Multifunctional Textiles from New Zealand Wool Coloured with Silver or Silver Halide Nanoparticles

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**A thesis submitted to Victoria University of Wellington
in fulfilment of the requirements for the degree of
Doctor of Philosophy
in Chemistry**

**Victoria University of Wellington
2009**

ABSTRACT

Significant opportunities exist for the development of innovative multifunctional textiles for high value market applications. Composites that combine the inherent properties of their all precursor components in a synergistic manner in particular are sought after. Thus the unique chemical and physical properties of silver or silver halide nanoparticles are combined with the traditional properties of wool, thereby producing an innovative multifunctional composite. The prepared wool - silver or - silver halide nanoparticle composites retain the elasticity, thermal insulation and softness of the wool, whilst the colour, conductivity and antimicrobial properties owing to the nanoparticles are also incorporated. Due to the multi functions of silver the resulting high quality, high value product has numerous applications within the fashion and interior furnishings industries. The wools employed for the preparation of wool - silver or - silver chloride nanoparticle composites are merino wool and crossbred wool. Merino wool provides the main focus of the research.

The experimental approach for the colouring of merino by silver or silver halide nanoparticles follows a novel and proprietary approach. The preparation of wool - silver nanoparticle composites includes two different procedures: 1) the synthesis of nanoparticles in the presence of wool fibres, using an external reducing agent/stabilising agent (trisodium citrate (TSC)), with the *in situ* binding of nanoparticles to the surface of the fibre; and 2) the synthesis of nanoparticles in the presence of the merino wool substrate, using the reducing nature of wool, with the *in situ* binding of nanoparticles within the fibre. Merino wool - silver nanoparticle composites range in colour from very pale yellow, through gold to tan and brown. The successful preparation of wool - silver halide nanoparticle composites includes the *in situ* precipitation of nanoparticles within the wool fibre. This is accomplished by doping the wool, with one of the halides, Cl^- , Br^- or I^- , prior to treatment with a silver containing solution. The colour of merino wool - silver halide nanoparticle composites can be tuned from pink to peach to purple.

The colour of the wool - silver or - silver halide nanoparticle composites is due to surface plasmon resonances, i.e. the interaction of electromagnetic radiation of visible

light with the nanoparticles. The reflected colour is dependent upon the size and shape of the nanoparticle, in addition to the refractive index of the stabilising agent surround the particle. The refractive index of silver chloride or silver bromide differs to that of the reducing/stabilising agent implemented, TSC, or merino, and thus the reflected colour is altered. The colour of silver iodide nanoparticles appears to be due to the interaction of light with the formed nanoparticles themselves and not due to the formation of silver nanoparticles within the silver iodide nanoparticles. In addition to the colour being measured by UV-vis in reflectance mode, the characterisation of the hues of the prepared composites were monitored by obtaining CIE L*, a*, b* values via the HunterLab Colourquest.

The morphological characterisation of merino wool coloured by silver or silver chloride nanoparticles was undertaken using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). When merino wool - silver nanoparticle composites are prepared using an external reducing agent, the formed nanoparticles predominantly bind to the wool fibres surfaces only. When the reducing nature of wool is used for composite preparation, nanoparticles are formed within the fibre and are dispersed throughout the fibres core, with few being present on the surface. Comparable studies of merino wool - silver halide nanoparticle composites showed that silver halide nanoparticles are formed and stabilised just below the fibres surface. The confirmation of silver or silver halide species within the prepared composites was undertaken using energy dispersive spectroscopy (EDS), scanning transmission spectroscopy (STEM), x-ray diffraction (XRD) and x-ray absorption near edge spectroscopy (XANES).

Colourfastness tests to washing, rubbing and exposure to chlorinated swimming pool water were undertaken to assess the robustness of the prepared composites in terms of their colour. These tests indicate that the colours of both merino wool - silver and - silver chloride nanoparticle composites are very stable. The leaching of silver during the washing process was noted to be insignificant, suggesting a strong and stable bond between the fibre substrate and the nanoparticles. X-ray photoelectron spectroscopy (XPS) was used to elucidate the chemical bonding between the wool fibre substrate and the silver or silver halide nanoparticles.

The colourfastness of merino wool - silver or - silver halide nanoparticle composites to light however, was not observed. When exposed to UV light for extended periods, a distinct change in colour occurs. Silver nanoparticle composites lighten considerably, whereas their silver chloride nanoparticle counterparts are noted to become grey in their colour. XPS was used in an attempt to determine what leads to the discolouration of the composites. Further research is required however, in order to reduce or halt the colour degradation of merino wool - silver or - silver chloride nanoparticle composites. Silver iodide nanoparticles, on the other hand, show great potential as colourants for wool, exhibiting stable colours over a long time period to light.

A range of desirable colours are obtained through the colouring of wool by silver or silver halide nanoparticles. These nanoparticles are strongly bound to the fibres and thus the colours are stable to washing and rubbing, exhibiting insignificant leaching of silver during such processes. Additionally, the prepared silver and silver halide nanoparticle composites tested positive for their antistatic properties, and their antimicrobial activity, providing a high value multifunctional material. Numerous applications within fashion and interior furnishing industries are therefore apparent. However, the evident setback for applications in these fields is the colour instability to light of silver, silver chloride and silver bromide nanoparticles, and thus further studies are required to eliminate this problem. Alternative options exist for the exploitation of the photosensitivity of silver halide nanoparticles within the merino wool composites, or the possibility of using silver or silver halide nanoparticles in combination with other strong dyes for the production of coloured woollen fabrics.

ACKNOWLEDGEMENTS

Firstly, I would like to express my thanks to my supervisor Professor Jim Johnston whom without such guidance and encouragement this project would not have been possible. You have acted as a director, a mentor, a friend, and have fostered me to become the specialist in my field that I am today. I have gained so much knowledge and accomplished so many things, which I never imagined would be achievable. I would also like to make special acknowledgment of Dr. Thomas Borrmann, whose aptitude to always make time for my problems I have much appreciated. The past three years have been invaluable; both challenging and very much rewarding. I look forward to new and exciting challenges in the future.

Relating to proposal writing for synchrotron beamtime and the acquiring and analysis of synchrotron radiation data, I would like to thank Dr. Bridget Ingham from the New Zealand Synchrotron Group. Her knowledge sharing and enthusiasm to help has been imperative for the successful understanding of the prepared merino wool - silver or - silver chloride nanoparticle composites. I would also like to give my thanks to Dr. Aaron Marshall from Massey University, Palmerston North, whom kindly ran synchrotron radiation XANES spectroscopy at the Photon Factory, Ibaraki, Japan, and to Dr. Kia Wallwork, whom oversaw the reactions undertaken on the powder diffraction beamline at the Australian Synchrotron.

