with varying concentrations of the stripping agent in solution, all followed by an ISO 105 C09 wash without TAED.

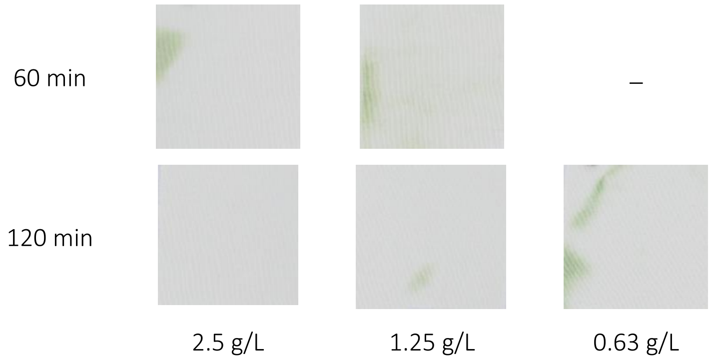


Figure 6.14 Visual appearance of PAE/pigment-padded cotton stripped with various concentrations and times, stripped and ISO 105 C09 (no TAED) laundered

As expected, a lower stripping agent concentration obtained inferior colorimetric results. However, the stripping method using 1.25 g/L and a treatment time of 120 minutes obtained satisfactory results with colorimetric values near to that obtained using double the stripping liquor concentration. For the 1.25 g/L with 120 minutes treatment time, the K/S was 0.04, ΔE was 1.4 and L* was 92.7 (Figures 6.15 - 6.17). This suggests that using the sequential Kybreak stripping/C09 (no TAED) method, satisfactory colour removal can be obtained using a minimum of 1.25 g/L with a treatment time of 120 minutes.

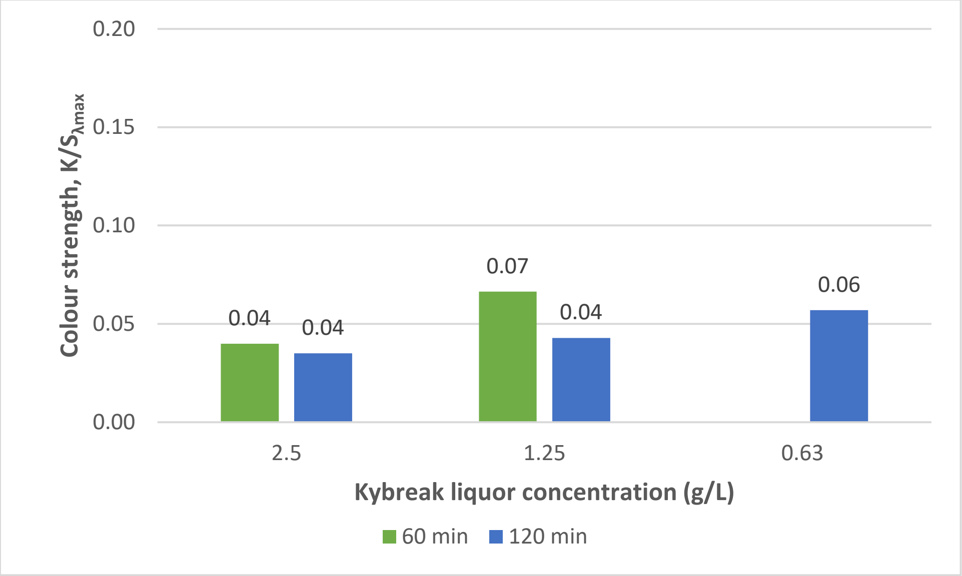


Figure 6.15 K/S values for fabrics treated with various Kybreak liquor concentrations, followed by ISO 105 C09 (no TAED) washing

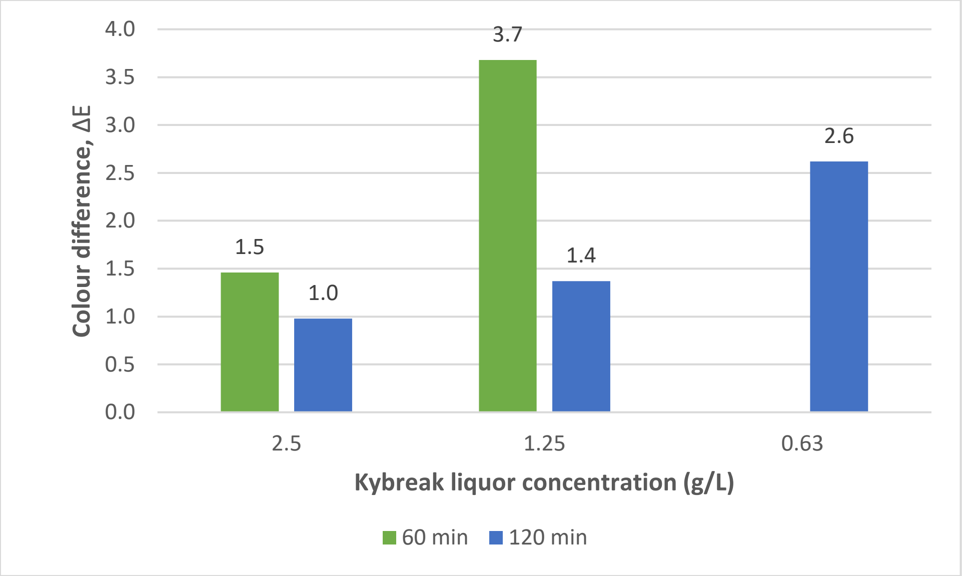


Figure 6.16 ΔE values for fabrics treated with various Kybreak liquor concentrations, followed by ISO 105 C09 (no TAED) washing

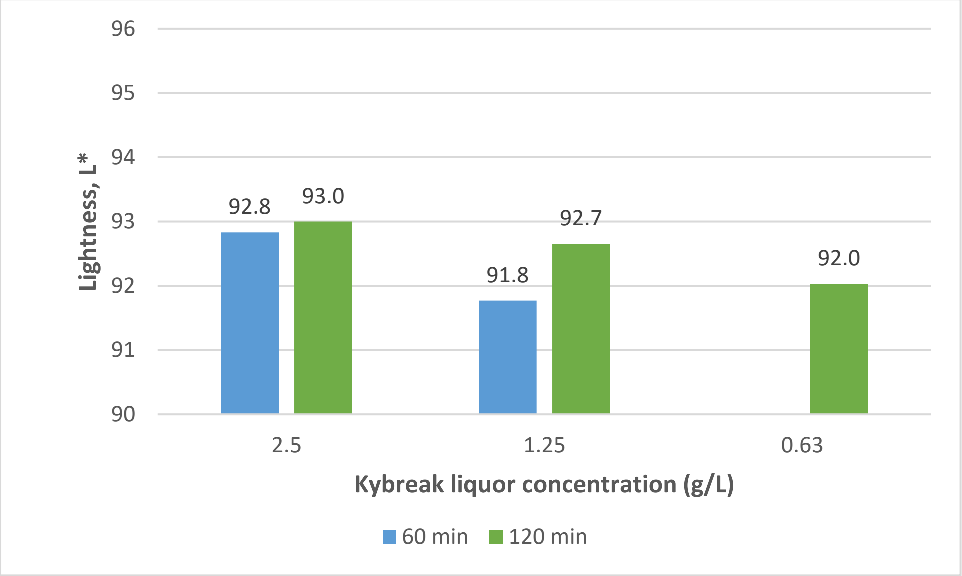


Figure 6.17 L* values for fabrics treated with various Kybreak liquor concentrations, followed by ISO 105 C09 (no TAED) washing

Reductive bleaching and sequential reductive bleaching/soaping

Figure 6.18 shows the fabrics stripped with either 2.5 g/L Kybreak for 60 minutes or 1.25 g/L Kybreak for 120 minutes, followed by Uniperol Bleach IT reductive bleaching. It can be observed from the visual images and from the associated colorimetric values in Figures 6.19 - 6.21, that additional soaping after reductive bleaching is very effective as it removes any residual green colour from the fabrics. For both methods, K/S and ΔE were significantly reduced after soaping and L* increased.

2.5 g/L 60 min Red. Bleach

2.5 g/L 60 min Red. Bleach + soaping

1.25 g/L 60 min Red. Bleach

1.25 g/L 60 min Red. Bleach + soaping

Figure 6.18 Visual appearance of PAE/pigment-padded cotton stripped with either 1.25 g/L or 2.5 g/L Kybreak for 60 or 120 mins, followed by reductive bleaching aftertreatment, with and without additional soaping

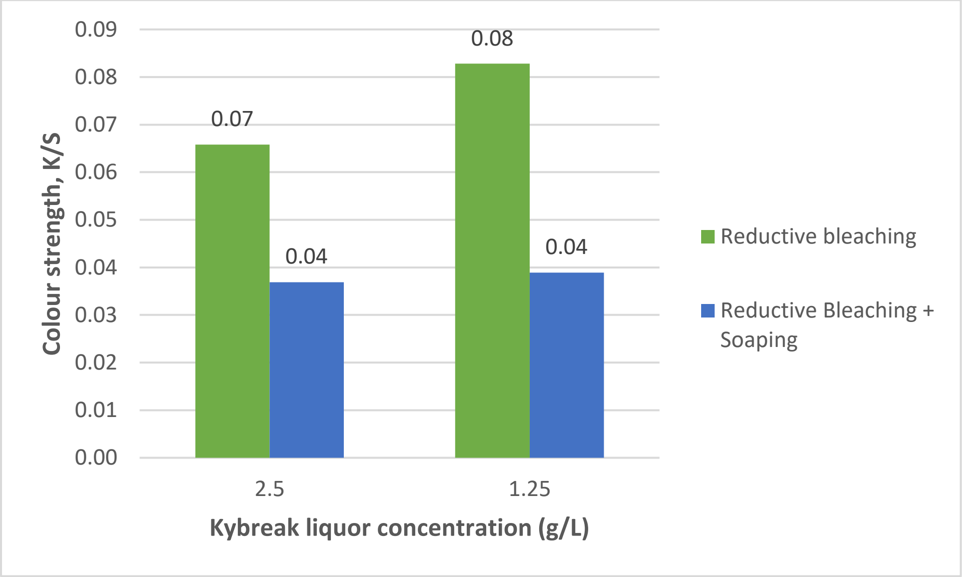


Figure 6.19 K/S values for fabrics treated with 1.25 g/L Kybreak for 120 mins or 2.5 g/L Kybreak for 60 mins, followed by reductive bleaching aftertreatment with or without additional soaping

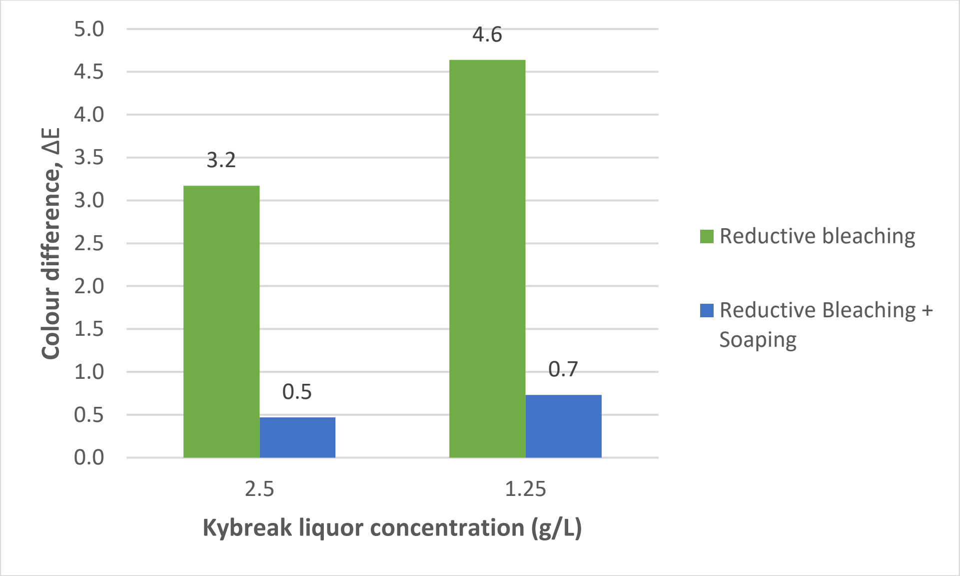


Figure 6.20 ΔE values for fabrics treated with 1.25 g/L Kybreak for 120 mins or 2.5 g/L Kybreak for 60 mins, followed by reductive bleaching aftertreatment with or without additional soaping

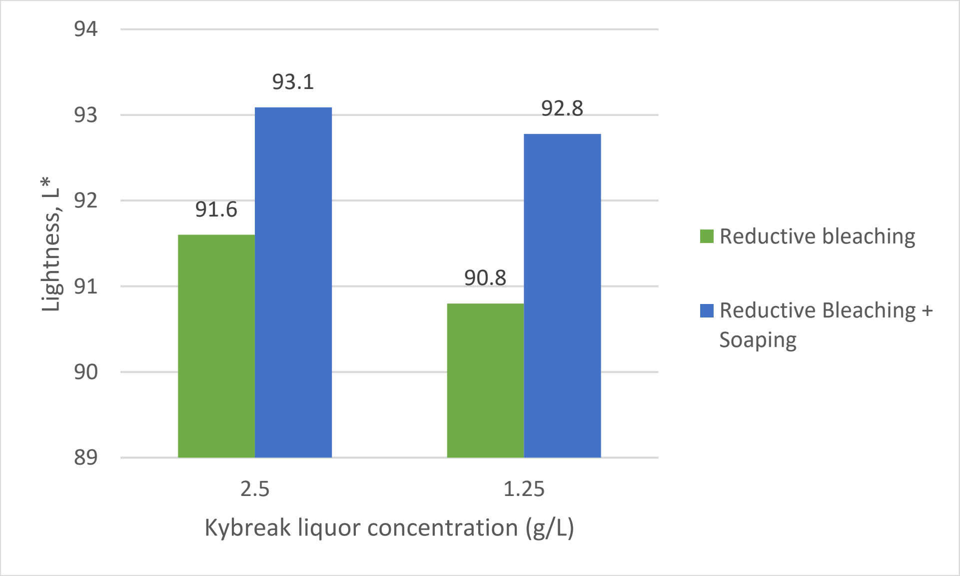


Figure 6.21 L* values for fabrics treated with 1.25 g/L Kybreak for 120 mins or 2.5 g/L Kybreak for 60 mins, followed by reductive bleaching aftertreatment with or without additional soaping

The effect of sequential reductive bleaching and soaping without the stripping treatment on the colour of the PAE/pigment-padded cotton fabrics was additionally tested. It was observed that the PAE/pigment formulation was not effectively stripped off from the cotton fabric by this treatment. This was supported by colorimetric values of K/S 2.2, ΔE 40.0 and L* 57.7. It could therefore be concluded that the previously observed colour removal could only be achieved with the full stripping/bleaching/soaping treatment.