Relating to processing the coloured wool after preparation, I would like to thank Dr. Peter Ingham and Steve McNeil from AgResearch, Christchurch, for facilitating the spinning of coloured crossbred wool from fibre to yarn, and also to Stephen Parsons from Wools of NZ Ltd, Ilkley, United Kingdom for the subsequent weaving into carpet samples. To Jo Reeve and to Janet Clark, thank you for all your time and effort in the respective spinning and weaving of coloured fine merino. It was very much appreciated. I would also like to mention Steve McNeil from AgResearch again for organising the numerous colourfastness tests on the prepared composites to be undertaken.

To all of my research group, both present and past, but in particular to: Aaron, Kerstin, Carla, James, Michael, Mathew. Also to my good friend and PhD peer, John. Thank you for acting as ‘sounding boards’, discussing/providing ideas and for being so much help with my multitude of questions. You have all been great company in the lab and within the SCPS community. I would also like to thank all the SCPS general staff, especially Jackie and Teresa, Sally and Lisa for their respective generosity of lending lab equipment and for the efficient running of stores. Additionally, a special mention would like to be made to David Flynn, whose time and effort spent preparing resin sections of composites and assistance on both the SEM and TEM instruments was very much appreciated.

To my wonderful family: Mum, Dad, Georgia, Matai and Annette, and to my fantastic friends René, Melissa, Rose, Chloé and Carrie. Thank you all so much for being there for me and showing a true interest in my research. You have listened to me go on about how wonderful merino wool coloured by silver nanoparticles is, as well as putting up with all my whinges and moans about the difficulties of life as a PhD student. A special mention would also like to be made to my best friend and companion René. You have shared the ups and downs with me over the past eight years of study and have always, always been so supportive. I just cannot thank you enough.

Finally, I would also like to acknowledge funding provided by the Bright Futures Top Achiever Doctoral Scholarship, the Victoria University of Wellington Postgraduate Scholarship for PhD Study, the Victoria University of Wellington PhD Submission Scholarship and the Curtis-Gordon Research Scholarship in Chemistry. I would also like to thank the New Zealand Synchrotron Group for funding the work undertaken at the Australian Synchrotron, and the New Zealand Postgraduate Study Abroad Award for providing financial assistance to attend an international conference.

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1 INTRODUCTION

1.1 Background

The development of new clothing products based on composite materials of textile fibres and nano-structured materials have become of increasing interest, within both academic and industrial sectors ¹⁻³. A wide range of nanoparticles and nanostructures exist and thus have great potential to be immobilised on fibres, subsequently imparting the functionality of the nanostructure to the final clothing product. Recently, much interest has been given to the development of ‘clean textiles’ through the surface modification of textile fibres with either anti-stain or self-cleaning coatings ^{4-7,2}. In the first approach, anti-stain coatings can be prepared by the deposition of a fluorinated layer ⁵ or through the use of coatings which roughness mimics the well-known lotus flower effect ^{6,7}. Self-cleaning surfaces have been designed through the use of titanium dioxide nanoparticles, for example, that can act as a photocatalyst under UV light ^{4,2}. In conjunction with the development of self-cleaning surfaces, other nano-textile applications have also been developed which include, but are not restricted to, antibacterial ^{8,9}, anti-static ^{10,11} and electronic or sensor properties ¹²⁻¹⁵. Numerous methods may be implemented for the surface modification of fibres with nano-structured materials. This includes the blending of nano-structured materials in a polymer matrix before the spinning of fibres ^{16,17} or the coating of fibres by the desired functional materials through chemical attachment to the fibre surface ¹⁸.

The main challenge in the development of multifunctional textiles, which are themselves composites, is maintaining or enhancing the desired properties of the combined components while eliminating or reducing their limitations. Materials that can successfully combine and retain the required inherent properties of both or all of the components are therefore desired. Ultimately, improved material performance and/or additional functional properties will be achieved.

For the most part, research in this field has had a major focus on those composite materials in which the base substrate is a synthetic textile. Common synthetic fabrics

are nylon (polyamide) ^{19,16,14}, spandex (polyurethane) ²⁰, acrylic (polyacrylonitrile) ²¹, rayon (regenerated cellulosic fibre) ²² and polyester ^{2,23}. Conversely, the use of natural fibres as the substrate, with the exception of cotton, has not been studied as extensively.

Nevertheless, it is believed that the production of such composites can lead to new materials of high value. In particular, by taking advantage of cheap, natural fibres, and by coating with specific nano-structured materials, in particular silver or silver halide nanoparticles, additional optical, chemical, electrical and antimicrobial functionality may be added to the fibre substrate whilst retaining the desired mechanical properties. The predominant natural fibre to be utilised will be fine merino wool. Cross bred wool will additionally be utilised. The resultant multifunctional nano-textile composites have application on their own (as textiles and fabrics for apparel and interior furnishings, including carpets etc). Yet it is also possible to incorporate the fibres into other host materials (conventional polymer sheeting and extrusions) thereby adding the combined functionality.

The following introduction will focus on the characteristics and properties of merino wool, and silver and silver halide nanoparticles, as the precursor components for the development of these new and exciting multifunctional textiles.

1.2 Merino and Crossbred Wool

Merino wool has a long history in its woven form as fabrics for apparel and drapery. Today, merino wool is utilised widely by the textile industry for high quality clothing and interior and industrial furnishings and are principally used for high-end luxury goods. Merino is obtained from the wool of Merino sheep (Fig. 1.1) and is a hair-like textile grown on top of the skin. Merino sheep were the first breed of sheep to be introduced to New Zealand by Captain Cook in 1773, and as such are found in abundance in New Zealand. It is the oldest and most numerous breed in the world, thought to have originated from Spain or North Africa. Figure 1.2 shows merino wool in its shorn fleece and spun yarn forms. Merino wool fibres are typically less than 25 micron in diameter. Based upon the diameter of the fibre, merino wool is divided into five different groups. Strong (broad) wool is typically 23 - 24.5 micron in diameter, with medium, fine, superfine and ultra fine wool being 19.6 - 22.9, 18.6 - 19.5, 15 -18.5, and 11.5 - 15 micron in diameter respectively ²⁴. The fine diameter of the fibre gives rise to the soft handle of merino wool.

Figure 1.1: Merino sheep.

Figure 1.2: Merino wool in its: a) shorn fleece and b) spun yarn forms.

When a fine wool sheep breed, such as merino, is mated to one of the British long-wool breeds, the resulting offspring is referred to as a crossbred sheep. The crossbred sheep breed combines the mutton qualities, early maturing and high lambing percentages of the long wool breeds with the high wool production of the fine wool sheep breed. Typical crossbreeds are romney marsh $\times$ merino, border leicester $\times$ merino and dorset horn $\times$ merino. Drysdale, perendale, coopworth and corriedale are names of crossbred sheep breeds which have been developed and become popular in New Zealand. The fibre diameters of crossbred wool are greater than that of merino wool, with the majority of crossbred sheep breeds producing wool in the 25 - 40 micron range. The end uses for wool 25 - 32 micron, referred to as mid-micron crossbred wool, are typically interior furnishings such as upholstery and curtain fabrics. To a lesser extent, crossbred wool is also used for medium-weight outerwear and bedding items ranging from blankets, duvets, pillows, mattress overlays, linings and fillings. Wool 33 - 40 micron is most often used in the carpet industry. Figure 1.3 shows crossbred wool in three forms: that of the fleece of the sheep, the shorn fleece and in their woven form as interior furnishings.

Figure 1.3: Crossbred wool: a) Perendale is an example of a New Zealand developed crossbred sheep breed; b) Mid-micron crossbred wool in its shorn fleece form; c) Crossbred woollen textiles in their woven form for interior furnishings.

Today the number of sheep, of all breeds, in New Zealand totals approximately 40.1 million ²⁵; merino sheep make up approximately 6.5%. New Zealand wool makes up a small percentage of merchandise exports, consisting of approximately 3% of the total in 2003. However this figure is a noted decrease from the years following (Table 1.1) ²⁶. This decrease is likely attributable to the reduction in sheep numbers due to declining profits compared to other types of farming. There is an opportunity for additional value to be added to merino wool fibres in their woven fabrics and crossbred wool in carpet form, through the use of chemistry and nanotechnology. The net worth of the commodity would be increased, therefore subsequently increasing the value of exports. Application in alternative areas also becomes available. Examples exist such as for responsive membranes, which are themselves closely woven knits, or the incorporation into polymer or plastic substrates whereby the functionality of the fibre is imparted.

Table 1.1: Wool Exports (\$NZ Million FOB) ^{26,27}.

September Year	Total Wool Sector	Total Merchandise Exports	Wool Sector as Percentage of Total Merchandise Exports
2002-03	817	28,730	2.8 %
2003-04	726	28,922	2.3 %
2004-05	663	29,396	2.1 %
2005-06	685	32,074	1.9 %
2006-07	625	33,105	2.3 %
2007-08	613	40,355	1.5 %

1.2.1 Chemical Structure of Wool

Wool fibres are made up of proteins. Proteins are natural polymers formed by the polymerisation of α -amino acids into long sequences. There are two main types of protein, globular and fibrous. Globular proteins, also known as spheroproteins, are soluble in aqueous media²⁸. Perhaps the most commonly known of the globular proteins is haemoglobin, a member of the globin protein family. However, their isolation is extremely difficult due to the ease in which subtle configurational changes may be induced. Changes to globular proteins may be brought about by, amongst other things, heat, irradiation with ultraviolet light, adsorption, storage, or by altering the pH of the environment. Conversely fibrous proteins, or scleroproteins, are long filamentous protein molecules, found only in animals²⁹. Unlike globular proteins, fibrous proteins are very stable and are insoluble in most solvents. The reason for which will presently be discussed in section 1.2.3.

Merino and crossbred wool, among other mammalian hair such as human hair, belong to a group of fibrous proteins consisting of α -keratins; protein molecules shaped in a helix amongst a complex mixture of proteins with irregular structure. The flexibility and elasticity of merino wool is due to the α -helix which essentially behaves like a spring. Keratin fibres have a characteristically high content of sulfur, mainly present in the form of the disulfide-containing amino acid cystine³⁰. Many other amino acid residues are found in merino wool excluding cystine. These are differentiated by their side chains and are outlined in Table 1.2³⁰. Figure 1.4 provides a schematic indicating the complexity of the primary protein structure of merino wool. The bonding between the amino residues, the cystine linkages and intramolecular hydrogen bonding are responsible for the shaping, setting and characteristics of the different protein fibres. Section 1.2.2 will discuss the physical structure of merino wool in further detail.

Table 1.2: Amino acid composition of wool keratin^{31,32}.

Amino acid	g amino acid per 100 g protein
Wool Keratin	
INERT	
Glycine	6.5
Analine	4.1
Valine	5.5
Leucine	9.7
Isoleucine	0.0
Phenylalanine	1.6
ACIDIC	
Aspartic acid	7.3
Glutamic acid	16.0
BASIC	
Lysine	2.5
Arginine	8.6
Histadine	0.7
HYDROXYL	
Serine	9.5
Threonine	6.6
Tyrosine	6.1
MISCELLANEOUS	
Proline	7.2
Cystine	11.8
Cysteine	0.1
Methionine	0.4
Tryptophan	0.7

Figure 1.4: Protein and bond structure of merino wool.³⁴

1.2.2 Physical Structure of Wool

Typically, α -keratin fibres consist of three essential components: the cuticle, the cortex and the medulla³⁰. The medulla comprises a series of cells, similar to honeycombs, down the length of the fibre that provide air spaces. Two forms of medulla exist, continuous or broken, with broken further classified as interrupted or fragmented (Fig. 1.5). Medullated fibres are lower in density and coarser than non-medullated fibres. As such, non-medullated fibres do not take up dyes or take up dyes irregularly, and thus show up white in the final product, they are generally considered contaminants for apparel end-uses³³. In general the absence of a medulla distinguishes fine wools from other hairs and as such will not be considered further for merino wool.

Figure 1.5: Types of medulla: a) non-medullated; b) fragmented; c) interrupted; and d) continuous.³⁰

The physical structure of an α -keratin fibre is very complex, as is observed schematically in Figure 1.6³⁴. An exterior thin sheath of overlapping cuticle shells surrounds the cortex, consisting of cortical cells. Cortical cells exist as two types, paracortical and orthocortical, with paracortical cells having characteristically higher sulfur contents³⁵. Both cells are long and cigar-shaped, occupying approximately half each of the interior of the fibre. These two types of cells absorb moisture to different extents and hence expand and contract inconsistently. This essentially causes bending of the fibre, which results in a crimp pattern along the length of fibre. The bisected arrangement is generally found to be more pronounced in finer wools and thus consequently have a more defined crimp. The crimp enhances the fibres elasticity and resilience, allowing it to be bent and twisted over 30,000 times without becoming damaged.

The cuticle is the outermost layer of α -keratin fibres, consisting of flat cuticle cells (scales) which overlap similar to roofing tiles. A key function of cuticle cells is to secure the fibres in the skin of the animal. Each cuticle cell points from the fibre root towards the tip, overlapping as such. This gives rise to a larger surface frictional value when a fibre is drawn in the against-scale direction than in the with-scale direction³⁶. It is this frictional difference that helps dirt and other contaminants to be expelled from the fleece.