Finally, the reductive bleaching/soaping sequence was also performed on fabrics stripped with 1.25 g/L Kybreak for 60 minutes or 0.63 g/L for 120 minutes, aiming to further lower the required stripping liquor concentration. The sequential bleaching/soaping method did not obtain satisfactory results on the fabric stripped with 0.63 g/L Kybreak, with K/S 0.1, ΔE 8.2 and L* 89.5. The sequential follow-up treatment was however effective on the fabric treated with 1.25 g/L Kybreak, with K/S 0.04, ΔE 0.5 and L* 93.0.

Figure 6.22 and Figure 6.23 show SEM images of the PAE/pigment-padded cotton fabrics stripped with 2.5 g/L and 0.6 g/L Kybreak solution, respectively. Visually, the fabric treated with 2.5 g/L Kybreak was perceived as white, in contrast to the fabric treated with 0.6 g/L Kybreak which was perceived to be light green. In general, the cotton fibres in the fabric are undamaged although there are localised regions in the micrographs where there could be cotton fibrillation and/or presence of the polymer binder material on the fibre surface. Fibrillation could be a result of the friction occurring in the C09 washing and the soaping process where the fabric comes in to contact with itself and with the steel balls. There appeared to be more surface contamination on the 0.6 g/L Kybreak treated fabric.

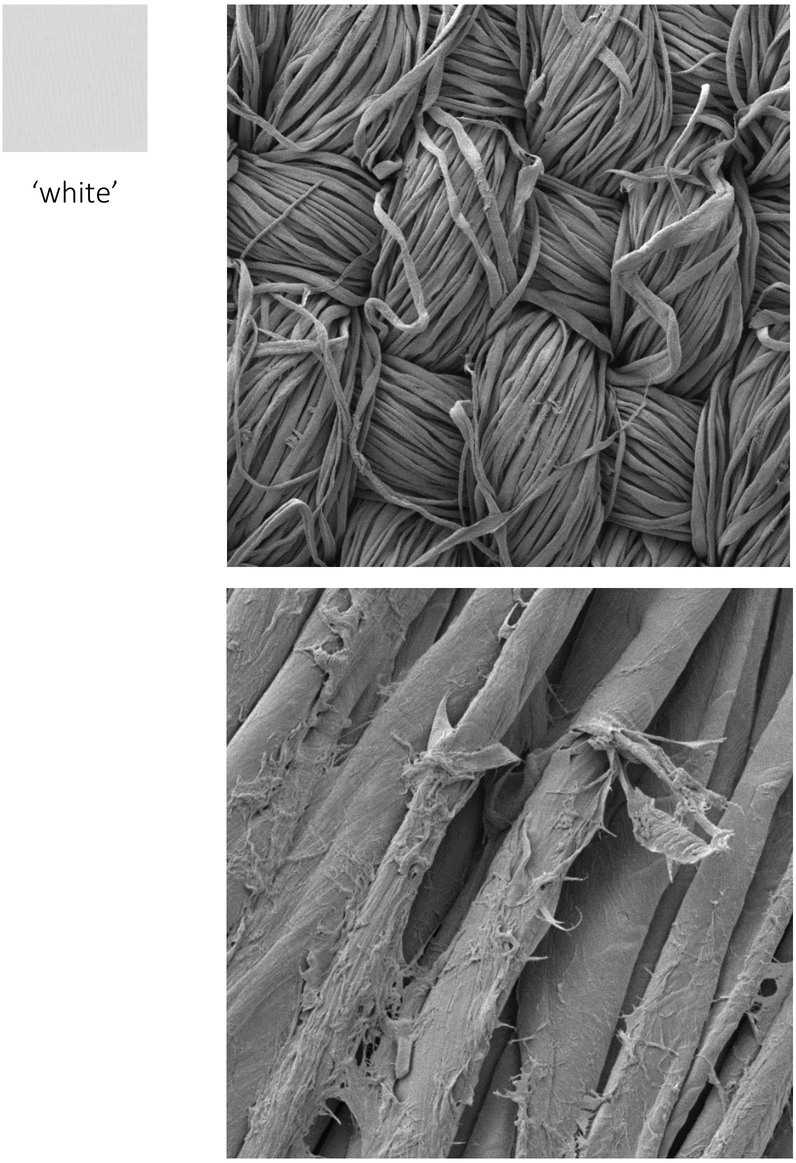


Figure 6.22 SEM images of PAE/pigment-padded cotton fabric stripped with 2.5 g/L Kybreak for 60 minutes, followed by sequential reductive bleaching and soaping

‘light green’

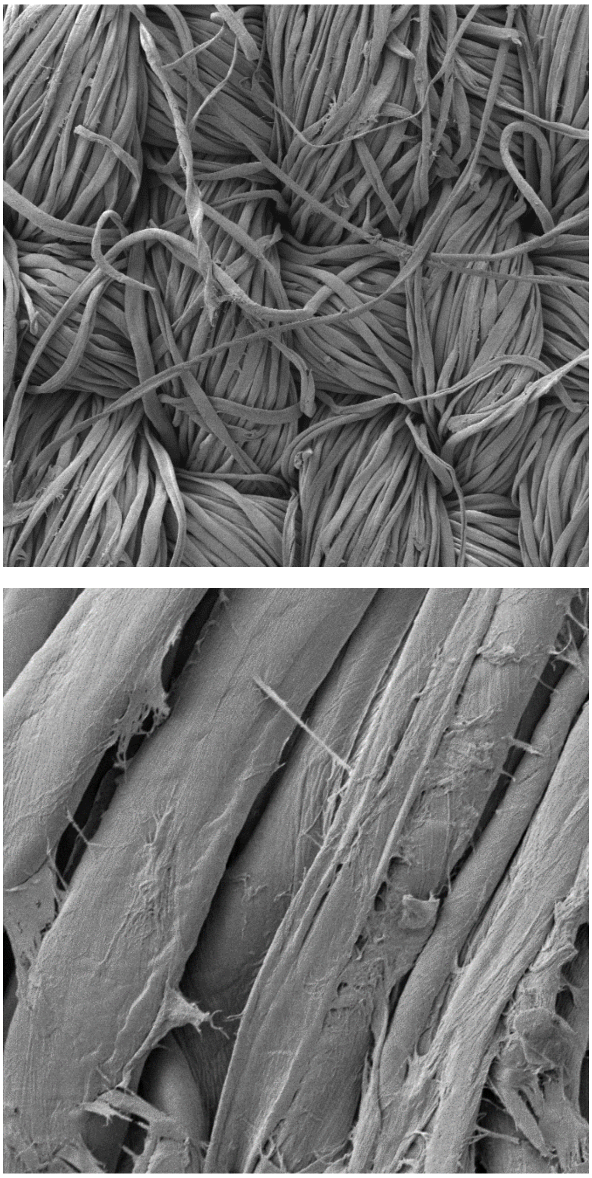


Figure 6.23 SEM images of PAE/pigment-padded cotton fabric stripped with 0.6g/L Kybreak for 120 minutes, followed by sequential reductive bleaching and soaping

6.4.1.4 Effect of Oxidising Agent on the Cotton Fibres

To observe any excessive oxidation effects on the cotton fabrics during the stripping treatment, untreated cotton fabrics were treated with the Kybreak formulation. Oxidation of cellulose fibres results in an increased amount of carboxyl groups and can be detected by application of Methylene Blue dye which binds to the carboxyl groups (Fras et al, 2002). The dyebath was prepared by adding 1.5 ml of a dilute Methylene Blue dye solution (1%) to 50 ml boiling water with a fibre to liquor ratio of 1:100. The fabric was then immersed in the dyebath and left for a suitable length of time so as to allow dyeing to occur. Analysis of the dyed fabrics that had been previously treated with 1.25 g/L Kybreak for 120 minutes and 2.5 g/L Kybreak treated for 60 minutes showed no obvious significantly higher staining, expressed in K/S, in comparison to the untreated cotton fabric, Figure 6.24.

Untreated cotton

K/S 2.5

2.5 g/L Kybreak for 60 mins

K/S 2.9

1.25 g/L Kybreak for 120 mins

K/S 2. 5

Figure 6.24 Visual appearance of 2.5 g/L (60mins) and 1.25 g/L (120 mins) Kybreak-treated cotton fabrics dyed with Methylene Blue

6.4.2 Stripping the PAE/Pigment Formulation from ''Large'' Cotton Fabrics

In Chapter 5 it was observed that after padding of cotton with PAE, signals appeared at ~1540 cm^{-1} and ~1640 cm^{-1}, which were assigned to the amide I and amide II bands of the polymer binder material. FTIR analysis of the large PAE/pigment-padded cotton fabric, followed by a C09 washing and sequential 2.5 g/L Kybreak stripping/bleaching/soaping treatment, shows that the signal around 1540 cm^{-1} significantly reduced, suggesting that the stripping treatment is effective in removing the PAE/pigment system from the cotton fabric, Figure 6.25.

Figure 6.25 FT-IR spectrum of PAE/pigment-padded and ISO 105 C09 washed cotton fabric treated with 2.5 g/L Kybreak, followed by sequential reductive bleaching/soaping aftertreatment compared to PAE/pigment-padded cotton fabric

The effect of the various Kybreak stripping methods on the larger surface area are visualised in Figure 6.26. Following the stripping of cotton-PAEP with 1.25 g/L Kybreak with either the C09 (no TAED) treatment or the sequential bleaching/soaping treatment both resulted in a decrease in K/S and ΔE and in increase in L* (Figure 6.27). The most dramatic change was observed after the bleaching/soaping treatment following stripping where K/S reduced from 1.7 to 0.2, ΔE reduced from 34.0 to 7.0 and L* increased from 64.2 to 90.5.