Figure 1.6: Physical structure of an α -keratin fibre.³⁴

The size and shape of cuticle scales characterise fibres from particular animal types and form the basis of fibre identification^{37,38}. Figure 1.7 gives a visual comparison between the cuticle scale structures of various keratin based fibres³⁹. Of those exhibited, alpaca, cashmere and both the coarse and fine wool fibres are α -keratin fibres. Each has discernable differences in their structures. Silk however is a fibroin protein with a much different morphological structure and cuticle scales are not evident.

Figure 1.7: Comparison of the cuticle structure of various fibres: a) crossbred wool; b) fine wool; c) alpaca; d) cashmere; and e) silk.³⁹

The epicuticle, the outermost membrane of the cuticle shells, is resistant to acids, alkalis, oxidising agents and enzymatic attack. However, unlike cell membranes in living systems the epicuticle of keratin fibres contains little or no phospholipids⁴⁰, disallowing the diffusion of molecules through the fibre's surface. Thus, due to its location on the exterior of the fibre, the epicuticle exerts a major influence on the surface properties.

The epicuticle membrane consists of approximately three quarters protein and one quarter lipid⁴¹. The hydrophobic character of the wool fibre surface is attributable to a layer of fatty acids covalently bound to fibre surface proteins^{42,43}. This quality makes facets of wool fibre processing, such as dyeing, considerably more difficult. Research into the structure of these surface proteins, and the nature of the chemical linkage between them and the fatty acids, has thus been the focus of much research in order to abridge processing^{44,45,42,46-48}.

Alcoholic alkali treatment has been seen to reduce the hydrophobic nature of the fibre^{47,45}. Important textile properties are enhanced by this, such as dye uptake and polymer adhesion^{42,48,44}. In work based on changes to the surface properties of wool induced by potassium *tert*-butoxide, Leeder and Rippon⁴⁸ proposed the presence of a lipid layer called the F-layer covalently bound to the exterior of the fibre's epicuticle by means of ester or thioester bonds. Evans et al.⁴⁶ demonstrated that treatment of wool

with potassium *tert*-butoxide released a fatty acid fraction which contained 71% of an unusual branched chain fatty acid with 21 carbon atoms. The fatty acid was identified on the basis of gas chromatography-mass spectrometry as 18-methyleicosanoic acid (18-MEA).

The epicuticle membrane is 5-7 nm thick and 18-MEA is about 2.8-3.0 nm long. Fatty acid chains are oriented away from the fibre to produce a “polyethylene-like” layer at the fibre surface, thus making the epicuticle resistant to the attack of different agents^{42,45}. As mentioned, the covalently bound lipid layer has a critical role in determining the surface properties of the fibre, which in turn, are important in many fibre-processing aspects. Thus it is often necessary to modify the fibre surface by removal of this layer, either chemically or physically, to achieve the required performance.

1.2.3 The Processing of Wool

The processing procedure of wool from fibre to yarn to woven form typically consists of a number of sequential steps. Initially, the wool must be scoured to remove impurities such as lanolin, sweat and vegetable matter. Following this, three mechanical processing steps are undertaken. The first of these involves the disentanglement and mixing of fibres, forming a continuous sliver. This is achieved by carding the fibres. The sliver is then prepared for spinning by aligning the fibres parallel to one another, through combing and drawing. The third step includes the fibres being spun into a yarn. This is accomplished through the drafting of fibres into a thin strand and inserting a twist. Interlacing the yarns, by weaving or knitting, forms a fabric product from the spun yarns. This is the final step.

Three alternative routes exist within the outlined series of processes, taking scoured wool to the yarn form. These are the worsted system, the semi-worsted system and the woollen system and are outlined in Figure 1.8. Appendix I may be consulted for additional information on terms referred to in this figure. There are similar features between the three systems, however, the routes also have significant differences (Table 1.3). For example, the number of steps required to produce a yarn, and the type of machinery used at each step, are different for each processing system. Additionally, the required route depends largely on the properties of the wool. For fine wools which are destined for high quality apparel, the worsted system is the preferred route. This is the most complex of the three routes. To achieve the required yarn quality, there are generally stringent requirements on the raw material. On the other hand, the woollen system, which is the most common route for coarser wools, can accept a wide range of crossbred wool types. The resulting yarn has quite different properties to a typical worsted yarn, but is well suited for carpets and heavy apparel. Between these two routes is the semi-worsted system. This is essentially a shortened version of the worsted route and produces a yarn that is intermediate in properties between worsted and woollen yarns.

Figure 1.8: The three main processing routes for wool (* indicates optional process).

Table 1.3: Comparison of the three processing routes.

	Woollen	Semi-worsted	Worsted
Wool requirements:	Can handle all wool types, but more suitable for shorter wools rather than very long. Usually a wide range of blend components. All fibre diameters used, from very fine to very coarse. Can use reprocessed wools of all types. Blend cost generally lowest.	Wools should be sound, staple length 75-125 mm, and low vegetable matter content. Usually a limited range of components in blend. Mainly medium fineness wools; 27 - 35 μm . Not suitable for short reprocessed wools. Blend cost higher than woollen.	Requires wools which for their diameter are longer, better style and sounder. Uses similar wools rather than a mixture of types. Mainly fine wools; less than 30 μm , usually less than 24 μm . Wastes never used. Blend cost highest.
Complexity of the processing system	The shortest route with fewest steps, large woollen card has low production rate. Card removes some vegetable matter, but cannot tolerate high levels. Carding is very critical because it sets the yarn count, and is the final opportunity for blending.	A compact, high production system, cheaper to operate than worsted system. Limited ability to remove vegetable matter and short fibres. Carding is less critical because of substantial blending and drafting in subsequent steps.	The most complex route; largest number of steps; card similar to semi-worsted card. Vegetable matter and short fibres removed by combing. Carding is less critical because of substantial blending and drafting in subsequent steps.
Properties of yarn:	Minimal alignment of fibres, many may be hooked. Yarn is hairy - many fibre ends protrude from surface. Yarn is bulky, soft and resilient.	Reasonable degree of fibre alignment. Less fibre ends and loops protrude from surface. Medium bulk and resilience.	Fibre alignment very high, giving most even yarn. Few fibre ends and loops protrude, so least hairy. Low bulk and firm handle.
End product uses:	Suitable for all purposes: apparel, carpets, furnishings.	Predominately carpets and knitwear.	High quality weaving and knitting yarns for quality apparel.

1.3 Silver and Silver Halide Nanoparticles

1.3.1 Silver Nanoparticles

1.3.1.1 Background – Metal Nanoparticles

Traditionally, metals such as silver and gold have been used for monetary, ornamental and jewellery applications in their respective lustrous white and yellow bulk metallic forms. However, if the particle size of either metal is reduced to the nanometre range¹, the conventional metallic colour is no longer observed. Instead a variety of brilliant hues are exhibited due to strong visible absorptions. The concept of creating colour with metal nanoparticles dates back to the Middle Ages when silver and gold in the form of colloids or sols, were unknowingly implemented in ornamental decoration by artisans as colourants for stained glass windows (Fig. 1.9a) and ceramics (Fig. 1.9b) throughout Europe and China.

Figure 1.9: Metal nanoparticles were used historically used in medieval times in ornamental decoration: a) stained glass; b) chinaware.

In the mid 17th century, Andreus Cassius discovered Purple of Cassius, a coated gold colloid, used as a pigment in glass enamel and chinaware. Subsequently, Johann Kunchel perfected the technique of making ruby-coloured stained glass. However, it was not until the work of Michael Faraday in 1856 that it was first proposed that the size of the metal particle gave rise to the colour observed⁴⁹. He postulated that the

¹ By definition, a nanoparticle is a particle in which at least one of its dimensions is less than 100 nm.

colour of ruby glass, as well as aqueous solutions of gold (mixed with either SO_3 or phosphorous), was due to finely divided gold particles of a particular size. Additionally he elucidated the mechanism of formation of colloidal metals and outlined the electrical discharge method for preparing aqueous gold colloids. Faraday's postulate did not have a theoretical framework, but was based on an intuitive understanding of highly reflective metals and scattering processes.

A theoretical explanation for the light scattered from very small metal particles was provided by Mie in 1908; a phenomenon which subsequently became named surface plasmon resonances (SPR)^{50,51}. SPR is a feature that can be attributed to the collective oscillation of conduction electrons as induced by the electromagnetic radiation of light⁵². In conducting materials, the electrons in the conduction band are delocalised. The effect of this is that the electron density is in constant flux. Therefore, when observed at a specific reference point in the material, the electron density appears to oscillate as a harmonic longitudinal wave. The fluctuations in the electron density induce a dipole in the particles electric field. This electron density is regarded as a quasi-particle; a plasmon. Figure 1.10 shows a schematic representation of plasmonic oscillation within spherical, metallic nanoparticles⁵³.

Figure 1.10: Plasmon oscillation in a metal nanosphere.⁵⁴

For incident electromagnetic radiation to couple with plasmon oscillations and instigate the transfer of energy, the energy and momentum of the two waves must be comparable. In an infinite metal, a theoretical material possessing no surface, the plasmons propagate as a longitudinal wave. In contrast, the incident light is a transverse wave, meaning there is no portion of the momentum of photons which is in the same direction as the

plasmons so there can be no coupling. However, when the conductive material has a small surface, the electric field induced by the plasmons is affected. This in turn changes the nature of the plasmon wave motion from being strictly longitudinal to possessing both longitudinal and transverse components. This allows coupling of incident photons with the plasmons. The resonance wavelength of this coupling is referred to as the surface plasmon resonance band (SPRB). The position and intensity of the SPRB is dependent upon a variety of factors, such as the size and shape of the particles, and also their dielectric environment ⁵².

The size of the particle affects the position of the resonance band with the wavelength being a function of the radius. However, in order for photon absorption to occur the surface must be pure, i.e. must have no oxide or sulfide layer. Additionally, as the size of the particle decreases the intensity of the resonance band decreases. This is due to a smaller resonant particle, but also to the damping of the surface plasmon modes through the scattering of conduction electrons on the surface. This follows a 1/radius relationship. The drop in intensity is also accompanied by a broadening of the resonance band.

As previously mentioned, the surface of the material affects the electric field induced by the plasmons of the metal and allows coupling between incident light and plasmon oscillations. A material with a flat surface will exhibit no resonance band. Plasmons will have a strictly longitudinal propagation that cannot couple with light and the electric field will be uniform. Thus the shape of the particle surface is of great importance when determining the presence and position of the SPRB.

In spherical particles a dipole is induced with the interaction of electromagnetic radiation, which oscillates in phase with the electric field of the incoming light. Spherical particles thus display one distinct plasmon band. Non-spherical particles however have a minimum of two plasmon bands. For example, particles such as ellipsoids or nanorods have two distinct plasmon bands present in their absorption spectra, whereas a cube shows six bands. The longitudinal oscillation is very sensitive to the aspect ratio of particles, and as such, slight deviations from spherical geometry lead to both transverse and longitudinal oscillations being observed ⁵⁵. Figure 1.11

offers a schematic representation of the interaction of electromagnetic radiation with spherical and non-spherical nanoparticles⁵².

Figure 1.11: Schematic of the interaction of electromagnetic radiation with a spherical nanoparticle (top) and non-spherical nanoparticle (bottom).⁵²

Finally, the contrast between the dielectric constants of the metal and the medium affect the position of the plasmon band. This is due to the ability of the local dielectric medium to refract incident photons, affecting their velocity and thus their energy. For small spherical particles, i.e. $\lambda \gg$ particle diameter, the dependence of the wavelength of the SPBR on the medium dielectric constant can be found spectroscopically from reflectance and absorbance measurements. It is described by the formula⁵⁶:

$$\lambda = \lambda_p \sqrt{(\epsilon_\infty + 2\epsilon_m)}$$

where λ is the resonance wavelength, λ_p is the wavelength of the bulk plasmon, ϵ_∞ is the high frequency dielectric constant of the metal and ϵ_m is the dielectric constant of the medium. As the dielectric constant of a medium is influenced by temperature, this factor also influences the SPRB wavelength.

In addition to interesting optical effects, metal nanoparticles often show unique and considerably changed physical, chemical and biological properties compared to their bulk counterparts⁵⁷. Synthesis of noble metal nanoparticles for applications such as catalysis, optics, electronics, environmental, and biotechnology is an area of increasing and continual interest⁵⁸⁻⁶⁴.

1.3.1.2 Silver Nanoparticles

Silver nanoparticles themselves have been used mostly for the synthesis of stable dispersions of nanoparticles, which are useful in areas such as catalysis in chemical reactions ^{65,66}, spectrally selective coatings for solar energy absorption ^{67,68}, surface-enhanced Raman scattering for imaging ^{69,70}, and antimicrobial sterilisation ^{71,72,57}. Because of their effective antimicrobial properties and low toxicity toward mammalian cells, silver nanoparticles have become one of the most commonly used nanomaterials in consumer products (104 out of 502 nanoproducts surveyed) ⁷³.