1.25 g/L Kybreak, C09 aftertreated

2.5 g/L, C09 aftertreated

1.25 g/L, Bleached/Soaped

2.5 g/L, Bleached/Soaped

Padded with softener 2.5 g/L, Bleached/Soaped

Figure 6.26 Visual appearance of ‘’larger’’ samples treated with Kybreak-formulation and after-treated according to various methods

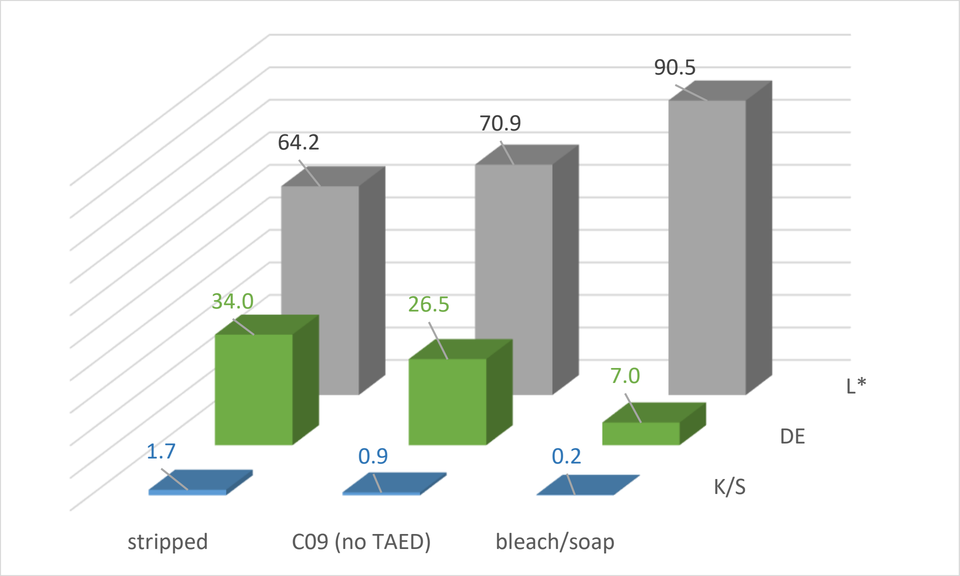


Figure 6.27 Colorimetric values for ‘’larger’’ PAE/pigment-padded cotton fabric after stripping with 1.25 g/L Kybreak, followed by either ISO 105 C09(no TAED) or sequential bleaching/soaping treatment

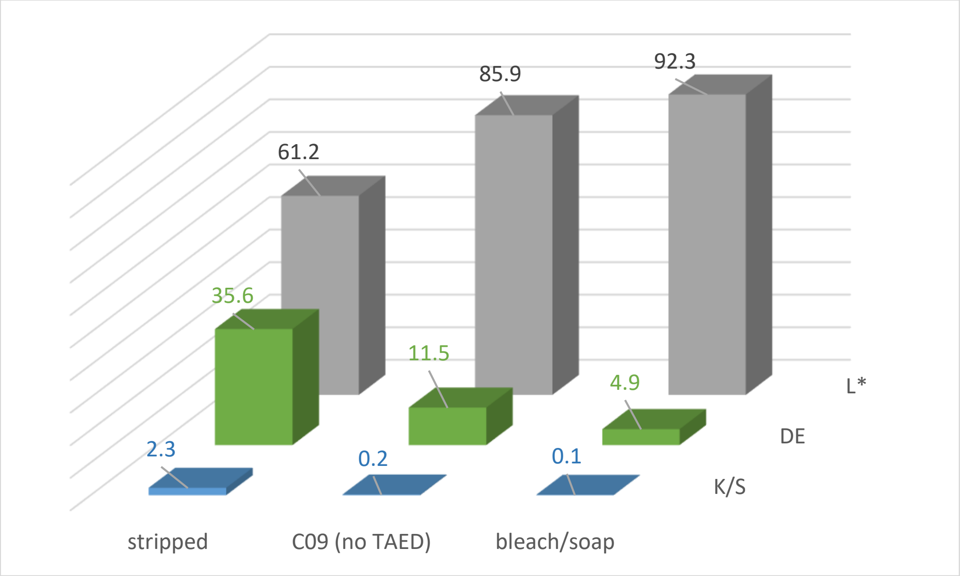


Figure 6.28 Colorimetric values for ''larger'' PAE/pigment-padded cotton fabric after stripping with 2.5 g/L Kybreak and followed by either ISO 105 C09(no TAED) or sequential reductive bleaching treatment

A similar observation was made for the fabrics treated with 2.5 g/L Kybreak, Figure 6.28. Following the stripping process with the sequential bleaching/soaping aftertreatment, K/S was reduced from 2.3 to 0.1, ΔE reduced from 35.6 to 4.9 and L* increased from 61.2 to 92.3. Notice that the 2.5 g/L Kybreak treatment obtained superior results where K/S and ΔE values were lower and L* was higher compared to the 1.25 g/L Kybreak treatment. This suggests that the 2.5 g/L Kybreak treatment was more efficient in colour removal from the cotton fabric.

Colorimetric parameters for the PAE/pigment-padded cotton fabric that incorporated a commercial cationic softener and was subsequently stripped are shown in Figure 6.29. Again, the K/S and ΔE values were reduced and L* increased after each step in the full process and the most significant change was observed after following the stripping treatment with the sequential bleaching/soaping treatment. The K/S value decreased from 1.8 to 0.1 after the stripping/bleaching/soaping process. Similarly, the ΔE value decreased from 36.5 to 4.0 while the L* value increased from 60.8 to 92.6.

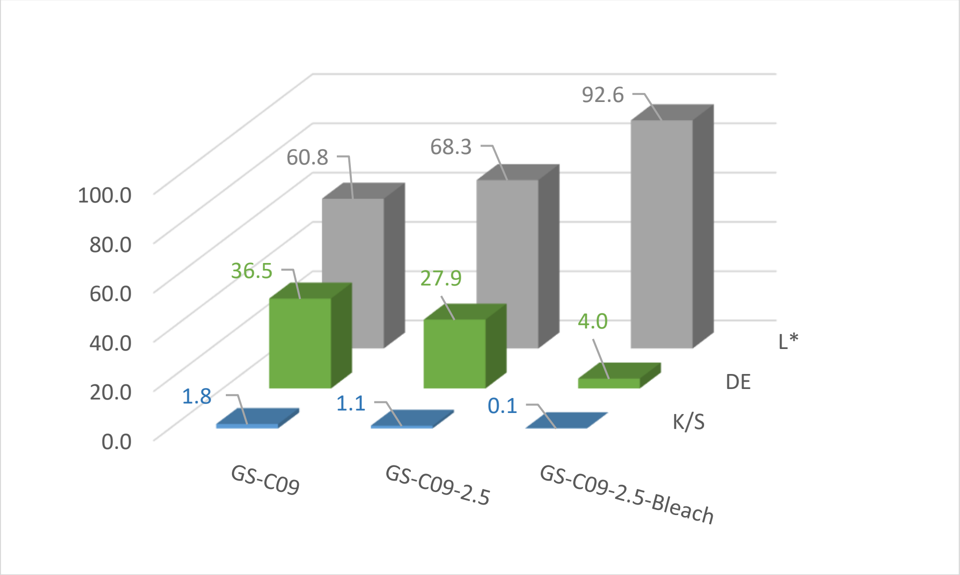


Figure 6.29 Colorimetric values for ''larger'' PAE/pigment-padded cotton fabrics after padding with softener (GS) and ISO 105 C09 washing, and after stripping with 2.5 g/L Kybreak and after stripping followed by sequential bleaching/soaping

Looking at the mass of the cotton fabrics in grams per m^2, it was observed that for untreated cotton fabric the mass in g/m^2 increased after blank padding/curing and the ISO 105 C09 laundering cycle from 142.8 to 159.0 g/m^2, respectively. This could be explained by the increase in fibre content per surface area due to shrinkage as a result of the ISO 105 C09 washing. After subjecting the cotton fabric to the Kybreak stripping treatment, the fabric mass increased slightly to 161.2 g/m^2, potentially caused by further shrinkage during aqueous processing. For the PAE/pigment-padded cotton fabric, the fabric mass decreased from 181.7 g/m^2 to 159.3 g/m^2 and to 168.8 g/m^2 after 2.5 g/L and after 1.25 g/L Kybreak treatment, respectively, in both cases followed by ISO 105 C09 (no TAED) aftertreatment, Table 6.4. For the cotton fabrics subjected to sequential reductive bleaching and soaping following Kybreak stripping the mass reduced to 158.1 g/m^2 and to 162.3 g/m^2 after 2.5 g/L and after 1.25 g/L Kybreak treatment, respectively. These reductions could be attributed to the removal of the initially fixed PAE/pigment after stripping, supporting the suggestion that the stripping treatment is efficient in removing the PAE/pigment from the cotton fabrics. Note that the fabric treated with the higher Kybreak concentration of 2.5 g/L obtained a higher reduction in fabric mass, suggesting that this concentration results in more efficient removal of the PAE/pigment formulation. Additionally, the difference in efficiency of the aftertreatments is observed especially in the fabrics treated with 1.25 g/L Kybreak, where the sequential reductive bleaching and soaping treatment had obtained a much higher reduction in fabric mass.

Table 6.4 Mass in g/m^2 of the cotton fabrics subjected to the Kybreak stripping treatment, followed by either ISO 105 C09 (no TAED) or sequential reductive bleaching/soaping

Stripping Treatment	**Aftertreatment**	
	C09 (no TAED)	**Red. Bleach /Soaping**
1.25 g/L Kybreak	168.8 g/m^2	162.3 g/m^2
2.5 g/L Kybreak	159.3 g/m^2	158.1 g/m^2

6.4.3 Objective Measurement of Fabric Handle

The Kawabata Evaluation System for Fabrics (KES-F) was used to assess the effects of different parameters of the stripping method on the handle of the cotton fabrics. The parameters include the stripping agent concentrations at varying stripping times, the aftertreatments following stripping treatment to remove any residue material on the fabric surface, and the addition of a cationic softener to the PAE/pigment padding liquor. Table 6.5 shows the tensile, shear and bending properties for all the tested fabrics.

Table 6.5 KES-F Tensile, shear and bending properties for various treated cotton fabrics

Fabric treatment	Kawabata Parameter				
	EMT (%)	G (gf/cm. degree)	2HG5 (gf/cm)	B (gf*cm^2/ cm)	2HB (gf.cm/ cm/)
Untreated	3.7	2.4	11.2	0.11	0.13
Untreated/C09	9.4	2.1	7.6	0.07	0.14
Untreated/C09/2.5gL Kybreak + Red Bleach + Soap	9.4	2.1	8.0	0.08	0.12
PAEP*	3.2	11.7	-45.3	-0.04	-0.32
PAEP/C09	5.1	5.7	10.2	-0.27	0.03
PAEP/C09/2.5gL Kybreak	6.8	3.9	11.3	0.06	0.07
PAEP/C09/2.5gL Kybreak + Red Bleach + Soap	8.3	2.0	8.2	0.10	0.14
PAEP/C09/2.5gL Kybreak + C09(no TAED)	8.0	2.4	8.8	0.19	0.24
PAEP/C09/1.25gL Kybreak	7.0	3.4	14.3	-0.35	-0.23
PAEP/C09/1.25gL Kybreak + Bleach	8.8	1.7	8.0	0.17	0.23
PAEP/C09/1.25gL Kybreak + C09(no TAED)	7.6	2.7	9.9	0.26	0.32
PAEP + softener	1.2	10.8	-42.3	-0.19	-0.28
PAEP + softener/C09	4.4	6.7	14.0	-0.14	-0.23
PAEP + softener/C09/2.5gL Kybreak	7.2	2.6	10.8	0.33	0.33
PAEP + softener/C09/2.5gL Kybreak + Red Bleach + Soap	8.6	2.2	8.6	0.08	0.16

NB. All values were produced by calculating the average of specific values for warp and weft.

* PAEP = PAE/pigment-padded

6.4.3.1 Effect of Padding, Laundering and Stripping on Fabric Mechanical Properties

Untreated white cotton was subjected to the stripping process in order to observe the effect of the processing steps of padding, laundering and stripping on the cotton fabric in comparison to the stripping of PAE/pigment-padded cotton or green cotton. Figure 6.30 shows examples of tensile curves, in this case for white cotton and green cotton, untreated, after padding, after ISO 105 C09 laundering and after stripping using 2.5 g/L Kybreak. With the KES-F tensile test, extension is applied along the required direction of the fabric. To create the tensile curve, the extension ε is plotted against the applied force F.

From the load-extension curves for white cotton it was observed that after blank padding and ISO 105 C09 washing the extensibility increased in comparison to the untreated fabric. Not much change is observed after the stripping treatment. These observations can be explained by several variables including the application of heat during baking of the padded fabrics and during washing and stripping. Furthermore, the deformation of the fabric due to agitation during washing and stripping, could also have contributed to the increase in extensibility of the fabric. In this case it is suggested that mainly the post-padding baking and laundering process is responsible for the increase in extensibility. Extensibility is related to the springiness or crimp per unit area. During baking and laundering the fabric is prone to shrinkage. Shrinkage increases the crimp per unit area and therefor the difference between the starting and ending point of extensibility at the same load applied increased after the fabrics had gone through the mentioned processes. The fabric was relaxed with the release of the weaving tension. For the green cotton the load-extension curve shifts both after the ISO 105 C09 washing and after the stripping treatment, most likely due to increase in crimp during laundering initially and secondly by removal of the binder material during stripping. Removal of the binder/pigment formulation from the cotton fabric caused relaxation of the fabric and breaking of the interfibre bonds. For both white and green cotton it is observed that extensibility is higher in when tensile force is applied in the weft direction, with bigger increases in extensibility after the process steps, in comparison to application of tensile force in warp direction. In woven fabrics, the weft direction tends to be more extensible than the warp direction and may therefore be more prone to relaxation shrinkage cause by laundering and stripping.

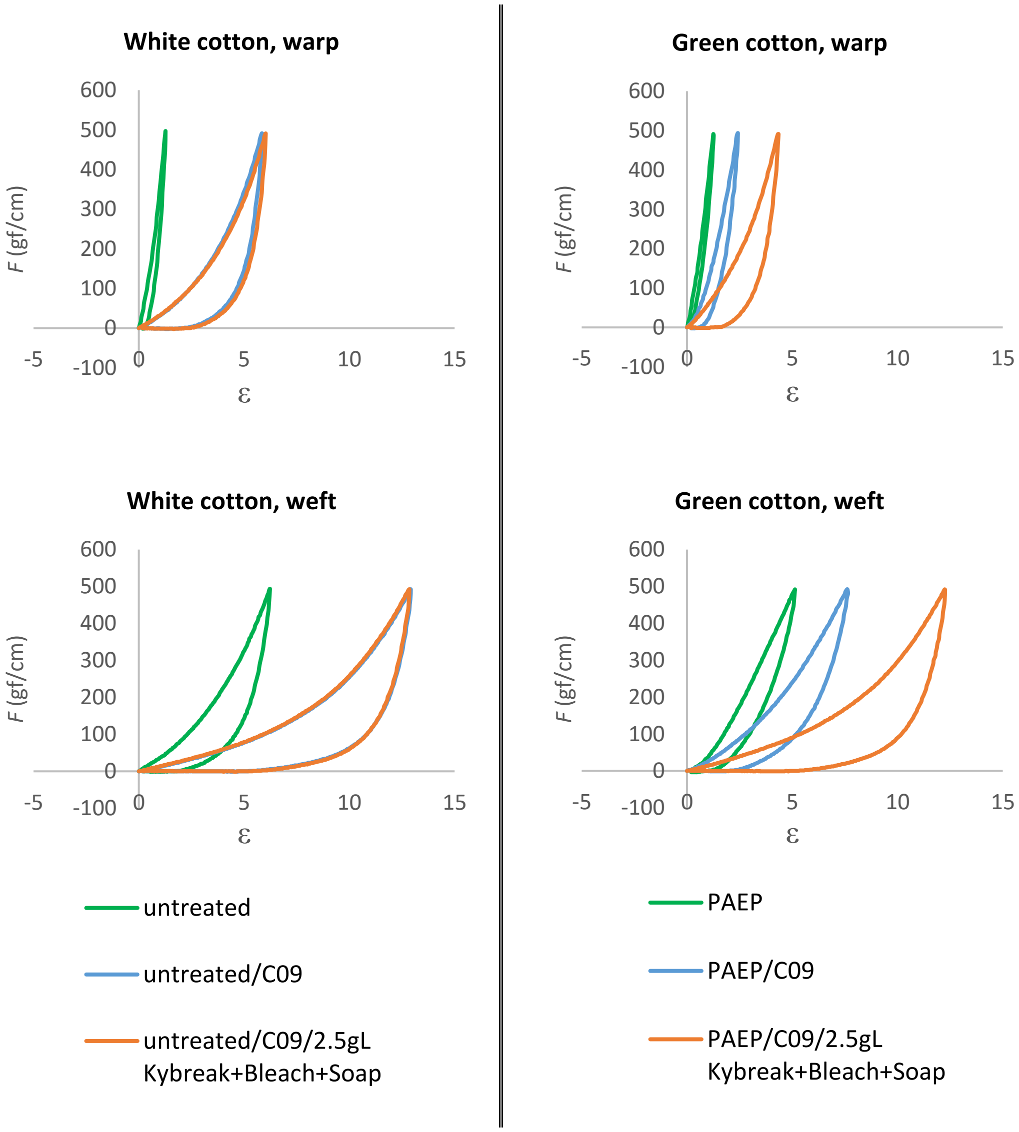


Figure 6.30 KES-F load-extension curves for untreated white cotton and PAE/pigment (PAEP)-padded green cotton fabrics, after ISO 105 C09 washing and after sequential Kybreak stripping/reductive bleaching/soaping

Figure 6.31 shows EMT for untreated 'white cotton', the blank padded fabric, cotton-PAEP, the fabrics after ISO 105 C09 washing and after 2.5g/L stripping treatment followed by sequential reductive bleaching/soaping. For both 'white cotton' and 'green cotton', EMT increased after each step. The most dramatic increase is found for white cotton after ISO 105 C09 washing where EMT increased from 3.7% to 9.4% in contrast to PAE/pigment-padded cotton with an increase from 3.2% to 5.0%. As discussed before with regards to the effect of the ISO 105 C09 laundering on colorimetric parameters and mass of the fabric, the blank padded cotton fabric is expected to be more prone to shrinkage in laundering in comparison to the PAE/pigment-padded cotton where the polymer binder material may prevent this.

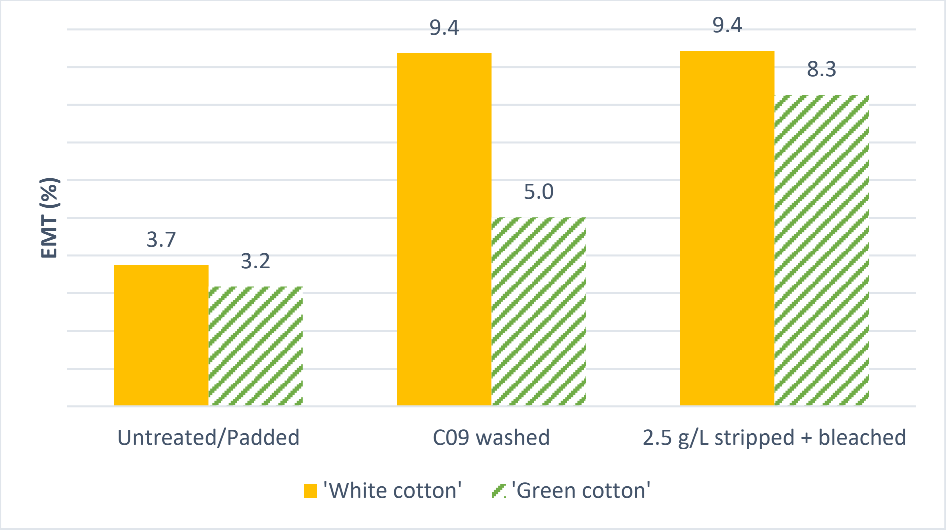


Figure 6.31 KES-F extensibility *EMT* for untreated white cotton and PAE/pigment (PAEP)-padded green cotton fabrics, after ISO 105 C09 washing and after sequential 2.5 g/L Kybreak stripping/reductive bleaching/soaping

After stripping, EMT increases most significantly for PAE/pigment-padded cotton from 5.0% to 8.3%, where the change for 'white cotton' is negligible. This change for the PAE/pigment-padded cotton can be appointed to the stripping process removing a significant amount of the PAE/pigment from the fabric and therefore the measured

EMT after stripping correlates to that of the textile material without support from the PAE/pigment. It cannot be said for certain whether all of the binder has been removed, however the amount of the binder that has been removed in this case appears to be sufficient to increase the extensibility of the fabric back to the level of the untreated white cotton as the control fabric. The higher extensibility of the fabric could also imply a low tensile modulus, suggesting that the stiffness of the coloured fabric decreased after the stripping process (Baig and Carr 2015).

Figure 6.32 shows examples of shear hysteresis curves, in this case for untreated cotton, the blank padded fabric, PAE/pigment-padded cotton, for the fabrics after ISO 105 C09 washing and after the 2.5 g/L Kybreak stripping treatment followed by sequential reductive bleaching/soaping. Hysteresis is a measurement of the energy that is lost during the deformation/recovery cycle, mainly caused by the interfibre and interyarn friction (Baig and Carr 2015). The KES-F shear hysteresis curve is produced by plotting the degree of shear deformation against the force *F* applied. From the hysteresis curves of white cotton, it can be observed that after laundering and stripping, little change occurs apart from a slight deformation in the recovery cycle. The hysteresis curves of the green cotton show that the force required to obtain shear deformation decreases both after laundering and stripping. Notice that the curve for PAE/pigment-padded cotton does not even reach the shear angles of -5° and 5°, suggesting they were too stiff to allow shear deformation to these angles. The curves for the PAE/pigment-padded cotton followed by the sequential 2.5 g/L Kybreak / reductive bleaching / soaping treatment appear to have taken a similar form as to that of untreated cotton.

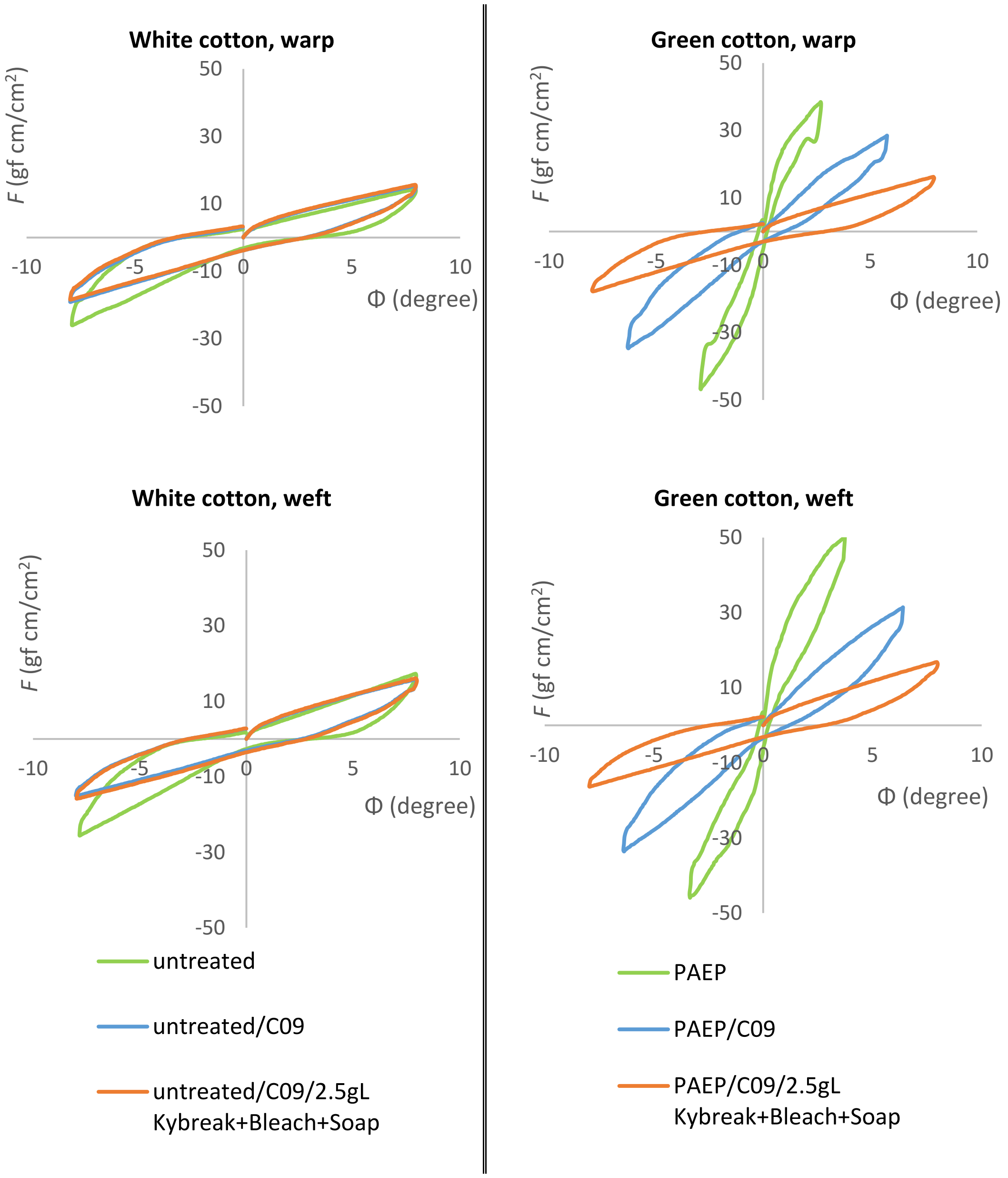


Figure 6.32 KES-F Shear hysteresis curves for untreated white cotton and PAE/pigment (PAEP)-padded green cotton fabrics, after ISO 105 C09 washing and after sequential Kybreak stripping/reductive bleaching/soaping

From the shear hysteresis curves several properties are calculated by the KES-F equipment. For this work shear rigidity (*G*) and the hysteresis of shear force measured at 5° (*2HG5*) are of most interest as the latter has been shown to be representative of fabric drape and softness, correlating to interyarn friction (Collier 1991). Figure 6.33 and Figure 6.34, respectively, show *G* and *2HG5* for untreated cotton fabric, PAE/pigment-padded cotton fabric, the fabrics after laundering and after sequential Kybreak stripping/reductive bleaching/soaping treatment. Laundering and the stripping sequence did not appear to significantly affect the force required to obtain shear deformation as for white cotton, negligible change for *G* was observed. The PAE/pigment-padded cotton fabric was stiffer by touch compared to untreated fabric, due to the presence of the PAE/pigment formulation, hence the higher G value initially. This then reduced both after laundering and after the stripping sequence from 11.7 to 5.7 and 2.0 gf/cm.degree, coinciding with the suggested reduction of PAE/pigment present on the fabric.