As previously discussed, it is understood that the optical absorption spectra of metal nanoparticles are dominated by surface plasmon resonances (SPR), which shift to longer wavelengths with increasing particle size ⁷⁴. In terms of silver nanoparticles it is well recognised that the absorbance of visible light depends mainly upon both the size and shape of the nanoparticle. The absorption spectra of individual silver nanoparticles have been correlated to the size (40-120 nm) and shape (spheres, platelets, decahedrons and triangular truncated pyramids) determined by TEM (Fig. 1.12 & 1.13) ⁷⁵. Spherical nanoparticles of silver ~40 nm in size absorb light in the blue region of the visible spectrum and thus to the eye appear yellow. Increasing the particle size from ~40 nm to ~90 nm progressively shifts the light reflected from yellow to red. Conversely, triangular pyramidal structures and platelets predominately absorb in the red region of the visible spectrum. As is true for the spherical example given, the colour reflected may be further tuned by controlling the size of non-spherical nanoparticles. For example, by manipulating the size of silver triangular prisms from ~60 nm to ~100 nm to ~120 nm the colour reflected may be respectively altered from purple to blue to green.

Figure 1.12: Correlation between the shape of silver nanoparticles with the colour of light absorbed. ⁷⁵

Figure 1.13: Correlation between size and shape of silver nanoparticles with wavelength of light absorbed.⁷⁵

Additionally, according to Mie theory a single SPR band is expected in the absorption spectra of spherical nanoparticles, whereas anisotropic particles give rise to two or more SPR bands depending on the shape of the particle. The number of SPR peaks increase as the symmetry of the nanoparticles decreases. Thus, spherical nanoparticles, disks, and triangular nanoplates of silver show one, two, and more peaks, respectively⁷⁶.

1.3.1.3 Preparation of Silver Nanoparticles

Many methods for the preparation of colloidal metals have been developed since Faraday's experiments in the 1850s. A summary of the research on the preparation of metal sols following Faraday can be found in the 1951 paper of Turkevich and co-workers⁷⁷. This paper describes in detail synthesis conditions and early electron microscope characterisation of gold sols prepared by the methods of Faraday, Bredig (electric arc between two gold electrodes under water), and Donau (action of carbon

monoxide on chloroauric acid) as well as a number of other methods involving the action of reducing agents on chloroaurate solutions.

These preparations introduce many of the methods used today in preparative metal colloid chemistry. The in-depth studies undertaken by Turkevich yielded a detailed knowledge of the nucleation, growth and agglomeration of metal nanoparticles. This ultimately led to a reproducible preparation method of gold sols with a narrow particle size distribution, in a range of mean sizes (ca. 2-100 nm), via the citrate reduction of HAuCl_4 ^{78,79}. Figure 1.14 offers a TEM image of a monodisperse 18 nm gold colloid prepared by such method⁸⁰.

Figure 1.14: TEM image of an 18 nm gold colloid prepared by the Turkevich method.⁸⁰

Presently a vast number of approaches are employed for the preparation of silver nano-materials. These include but are not limited to the chemical reduction of silver ions in aqueous solutions^{69,81} or non-aqueous solutions^{82,83}, template methods^{84,85}, seeds^{86,87}, electrochemical or ultrasonic-assisted reduction⁸⁸⁻⁹¹, photoinduced or photocatalytic reduction⁹²⁻⁹⁵, microwave-assisted syntheses^{96,97}, irradiation reduction^{98,99}, microemulsion methods^{100,101} and biochemical reduction¹⁰²⁻¹⁰⁴. Solution phase synthesis of metal nanoparticles is, in general, the most popular method for the formation of metal nanoparticles as it allows the greatest degree of control over size, structure and composition⁸⁰.

Colloidal particles, such as silver nanoparticles, prepared in the solution phase have a tendency to agglomerate due to attractive van der Waals forces. In the absence of repulsive forces to counteract this attraction an unprotected sol would coagulate. Thus it becomes necessary to protect them with appropriate stabilisers. In classical gold sols, for example, prepared by the reduction of HAuCl_4 by sodium citrate, the gold nanoparticles are surrounded by an electrical double layer formed by adsorbed citrate and chloride ions and associated counter ions. Figure 1.15 schematically shows the resulting Coulombic repulsion between particles⁸⁰.

Figure 1.15: The attractive and repulsive forces present upon colloidal particles in solution.⁸⁰

Additionally, surfactants or polymeric ligands, such as polyvinylpyrrolidone (PVP), sodium dodecylsulfonate (SDS), cetyltrimethylammonium bromide (CTAB), polyethyleneimine (PEI), poly(acrylic acid) (PAA) or poly(methacrylic acid) (PMAA) may be implemented to counter attractive forces between particles. A variety of reducing agents have been employed for reduction, including electrides, alcohols, glycols and certain specialized reagents such as tetrakis(hydroxymethyl) phosphonium chloride¹⁰⁵.

1.3.2 Silver Halide Nanoparticles

1.3.2.1 Background – Silver Halides

Silver halides refer to a group of compounds formed between silver and one of the halogens. These compounds are commonly used, with great importance, as photographic materials, solid electrolytes and liquid semiconductors¹⁰⁶⁻¹⁰⁸. For example, Calzaferri et al. has reported that thin silver halide layers on SnO₂-coated glass plates could catalyze the splitting of water in the presence of a small excess of Ag⁺ ions in aqueous solution under near-UV illumination¹⁰⁹. In addition, silver chloride is a well known antibacterial agent. It has been known to be used in hospitals for wound dressing applications and as catheter coatings in addition to being mixed with PMMA for bone cement applications¹¹⁰⁻¹¹².

As a group, the silver halides are given the pseudo-chemical notation AgX, where X indicates one of fluorine, chlorine, bromine or iodine. However, for the purpose of this thesis X will refer only to chlorine, bromine and iodine as silver fluoride is an anomaly to the properties of the remaining silver halides. For example, silver exists in the +1 oxidation state in all cases, with the exception of silver fluoride where silver may exist in either the +1 or +2 oxidation state. Additionally, silver halides are known for their very low solubility in water, once again with the exception of silver fluoride. The solubility of silver fluoride is approximately 6×10^7 times greater than AgI (Table 1.4). This difference in solubilities can be attributed to the solvation enthalpy of silver fluoride being abnormally large, in comparison to the remaining silver halides.

Table 1.4: Solubility of silver halides

Compound	Solubility (g/100g H ₂ O)
AgF	1.7×10^2
AgCl	1.9×10^{-4}
AgBr	1.4×10^{-5}
AgI	3.0×10^{-6}

Silver chloride and silver bromide crystallise under normal conditions in the face-centred cubic (fcc) rock-salt (NaCl) lattice structure, a form that is common with the majority of the alkali halides (Fig. 16a). Silver iodide, on the other hand, exists in a hexagonal wurtzite lattice structure at room temperature, with iodide ions arranged in a hexagonal close packed structure and with the silver ions occupying a sublattice of interstitial tetrahedral sites (Fig. 16b).