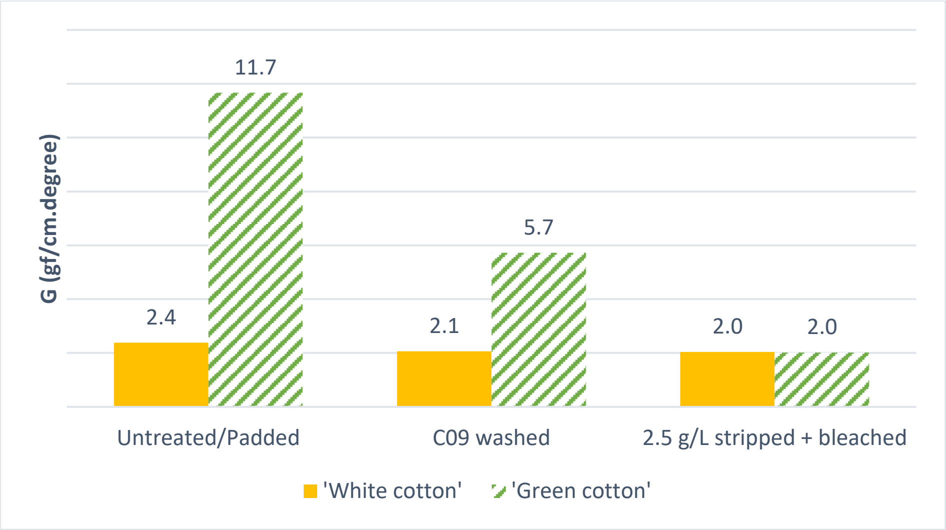


Figure 6.33 KES-F Shear rigidity *G* for untreated white cotton and PAE/pigment (PAEP)-padded green cotton fabrics, after ISO 105 C09 washing and after sequential Kybreak stripping/reductive bleaching/soaping

Figure 6.34 KES-F Shear stress *2HG* for untreated white cotton and PAE/pigment (PAEP)-padded green cotton fabrics, after ISO 105 C09 washing and after sequential Kybreak stripping/reductive bleaching/soaping

The energy loss during the deformation-recovery cycle measured at a shear angle of 5°C or *2HG5* for 'white cotton' reduced after laundering, from 11.2 to 7.6 gf/cm before slightly increasing to 8.0 gf/cm. The initial decrease suggested a lower energy loss during the deformation/recovery cycle potentially due to relaxation shrinkage of the fabric caused by the laundering cycle. *2HG5* showed a more dramatic change for cotton-PAEP from -45.2 to 10.2 gf/cm. The negative value for cotton-PAEP is due to the stiff fabric not allowing deformation up to 5° as can be observed in the shear hysteresis curve for green cotton.

Figure 6.35 shows examples of bending curves obtained after KES-F measurement. In this case the curves represent untreated cotton fabric, PAE/pigment-padded cotton, the fabrics after laundering and the fabrics after sequential 2.5 g/L Kybreak stripping/reductive bleaching/soaping treatment. The KES-F bending curve is produced by plotting the fabric bending curvature *K* against the applied bending moment *M*.

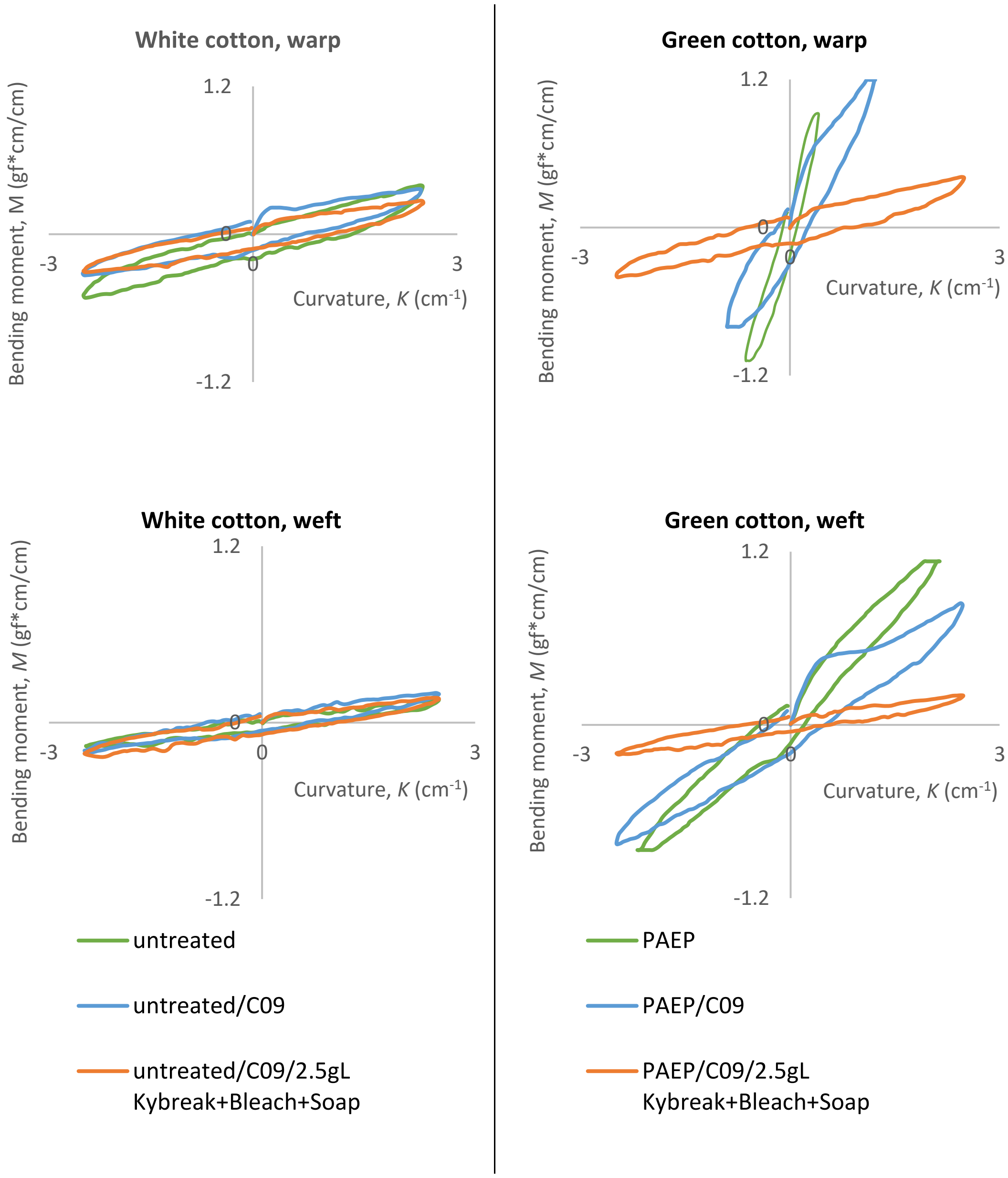


Figure 6.35 KES-F Bending curves for untreated white cotton and PAE/pigment (PAEP)-padded green cotton fabrics, after ISO 105 C09 washing and after sequential Kybreak stripping/reductive bleaching/soaping

The bending hysteresis curve for white cotton barely changes after laundering and stripping treatment. For green cotton the bending hysteresis curve for the fabric after padding (and also after laundering for warp direction), does not reach the expected maximum bending deformation of the fabric expressed in curvatures -2.5 and 2.5 cm^{-1}, suggesting that similarly to the shearing test, the fabrics were too stiff to actually be bent to the full extent. The hysteresis curves of PAE/pigment-padded cotton fabric followed by sequential 2.5 g/L Kybreak / reductive bleaching / soaping treatment, shifted to the shape similar to that of untreated cotton.

From the bending hysteresis curves a number of properties are calculated by the KES-F equipment. For this work, both the bending rigidity *B* and the hysteresis of bending (measured at K=0.5cm^{-1}) *2HB* were of interest to assess the effect of the varying processes on the fabric bending properties.

Figure 6.36 KES-F Bending rigidity *B* for untreated white cotton and PAE/pigment (PAEP)-padded green cotton fabrics, after ISO 105 C09 washing and after sequential Kybreak stripping/reductive bleaching/soaping

Figure 6.36 and Figure 6.37, respectively, show *B* and *2HB* for untreated cotton, PAE/pigment-padded cotton, the fabrics after laundering and after sequential 2.5 g/L Kybreak stripping/reductive bleaching/soaping treatment. Bending properties for white cotton were relatively unchanged with a marginal reduction in rigidity. For PAE/pigment-padded cotton initially negative values were obtained with *B* -0.04 gf.cm^2/cm after padding and *B* -0.27 gf.cm^2/cm after laundering, before obtaining similar bending rigidity as untreated cotton. *2HB* for cotton-PAEP increased from -0.32 to 0.03 gf.cm/cm until after stripping obtaining a value similar to that of untreated cotton.

Figure 6.37 KES-F Bending moment *2HB* for untreated white cotton and PAE/pigment (PAEP)-padded green cotton fabrics, after ISO 105C09 washing and after sequential Kybreak stripping/reductive bleaching/soaping

The increase of bending rigidity *B* to after laundering may be due to some shrinkage in the fabric and a consolidation in structure. Table 6.6 shows the data obtained for PAE/pigment-padded cotton fabric and for the same fabric after additional ISO 105 C09 washing, in both warp and weft direction. From the data it can be observed that both the PAE/pigment-padded fabric and the padded and washed fabric both obtained negative bending rigidity and bending stress values, suggesting that both fabrics did not allow adequate bending deformation required for this test. Examination of the data for both fabrics in the weft direction, showed that the bending rigidity of the fabric actually reduced after ISO 105 C09 washing. This correlates to the removal of excess PAE/pigment and relaxation shrinkage caused by laundering.

Table 6.6 KES-F bending properties for PAE/pigment-padded cotton fabric and of the fabric after additional ISO 105 C09 washing for warp and weft directions

Fabric Treatment	Bending Parameter		
	B (warp)	B (weft)	Mean
PAE/pigment-padded	-0.52	0.44	-0.04
PAE/pigment-padded + C09 washed	-0.74	0.20	-0.27
	2HB (warp)	2HB (weft)	Mean
PAE/pigment-padded	-0.88	0.24	-0.32
PAE/pigment-padded + C09 washed	-0.19	0.26	0.03

The effect of laundering and stripping on the shearing and bending properties can be related to the effect of aqueous processing on the interyarn interaction. Laundering relaxes the yarns in the fabric and decreases the interyarn friction at yarn crossover points, resulting in the laundered fabrics being deformed (shearing and bending) more easily and recovering to their original planar form more easily (Collier 1991). This increase in drapeability is further increased by the stripping treatment removing the PAE/pigment formulation from the fabric and allowing the fabric to regain its natural drape properties.

In summary, it was observed that the ISO 105 C09 laundering process greatly affects the extensibility of the blank padded fabric. No significant effect of laundering was found for shear and bending properties of the blank padded fabric. Furthermore, the stripping process seemed to not greatly affect the cotton fabric in terms of extensibility, shear or bending properties. For PAE/pigment-padded cotton extensibility increased after laundering, correlating to the removal of excess PAE/pigment and relaxation of the yarns, further enhanced by the stripping sequence, reducing the presence of PAE/pigment from the fabric. As with the extensibility of the PAE/pigment-padded cotton fabric, changes in shear and bending properties also show that after the stripping process, the properties are similar to that of the ‘white cotton’ fabric.

6.4.3.2 Effect of stripping liquor concentration on fabric mechanical properties

The Kybreak stripping treatment using different stripping liquor concentrations (1.25 g/L for 120 minutes or 2.5 g/L for 60 minutes) produced a similar effect on the tensile properties for both methods, with EMT 7.0% using 1.25 g/L Kybreak and 6.8% using 2.5 g/L Kybreak (Figure 6.38).

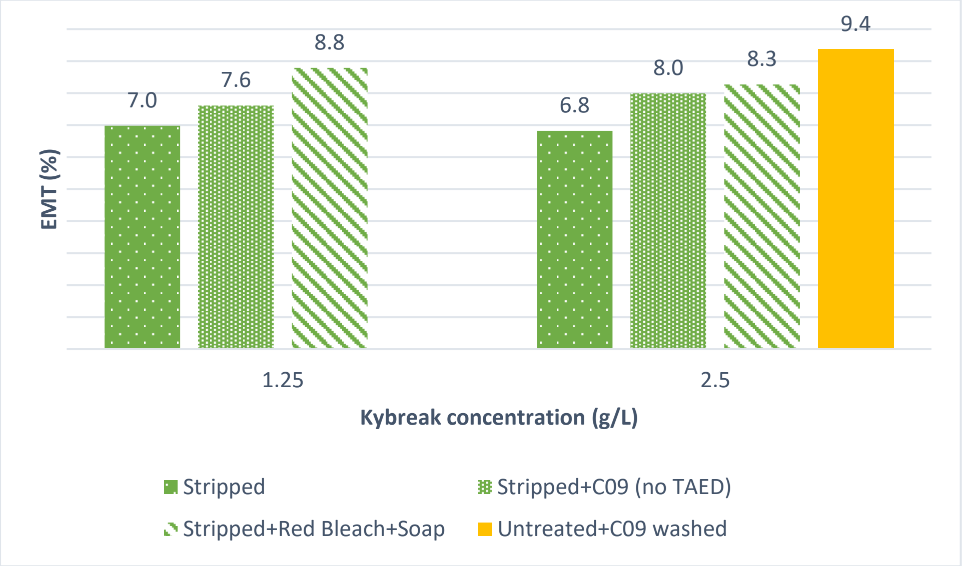


Figure 6.38 KES-F extensibility *EMT* for fabrics stripped with 1.25 g/L and 2.5 g/L Kybreak, after stripping, after stripping/C09(no TAED) and after stripping/bleaching/soaping, with untreated and ISO 105 C09 washed cotton fabric as a reference standard

The shear properties of the fabrics stripped with the 1.25 g/L and 2.5 g/L Kybreak, respectively, are shown in Figure 6.39 and Figure 6.40. Shear rigidity for the fabrics treated with different stripping concentrations was similar, with 3.4 gf/cm.degree using 1.25 g/L Kybreak and 3.9 gf/cm.degree using 2.5 g/L Kybreak. Shear stress for

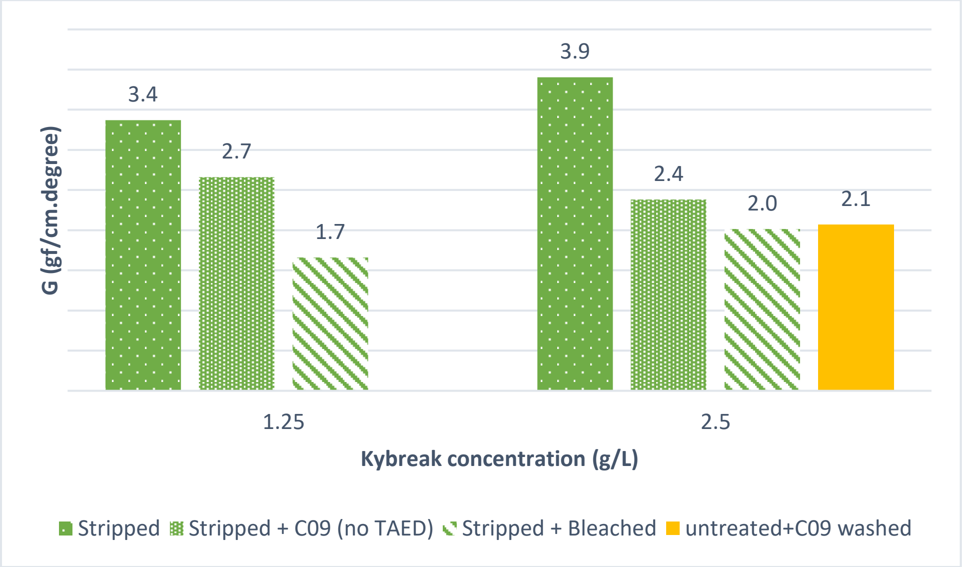


Figure 6.39 KES-F shear rigidity *G* for fabrics stripped with 1.25 g/L and 2.5 g/L Kybreak, after stripping, after stripping/C09(no TAED) and after stripping/bleaching/soaping, with untreated and ISO 105 C09 washed cotton fabric as a reference standard

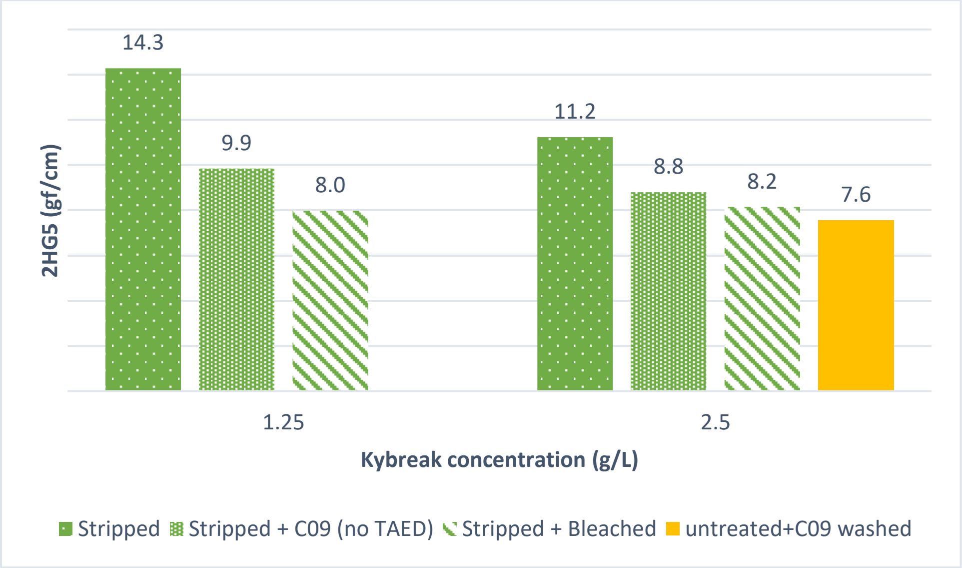


Figure 6.40 KES-F shear stress *2HG5* for fabrics stripped with 1.25 g/L and 2.5 g/L Kybreak, after stripping, after stripping/C09(no TAED) and after stripping/bleaching/soaping, with untreated and ISO 105 C09 washed cotton fabric as a reference standard

the fabric treated with 2.5 g/L Kybreak was lower than that obtained by the 1.25 g/L Kybreak treatment, with *2HG5* 11.2 gf/cm and 14.3 gf/cm, respectively.

The bending properties of the fabrics stripped with the 1.25 g/L and 2.5 g/L method, are shown in Figure 6.41 and Figure 6.42. The low values *B* 0.06 gf.cm2/cm and *2HB* 0.07 gf.cm/cm for the cotton fabric treated with 2.5 g/L Kybreak can again be related to the increase rigidity in the padded fabric. Figure 6.43 shows the bending hysteresis curves for the fabrics stripped using different stripping concentrations. It can be observed that for the cotton fabric treated with 1.25 g/L Kybreak, when bent in warp direction, the curvatures of -2.5 and 2.5 cm^{-1} were not reached. This is also represented by the negative values show in Table 6.7, with *B-warp* -0.95 $gf.cm^2/cm$ and *2HB-warp* -0.88 gf.cm/cm. Based on the data in the table, for both fabrics difficulties were found to obtain the required bending deformation curvature. Looking at the data for the fabrics bent in weft direction, it can be observed that both bending rigidity and bending stress values reduced with increase in stripping liquor concentration.

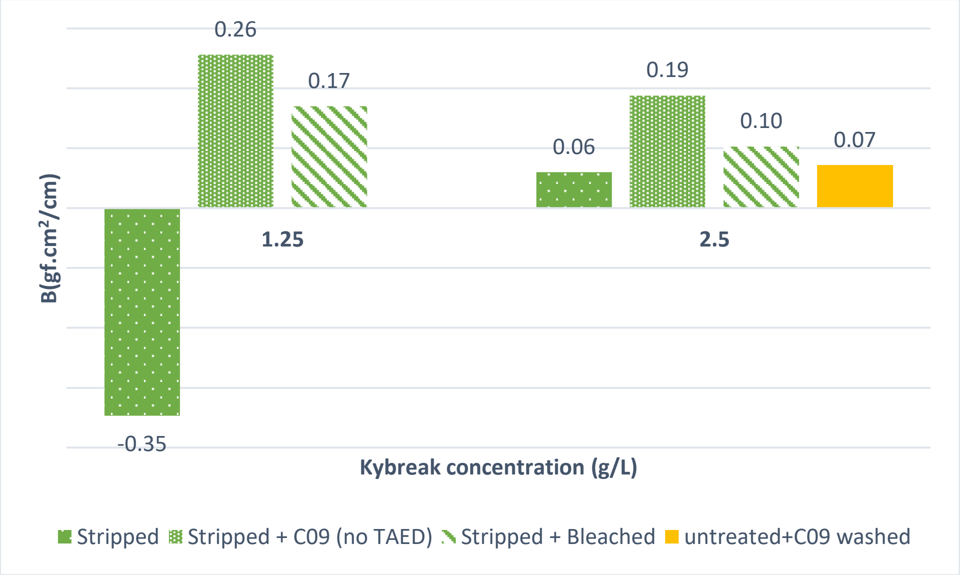


Figure 6.41 KES-F bending rigidity *B* for fabrics stripped with 1.25 g/L and 2.5 g/L Kybreak, after stripping, after Kybreak stripping/C09(no TAED) and after Kybreak stripping/bleaching/soaping

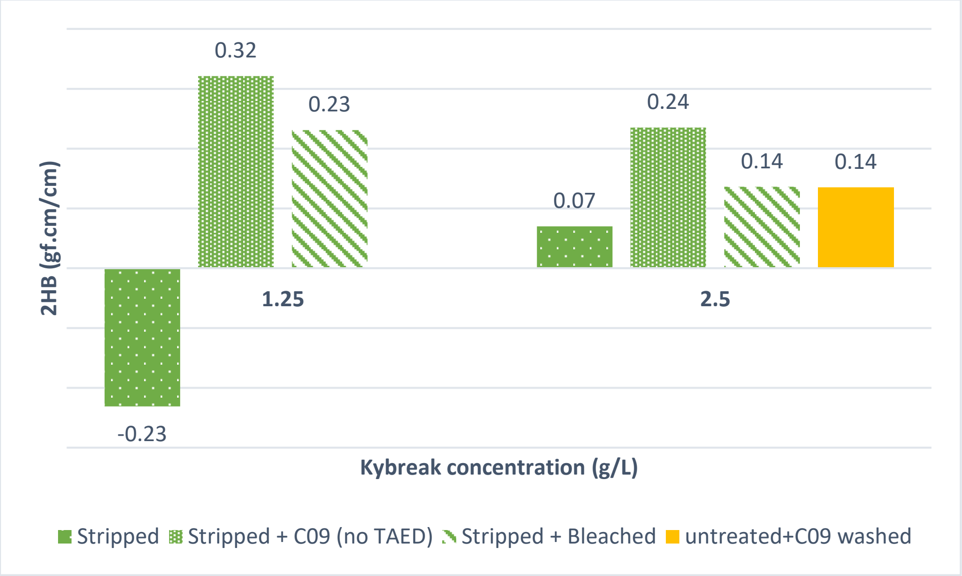


Figure 6.42 KES-F bending moment *2HB* for fabrics stripped with 1.25 g/L and 2.5 g/L Kybreak, after stripping, after Kybreak stripping/C09(no TAED) and after Kybreak stripping/bleaching/soaping

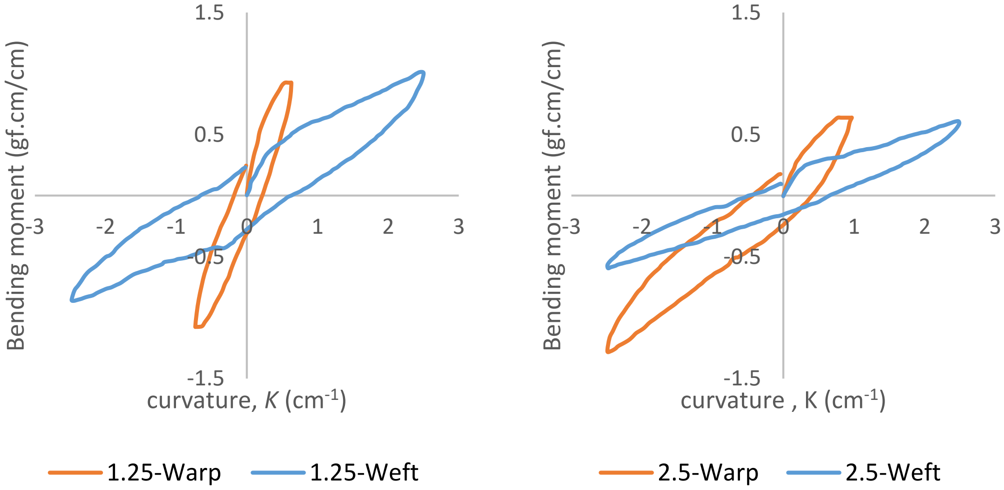


Figure 6.43 KES-F bending hysteresis curves for PAE/pigment-padded cotton fabric treated with 1.25 g/L Kybreak (left) and with 2.5 g/L Kybreak (right)

Table 6.7 KES-F bending properties PAE/pigment-padded cotton fabric treated with 1.25 g/L and with 2.5 g/L Kybreak™ 500 for warp and weft direction

Fabric Treatment	Bending Parameter		
	B (warp)	B (weft)	Mean
1.25 g/L Kybreak	-0.95	0.25	-0.35
2.5 g/L Kybreak	-0.04	0.16	0.06
	2HB (warp)	2HB (weft)	Mean
1.25 g/L Kybreak	-0.88	0.42	-0.23
2.5 g/L Kybreak	-0.09	0.24	0.07

In summary, when comparing the stripping treatment using 1.25 g/L Kybreak and 2.5 g/L Kybreak it was observed that the difference in effect on the extensibility of the fabrics was negligible. Shear rigidity was also similar for both fabrics. Superior results were obtained for the method using the higher concentration of 2.5 g/L Kybreak, with reduced shear stress, bending rigidity and bending stress.

6.4.3.3 Effect of Aftertreatment Following Kybreak Treatment on Fabric Mechanical Properties

The tensile properties of the cotton fabrics stripped with 1.25 g/L and 2.5 g/L Kybreak followed by sequential reductive bleaching and soaping, in terms of extensibility were near to that of untreated and ISO 105 C09 washed cotton as a reference (Figure 6.38). Following the Kybreak stripping treatment with the sequential bleaching/soaping treatment, *EMT* was increased from 7.0 % to 8.8 % (1.25 g/L Kybreak) and from 6.8 % to 8.3 % (2.5 g/L Kybreak). *EMT* for both stripped fabrics were near that of untreated and ISO 105 C09 washed cotton with *EMT* 9.4 %.