Figure 1.16: Crystal structures of silver halides at room temperature : a) silver chloride and silver bromide exist in the NaCl lattice arrangement, whereas b) silver iodide exists in the wurtzite lattice arrangement

Silver chloride, silver bromide and silver iodide have ionic semiconductor properties, with an electrical conductivity lying between a conductor and insulator at room temperature. Current transport is governed by intrinsic ionic Frenkel defects; interstitial silver ions and silver ion vacancies within the crystal lattice. Such defects are formed by the movement of a silver ion from a lattice site that subsequently becomes lodged in an interstitial position nearby in the crystal. Both interstitial ions and vacancies may be mobile and so contribute to ionic conduction, however interstitial silver is the high mobility carrier and thus dominates conductivity.

Doping silver halides with ions of different charge may change the defect concentrations and thus the conductivity. For example, if AgBr is doped with a small concentration of CdBr_2 , each Cd^{2+} replaces two Ag^+ ions. The concentration of Ag^+ vacancies is thereby increased and that of interstitials decreased. As the interstitials are

more mobile than the vacancies in AgBr, the initial effect of doping is to decrease the ionic conductivity. However, as the concentration of Cd^{2+} is increased the vacancies become increasingly numerous to dominate the conduction process and so conductivity rises again ¹¹³.

Typical to semiconductors inherent properties, the electrical conductivity of the silver halides increases with rising temperature. Silver chloride and silver bromide remain in the face-centred cubic arrangement with increased temperatures and increased conductivity is due to the greater mobility of silver ions. Silver iodide, on the other hand, undergoes a phase transformation at 420 K converting from the original hexagonal wurtzite structure (β -phase) to a rigid body-centred cubic arrangement (α -phase). The silver iodide α -phase is a superionic conductor and the silver ion conductivity is seen to increase swiftly by about six orders of magnitude above to that at room temperature ¹¹⁴. The high temperature phase of silver iodide contains two silver ions per unit cell distributed over 42 available sites, thus taking an average structure. This structure corresponds to a “liquid-like” state of the silver ions; providing readily available vacant sites to accommodate rapid silver ion motion ¹¹⁵.

1.3.2.2 Photochemistry of Silver Halides

1.3.2.2.1 Photography

The photosensitivity of natural silver salts has been known by scientists for centuries. In 1727, J. H. Schulze became one of the earliest scientists to observe that a mixture of silver nitrate and chalk darkened on exposure to light. In the early 19th century it was found that silver nitrate’s sensitivity could be increased by combining it with a halogen. However, the first photograms which were produced were not permanent and exposure of the entire photogram to ordinary light darkened it entirely.

In the following decades the photographic process was broken down into several components forming the basis of the development of photographic films today. The silver halide, typically microcrystals suspended in a gelatine matrix and applied as a

thin coating on a glass (now polymer base), could firstly be exposed to light. The darkening of the image could then be amplified by an appropriate chemical, a *developer*. The unexposed halide could lastly be removed, *fixing* the image.

Although the photographic processes were being developed following Schulze's discovery, the darkening process of the silver halides was not theoretically understood until the early 20th century. According to the mechanism first proposed by Gurney and Mott in 1938 absorption of a photon by the silver halide promotes an electron from the valence band to the conduction band, forming an electron hole in the valence band. Both charge carriers may recombine or the photo-electron may migrate to a trap in the lattice (either a defect or an impurity centre) ¹¹⁶. Mobile interstitial silver ions in the crystal become attracted to the traps and are consequently reduced to atomic silver. Subsequent photo-electrons and interstitial silver ions migrate alternately to the same trap to enhance the cluster of silver atoms. The positive hole also generated by the electron transfer can migrate to the surface of the crystal, where it oxidises a halide ion to a halogen atom, which can subsequently be removed if some kind of halogen acceptor is in the environment. If not removed, the free halogen may reverse the process by re-oxidising the silver atoms.

Equations 1 and 2 show a schematic representation of silver halides when exposed to light or radiation of an appropriate wavelength.

The silver ion can then combine with the electron to produce a silver atom:

The few silver atoms present in a silver halide grain following exposure act as catalyst in the development process, so that the rest of the silver ions in the grain are reduced to metallic silver.

1.3.2.2.2 Colour

The silver formed through the procedure outlined above is commonly known as photolytic silver and has colloidal dimensions in the nanometre region. With particle sizes less than the wavelength of light, colloidal silver displays interesting optical characteristics due to surface plasmon resonances; the collective oscillation of conduction band electrons (see section 1.5.1.1). The scattered colour from silver nanoparticles is dependent on several factors, including the size and the shape of the particle. The refractive index of the immediate environment the nanoparticle resides additionally affects the reflected colour. For example, if the refractive index, n , of the host matrix is increased, the maximum of the silver absorption band will move to a longer wavelength.

According to Ware, this may account for the purple appearance of silver chloride when exposed to UV radiation, and the lilac hues of highlights of a silver chloride fixed photograph¹¹⁷. It is thought that the purple colour of silver chloride when exposed to UV light arises from silver nanoparticles *c.* 10 nm in diameter being included within the silver chloride crystal lattice, leading to an absorption band centered at 550 nm. The effect of the higher refractive index of the silver chloride matrix ($n = 2.071$) is to shift the absorption band characteristically found at *c.* 390-400 nm in silver hydrosols ($n = 1.0$) to the longer wavelength¹¹⁷. When a silver chloride fixed photograph is treated with thiosulphate, the silver chloride matrix is dissolved leaving the colloidal silver in an environment with a much lower refractive index. Therefore a profound change in colour from lilac to pale yellow occurs. The absorption band returns from 550 nm to the typical silver hydrosol absorption band of 400 nm¹¹⁷.

Impurities present in the gelatine matrix of a photograph will also greatly affect the plasmon absorption band. It has been conveyed in studies that changes in optical absorption are usually coupled with spectroscopic observations of the ligand vibrations by means of the 'surface enhanced Raman effect'. For example, Liu *et al.* noted a red shift of the 390 nm band of a silver sol (yellow) to 510-550 nm due to the surface adsorption of thiolic ligands¹¹⁸. Herne and co-workers observed that the adsorption of aromatic amino acids and dipeptides turn a yellow silver sol pink, but aliphatic amino

acids turn it orange ¹¹⁹. Additionally, Suh and co-workers reported a change in colour from yellow to blue on addition of p-aminobenzoic acid to a silver sol ¹²⁰.