Similarly, shear properties *G* and *2HG5* of the stripped fabrics followed by sequential bleaching/soaping treatment showed superior results compared to the stripping treatments followed by ISO 105 C09 (no TAED). Shear rigidity reduced from 3.3 to 1.7 gf/cm.degree (1.25 g/L) and from 3.9 to 2.0 gf/cm.degree, both nearing that of untreated and C09 washed cotton with *G* 2.07 gf/cm.degree, Figure 6.39. The bleaching/soaping follow-up treatment obtained reduction in shear stress from 14.3 to 8.0 gf/cm and from 11.2 to 8.2 gf/cm, Figure 6.40. Shear properties of cotton fabric were slightly superior after the treatment using 1.25 g/L Kybreak for 120 minutes in comparison to the higher stripping concentration.

Bending properties *B* and *2HB* of the stripped cotton fabrics followed by sequential reductive bleaching and soaping also showed to be superior to those stripped followed by a ISO 105 C09(no TAED) aftertreatment, Figure 6.41 and Figure 6.42. In contrast to the effect on the shear properties, the 2.5 g/L Kybreak treatment produced slightly lower bending rigidity with *B* 0.10 gf.cm2/cm and *2HB* 0.14 gf.cm/cm which are nearest to that of untreated and ISO 105 C09 washed cotton with *B* 0.07 gf.cm2/cm and *2HB* 0.14 gf.cm/cm. The effect as a result of the two follow-up treatments can be observed in Figure 6.44, where the 2.5 g/L Kybreak stripping treatment followed by sequential reductive bleaching and soaping produced a fabric with a colour appearance similar to that of untreated cotton and the stripped fabric followed by the ISO 105 C09 (no TAED) treatment remained green-stained.

In summary, the visual assessment of the aftertreatments ISO 105 C09 (no TAED) and sequential bleaching/soaping after stripping, with the two different stripping liquor concentrations, indicated that in both cases, the sequential bleaching/soaping method was most the most effective aftertreatment following Kybreak stripping. This was expressed in higher extensibility and lower shear and bending properties of the fabrics. There was only a slight difference observed in the results between the two stripping liquor concentrations.

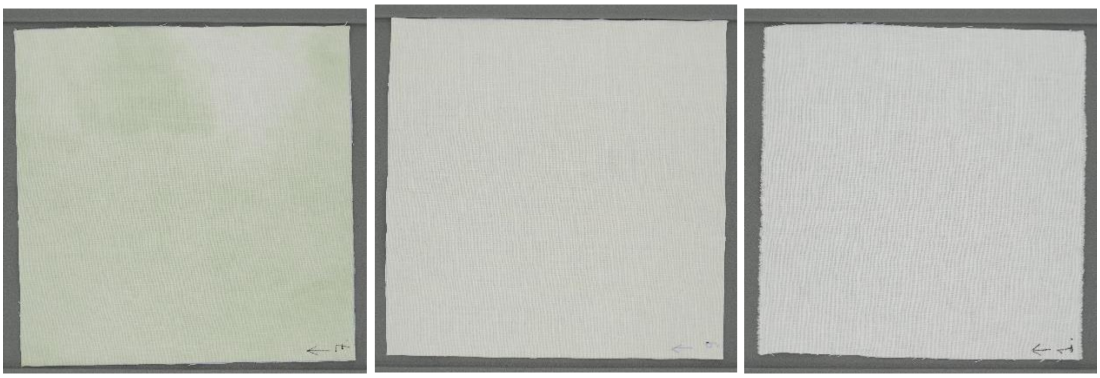


Figure 6.44 Visual appearance of PAE/pigment-padded cotton fabrics treated with 2.5 g/L Kybreak followed by ISO 105 C09 (no TAED) treatment (left) and followed by sequential reductive bleaching and soaping (middle) and untreated cotton fabric (right)

6.4.3.4 Effect of Incorporating a Softener on Fabric Mechanical Properties

The effect of the application of the PAE/pigment formulation on the handle of the cotton fabrics was readily detected subjectively. Therefore, the effect of incorporating a cationic softener into the pigment formulation was evaluated. The KES-F extensibility of the PAE/pigment/softener-padded cotton fabric was slightly lower than that of the untreated and ISO 105 C09 washed cotton fabric, with EMT 4.4% and EMT 5.0%, Figure 6.45, whereas the extensibility of untreated white cotton was 9%. Both shear rigidity and shear stress was relatively higher for the cotton fabric with the incorporated softener with *G* 7.0 gf.cm/degree and *2HG5* 14.0 gf/cm, Figure 6.46 and Figure 6.47. For untreated and ISO 105 C09 washed cotton as a reference standard, G was 2.1 gf.cm/degree and 2HG5 was 7.6 gf/cm. As with the previously mentioned results, bending properties of the padded fabrics produced negative values due to the stiffness of the fabric inhibiting the required fabric deformation, Figure 6.48 and Figure 6.49. Table 6.8 shows the bending properties for the cotton fabrics padded with and without incorporation of a softener into the padding formulation. Both bending rigidity and bending stress were higher for the fabric padded with the softener in comparison to the fabric without softener, with *B* 0.27 gf.cm^2/cm and *2HB* 0.39 gf.cm/cm for weft direction. For the untreated and ISO 105 C09 washed cotton as a reference standard, B was 0.07 gf.cm^2/cm and 2HB was 0.14 gf.cm/cm.

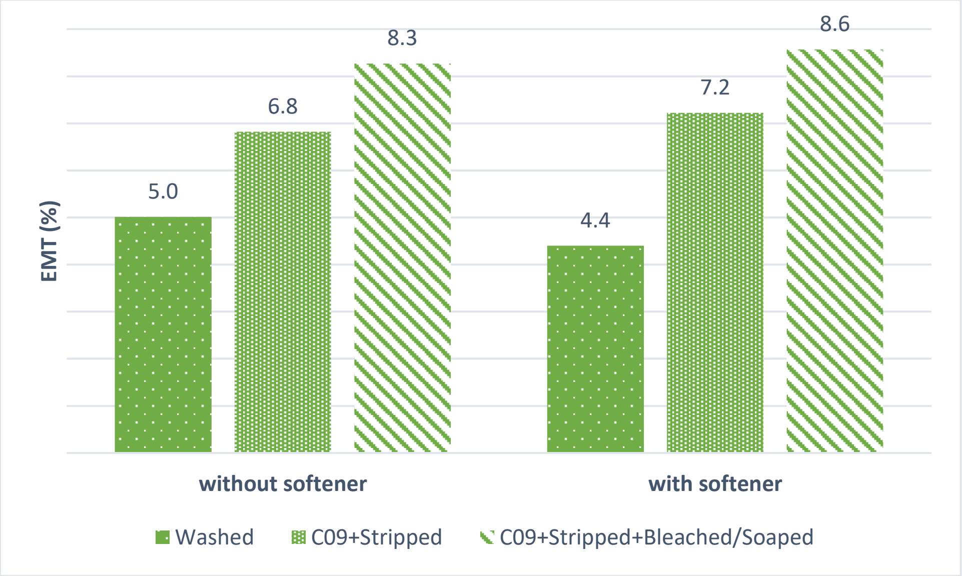


Figure 6.45 KES-F extensibility *EMT* for PAE/pigment-padded cotton fabrics with and without incorporation of a commercial cationic softener (Easy), stripped with 2.5 g/L Kybreak, from padding to sequential Kybreak stripping/bleaching/soaping

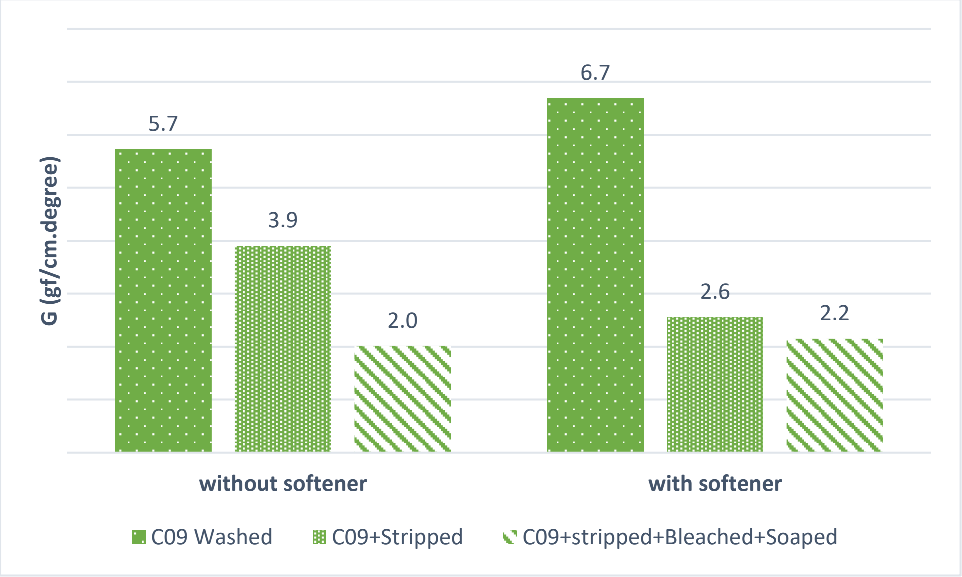


Figure 6.46 KES-F shear rigidity *G* for PAE/pigment-padded cotton fabrics with and without incorporation of a commercial cationic softener (Easy), stripped with 2.5 g/L Kybreak, from padding to sequential Kybreak stripping/bleaching/soaping

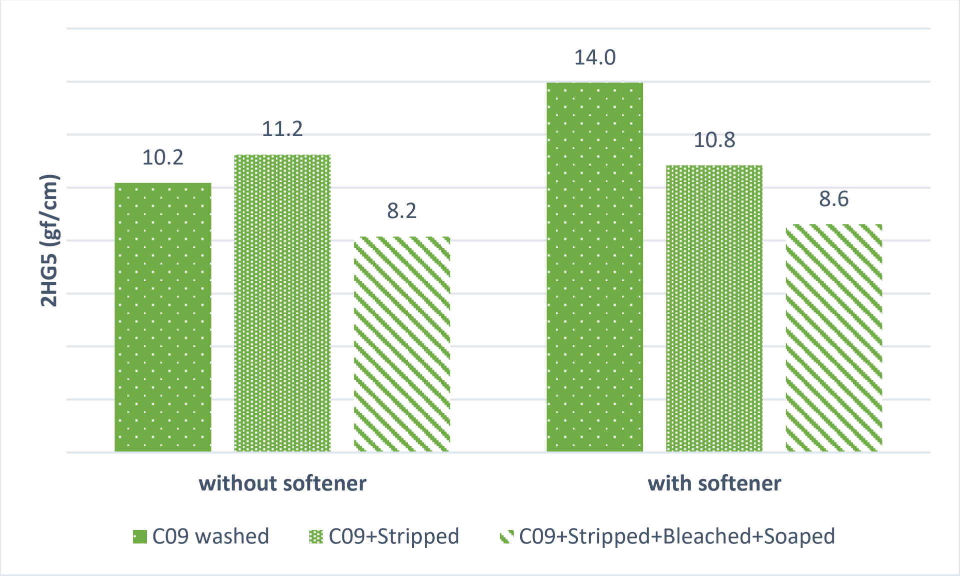


Figure 6.47 KES-F bending hysteresis *2HG5* for PAE/pigment-padded cotton fabrics with and without incorporation of a commercial cationic softener (Easy), stripped with 2.5 g/L Kybreak, from padding to sequential Kybreak stripping/bleaching/soaping

Figure 6.48 KES-F bending rigidity *B* for PAE/pigment-padded cotton fabrics with and without incorporation of a commercial cationic softener (Easy), stripped with 2.5 g/L Kybreak, from padding to sequential Kybreak stripping/bleaching/soaping

Figure 6.49 KES-F bending hysteresis *2HB* for PAE/pigment-padded cotton fabrics with and without incorporation of a commercial cationic softener (Easy), stripped with 2.5 g/L Kybreak, from padding to sequential Kybreak stripping/bleaching/soaping

Table 6.8 KES-F Bending properties for PAE/pigment-padded cotton fabric with and without incorporation of a commercial cationic softener (Easy) in warp and weft direction

Fabric Treatment	Bending Parameter		
	B (warp)	B (weft)	Mean
PAE/pigment-padded +C09 washed	- 0.74	0.20	-0.27
PAE/pigment/softener-padded + C09 washed	- 0.54	0.27	-0.14
	2HB (warp)	2HB (weft)	Mean
PAE/pigment-padded +C09 washed	-0.19	0.26	0.03
PAE/pigment/softener-padded + C09 washed	-0.85	0.39	-0.23

The incorporation of a softener is expected to provide lubrication of the fibres and yarns in the fabric, giving the fabric a softer and more flexible ‘’feel’’ (Juodsnukyte, Gutauskas, Krauledas 2005). Interfibre and interyarn friction should be limited going hand in hand with the increased ability of the fibres and yarns to slide. Extensibility is then expected to increase to a certain extent and the forces required to obtain deformation of the fabric by bending and shearing should decrease with the incorporation of the surfactant (Tzanov, Betcheva, Hardalov 1998; Inoue et al, 2012). Based on the KES-F results, the addition of 0.5 g/L of the commercial cationic softener did not improve the handle of the fabric. It is possible that the amount of softener incorporated into the padding liquor is not sufficient to obtain the desired effect on the fabric mechanical properties. Other studies into softener application have exploited various concentrations with a range of 3-50 g/L, where the optimal concentration may depend on the specific softener chemistry (Tzanov, Betcheva, Hardalov 1998; Gong and Bhatia 2009; Zuber et al, 2011). Increasing the concentration of the softener in the padding liquor and looking into alternative softeners may improve the handle properties of the padded fabrics and is suggested to be studied in future works.

6.5 Conclusions

The Kybreak stripping treatment removes the PAE/pigment formulation from the treated cotton fabric. The effectiveness of the Kybreak oxidative system is best enhanced by a reductive bleaching and after-soaping process which effectively returns the fabric back to its original whiteness and mechanical properties, that is, the green coloured polymer binder formulation has been removed. The removal of the green coloured polymer binder formulation was effective at both Kybreak concentrations examined.

The KES-F has been successfully applied to establish the ‘’handle’’ of the printed fabrics following various aqueous aftertreatments and has sensitively characterised the mechanical properties of the treated fabrics. In particular G, 2HG5, B and EMT have been useful in evaluating the impact of the polymer binder on fabric ‘’handle’’ and its subsequent removal.

The effect of a softener on the mechanical properties of the pigment print system was minimal and further work is required to optimise the softener application concentration and also assess alternative softeners.

Chapter 7 – Summary of Conclusions and Suggestions for Future Work

As is well known, the production of cotton generally requires large amounts of land, water, and the use of fertilisers and pesticides to produce appropriate yields. Despite regulated irrigation systems and improved technology such as genetic engineering to reduce the amount of fertilisers and pesticides needed, the production of cotton still remains a contentious issue mostly due to the high levels of water usage and the environmental impact. Therefore, any process developments that can reduce water usage is beneficial and welcome.

Of all the dyeing processes for cotton, reactive dyeing of cotton is the most prevalent and potentially poses a threat to the environment due to the process producing effluent contaminated with salts and hydrolysed dyestuff. For fashion garments where there is a relatively short lifetime, the high colour durability provided by reactive dyes is often unnecessary. Furthermore, when it comes to recycling of the garments after their end-of-life, the covalently bound contaminants such as dyes may pose a problem to the fibre recycling process. Therefore, there is a clear need for a different approach for designing fashion apparel. One approach is to re-evaluate current colouration technology by developing a method of colouration that allows for the application of colour which is durable to consumer usage such as laundering but can be removed from the garment after its first lifetime. In this way fibre waste could be reduced while simultaneously limiting the need for growing ʻʻnewʼʼ cotton crops. This approach would allow reuse or recycling of waste garments with faulty dyeings created along the production line as well as leasing or selling garments to companies and/or consumers and reuse the full garments or even allow fibre to fibre recycling through the lyocell process. This approach could also eliminate the complex issue of having to design a dye-specific colour removal method.

For the thesis research, attempts were made to produce Bunte salt terminated polymers, using wool or PAE as a starting material, to function as binder materials for the colouration of cotton fabrics. The efficient production of Bunte salt functional groups were confirmed by FTIR analysis. Formulation of the wool-derived functional polymer into an ink and application onto fabrics showed to be complex in terms of ink stability, printability and fixation. Nevertheless, Bunte salt chemistry specifically using wool remains of high interest as it provides a platform for the use of bio-based or even bio-waste materials for the colouration of textiles such as cotton.

Modified as well as unmodified PAE showed excellent potential when applied as a binder material for the pigment colouration of cotton. The material provided the cotton fabric with a durable colour appearance as well as allowed colour removal when subjecting the coloured fabric to specific ‘’stripping’’ conditions.

7.1 Conclusions

Objective I. Assessing the use of bio-based resources and exploring Bunte salt chemistry for the production of potential binder materials

The initial investigation into the development of a novel colouration method using potential binder materials based on Bunte salt chemistry was described in Chapter 4. The potential of polymers with Bunte Salt ($R\text{-}SSO_3$) terminations to function as a binder material lies in its ability to form disulphide crosslinks under controlled conditions. One approach using the Bunte salt chemistry used wool as a resource for the binder material, with the idea in mind that the choice of using a bio-based material minimises the need to produce the starting material in the first place. FT-IR analysis showed the efficient production of the Bunte salt groups, more so after acid sensitisation of wool at 80°C prior to oxidative sulphitolysis, with the signal intensities at around 1025 cm^{-1} and 1200 cm^{-1}. However, films as well as the formulated ink printed onto cotton did not show to be durable to water. Films dissolved, and prints were partially or fully removed after wet rubbing and laundering, respectively. These results suggest that perhaps no significant disulphide bond formation had occurred, as a result of ink instability.

An attempt was made to produce Bunte Salt-terminated compounds from the commercial PAE, Hercosett™ 617, by a reaction with sodium thiosulphate. Examination of the FT-IR spectrum of the isolated Bunte salt-terminated PAE derivative (PAE-BS) showed the presence of the Bunte salt groups with signals around 1022 cm^{-1} and 1190 cm^{-1}. Heat drying of the PAE-BS solutions successfully produced water-insoluble films. The evident presence of sulphur in the films was detected by EDX analysis. Raman lines were centred at 998 cm^{-1}, 660 cm^{-1} and around 430 cm^{-1} which could be assigned to symmetrical $-SO_3$, C-S and $S-SO_3$ stretching vibrations of the Bunte salt groups, respectively. Unfortunately, no Raman lines were observed correlating to the S-S stretching vibration. This suggests that no significant disulphide bond formation had occurred. Nevertheless, padding of the cotton fabrics followed by drying at 80°C and baking at 150°C showed satisfactory colour fastness to washing, suggesting the potential of the PAE-BS as a binder for pigment colouration of cotton fabrics. The work described in this chapter showed the potential of Bunte salt polymers to function as binders for pigment colouration of textiles such as cotton fabrics. However, for future work a thorough focus is suggested on the characterisation of the Bunte salt-terminated polymer and the potential crosslinking mechanism involved in colour application onto the fabrics.

Objective II. Assessing the suitability of polyamide epichlorohydrin (PAE) as a binder material for pigment coloration

A simpler method for the colouration of cotton fabrics involved the use of the commercial PAE solution Hercosett™ 617, without modification, as a potential binder material. It was established that the PAE could be used for the colouration of cotton fabrics with pigments. With the application of colour onto textiles that are purposed to be garments, it is expected that the coloured textiles have an acceptable and appropriate washing, rubbing and light fastness. The colour fastness and fixation of the PAE/pigment formulation on cotton was assessed by subjecting the PAE/pigment cotton fabrics to laundering tests according to the ISO 105-C09 standard. Satisfactory results were obtained and supported by colorimetric data of the fabrics before and after washing. Considering the purpose of the ISO 105-C09 test is to simulate multiple domestic/commercial laundering cycles, it may be concluded that Hercosett™ 617 is suitable to function as a binder material in pigment padding of cotton for the purpose of garments. KES-F analysis showed that the application of the PAE/pigment formulation at the relatively high levels used in this study, imparted a stiffer handle to the fabrics, which may not be appropriate for the use of the padded fabric in garments with regards to comfort.

Objective III. Stripping of the binder/pigment formulation from cotton fabrics

In order to remove the fixed PAE/pigment formulation from the cotton fabrics, ʻʻstrippingʼʼ tests were carried out using potassium persulphate or Kybreak™ 500, a commercial re-pulping agent, as described in Chapter 5 and 6. Initial stripping tests showed that Kybreak was superior in comparison to potassium persulphate alone in its efficiency for the removal of PAE and recovering white cotton fabric. These initial stripping studies used a relatively high concentration of the stripping agent of 30 g/L. Considering the aim was to design this colouration method for commercial purposes, it is desirable to reduce the chemical concentrations in order to minimise the costs and potential deleterious effects on the fabric properties. A more thorough investigation showed that the Kybreak stripping method was successful down to a minimum concentration of 1.25 g/L Kybreak with a stripping time of 120 minutes or by using 2.5 g/L Kybreak with a stripping time of 60 minutes. Stripping appeared to be successful in the degradation of the PAE and to allow removal of most of the colour from the fabric. Some pale colour remained on the cotton fabric, and therefore required a further decolorising treatment. The methods tested included a ISO 105 C09-based washing method, a reductive bleaching method using the commercial reductive bleaching agent Bleach IT, and a sequential reductive bleaching/soaping method using a simple solution of sodium carbonate and Hostapal NIN following reductive bleaching. The most satisfactory result was obtained by the sequential Kybreak stripping/bleaching/soaping method, where the stripped or recovered fabric had colorimetric-, extensibility-, shear- and bending properties similar to that of washed white cotton fabric.

7.2 Suggestions for Future work

The work described in this thesis demonstrated the potential for using a commercial PAE solution as a binder material for the pigment dyeing of cotton fabrics. Additionally, a method for the removal of the binder/pigment system was developed. The focus of the work was to simply investigate the fixation and removal of the PAE as a binder material. Future work should include refining of the application and removal methods and evaluation of the costs associated with this potentially commercial technological application.

7.2.1 Producing Binder Materials from Renewable Resources

It is highly recommended that further investigation is carried out into the use of wool as a potential bio-based resource to function as a binder material. For the development of a circular colouration and colour removal method, it would be expected that the resources are renewable. Waste keratin-rich materials such as wool could be of excellent use, potentially replacing synthetic non-renewable resources. Characterisation of the Bunte-salt terminated polymers and finetuning of the process variables as well as ensuring the resulting solution stability are highly recommended prior to application onto fabrics. Additionally, it is recommended to study the potential of applying these polymers onto fabrics using an eco-friendly method such as inkjet printing.

7.2.2 Colour Levelness

Since the thesis work was mainly focussed on the suitability of the PAE as a binder material and its subsequent removal, no consideration was given towards uniform colour appearance on the coloured fabric. Unfortunately, the mixer used in this work was ineffective in fully dispersing the pigment in the polymeric binder and gave rise to the visual unevenness. A new mixer has now been purchased will provide the ability to produce homogenous pigment dyeing/print formulations. In addition, effective dispersion of the pigments could be improved with other auxiliary agents such as anti-migrants. An optimised pigment solution may be identified through an investigation into the preparation of the padding liquor and of the padding and curing process, which may include the addition of auxiliary agents or adjustments of viscosity, choice of pigment, pigment concentration, binder concentration, and padding and curing conditions.

7.2.3 Fabric Handle

The application of the PAE/pigment formulation onto cotton fabric imparted a stiff handle to the fabric. This is highly undesirable when aiming to use this method of colouration for garments. The rigidity of the PAE/pigment formulation may be influenced by a variety of factors. An investigation into the composition of the padding liquor including the addition of a softener, the percentage of wet pick-up due to padding and the degree of crosslinking of the PAE may allow improvement of the fabric handle of the padded fabric.

7.2.4 Continuous Colour Application and Removal

The work described in this report involved a single colour application and removal. Ideally, the process can be carried out with other colorants to allow a universal reuse of the fabric. It would be of great interest to investigate the potential of the fabric to be coloured and stripped according to the established stripping sequence, before colour build-up and/or fabric degradation occurs. The analysis of degradation of the cotton material could involve testing the mechanical properties such as measuring the tensile strength of the treated fabrics. Additionally, dissolution of the cotton fabric in copper(II)ethylenediamine could be tested to calculate the limiting viscosity number and the degree of polymerisation of the material as an indirect measurement of degradation of the cellulosic material as well as for the assessment of dissolution potential of the cotton fibres for chemical recycling.

7.2.5 PAE Crosslinking and Degradation

The fixation and removal of the PAE/pigment formulation onto and from cotton was indirectly assessed through colorimetric analysis and FT-IR analysis. However, these analysis methods neither allow exact assessment of the crosslinking mechanism of the PAE nor of the efficiency of the stripping sequence on the degree of degradation of the PAE. Therefore, it could not yet be concluded what the fixation mechanism of PAE was or to what extent the PAE had been removed from the cotton fabrics after stripping. It is suggested to analyse the PAE resin to specify the components and accordingly characterise the PAE and PAE/pigment films, and the padded and stripped fabrics. Methods for this may include liquid ^{1}H and ^{13}C-nuclear magnetic resonance (NMR) and colloidal titration for determining the AZR content and degree of polymerisation of PAE (Obokata and Isogai 2004; Obokata and Isogai 2005). Furthermore, dynamic mechanical thermal analysis (DMTA) could provide additional insight of the crosslinking of PAE when assessing PAE films (Siqueira 2012). For the analysis of PAE applied onto fabrics, FT-IR, and X-ray photoelectron spectroscopy (XPS) could be useful for assessing the presence of the functional polymer before and after stripping.

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