1.3.2.3 Preparation of Silver Halide Nanoparticles

Among the methods utilised for the synthesis of silver halide nanocrystals, the reverse micelle and water-in-oil microemulsion systems are most commonly cited ¹²¹⁻¹²⁵. These preparation methods provide a highly homogeneous product, due to the efficient mixing at the molecular level. Theoretically, if reactants Ag^+ and X^- are respectively dissolved in the aqueous phases of two identical water-in-oil microemulsions, upon mixing, due to collision and Brownian diffusion, surfactant layers will open up and reactants Ag^+ and X^- will diffuse and come in contact with each other, forming an AgX precipitate (Figure 1.17). Alternatively, a silver containing aqueous solution can be introduced in an organic microemulsion that contains a halide releasing material, or vice versa.

Figure 1.17: Schematic representation of the synthesis of using two microemulsions.

The precipitate formed is confined to the interior of the microemulsion droplets and in many cases the size and shape of the particle formed may reflect the interior of the droplet. This is one of the principles utilized in producing nanoparticles using microemulsions ¹²⁶. It has also been suggested that many other factors can influence the

final nanoparticle size, shape and their distribution, such as the number of reagent molecules per reversed micelle, the reversed micelle concentration, and the nature of the solvent medium¹²⁷. This is because a change of these factors may affect the rates of intermicellar material exchange, nucleation and growth. It has also been found that an increase in the reagent concentration leads to an increase of the nanoparticle size. For example, the effect of various parameters on the synthesis of silver chloride nanoparticles by way of microemulsions has been investigated by Husein et al.¹²⁸. Aqueous solutions of silver nitrate were titrated into a dioctyldimethylammonium chloride/n-decanol/isooctane microemulsion. The silver cation reacted with the chloride counterion of the surfactant to form nanoprecipitates of silver chloride contained within the water pools of the microemulsion. It was observed that i) an increase of the surfactant or water concentrations caused an increase of the particle size, ii) an increase in the concentration of silver nitrate led to the formation of more nuclei and consequently smaller nanoparticle, iii) high n-decanol concentration or water to surfactant molar ratio induced destabilisation of reversed micelles and consequently nanoparticle agglomeration and flocculation was observed.

1.3.3 Antimicrobial Properties of Silver Species

It has been known since ancient times that silver has strong inhibitory and bactericidal effects¹²⁹⁻¹³³. Indeed, silver ions and silver-based compounds have shown strong biocidal effects on as many as 650 species of microbes including *E. coli*^{134,135}, *Staphylococcus Aureus*^{136,137}, and HIV-I¹³⁸. Historic examples of silver include the use of solutions of silver salts in the antiseptic treatment of newborn eye infections and in the treatment of burn wounds. Presently, silver-containing agents are implemented in the formulation of dental resin composites^{139,140}, ion exchange fibres¹⁴¹, clinical wound dressings (e.g. silver sulfadiazine)¹⁴² as well as in the coatings of biomedical materials (e.g. silver impregnated catheters)^{134,143}.

Various chemical forms of silver are known to exhibit antimicrobial activities. Silver ions (Ag^+), in the form of silver nitrate solution, is the most typical silver species to exhibit such effects. In addition, tarnished bulk silver has also been reported to actively inhibit the growth of microbes. This activity may be ascribed to its surface oxide layer

and/or release of the Ag^+ species¹⁴⁴. Several proposals have been developed to explain the inhibitory effects of silver ions/metals on bacteria.

It has been proposed that ionic silver will interact with multiple target sites within the cell¹²⁹. The silver cation released is a highly reactive chemical species that binds strongly to electron donor groups containing sulfur, oxygen, or nitrogen. Bacteria generally contain all these components in the form of thio, amino, imidazole, carboxylate, and phosphate groups. It is suggested that silver ions act by displacing other essential metal ions such as calcium or zinc¹⁴⁵. The binding of silver ions to bacterial DNA may inhibit a number of important transport processes, such as phosphate and succinate uptake.

Recently, many studies have offered that silver ions react with microbes by combining specifically with the thiol (-SH) groups of the protein^{146,147}. This in turn hinders the transport of vital cations in the pores of the microbial cell membranes, affecting the electron transfer system necessary for basic bacterial phosphorylation, metabolism and respiration¹⁴⁸. In addition, higher concentrations of silver ions have been shown to interact with cytoplasmic components and nucleic acids^{149,150}.

However, despite the damaging effect silver ions have on fungal, bacterial and viral microbes, studies have revealed that silver deposits are non toxic to human cells *in vivo* and are reported to be biocompatible¹⁵¹⁻¹⁵³. Recent advances have prompted the use of silver in the form of nanoparticles in various biomedical applications. The high specific surface area and high fraction of surface atoms of silver nanoparticles effectively leads to an increased contact area available for chemical reactions to occur. Thus higher antimicrobial activity compared to bulk Ag metal can be expected^{154,147}.

Electron microscopy studies have revealed that the majority of silver nanoparticles became localised in the membranes of treated *E. coli* cells, while some penetrated into the cells (Fig. 1.18)^{134,147}. Studies furthering this work demonstrated through proteomic and biochemical evidence that the pivotal antimicrobial action of silver nanoparticles is equivalent to that of ionic silver. This involves the destabilisation and de-energisation in bacteria through the disruption of the outer membrane components.

As the binding to protein thiol groups is central in the deactivation of microbes it is assumed that silver nanoparticles, like ionic silver, hinder such groups in *E. coli* from further function.

Figure 1.18: Transmission electron micrograph of *E. coli* cell treated with: a) $50 \mu\text{g cm}^{-3}$ of silver for 1 h; and b) enlarged view of the membrane of this cell ¹³⁴.

It appears the only significant difference between silver nanoparticles and ionic silver in their antimicrobial activity is the effective concentrations necessary. Silver nanoparticles prove appreciably more effective than silver ions, as concentrations required for the same results are in the nano-molar and micro-molar ranges, respectively ¹⁴⁷.

Nanoparticles of silver have been immobilised on textile fibres through numerous methods, in order to impart their antimicrobial effects ^{155,9,156,157,137,23,1,158,159}. Synthetic fibres with silver nanoparticles, in general, incorporate prepared nanoparticles with other precursor components in the spinning process. For example, polypropylene – silver nanoparticle composite fibres were produced via the general melt-spinning method using polypropylene chips and silver nanoparticles as the precursors ¹⁵⁶. Alternatively, ultrafine cellulose acetate fibres with silver nanoparticles have been reported to have been prepared by the direct electrospinning of a cellulose acetate solution with small amounts of silver nitrate followed by subsequent photoreduction in order to form nanoparticles ¹⁵⁷.

For pre-woven fabrics, both synthetic and natural, the silver nanoparticles must be attached to the fibre surface, chemically or otherwise. Cotton and polyester fabric composites with silver nanoparticles have been achieved through a padding method¹. Additionally, silver nanoparticles have been immobilised on cotton textiles through boiling the textile in a solution containing silver nitrate, aqueous ammonia solution and isopropanol¹⁵⁹. Information on the presence or nature of a chemical bond between silver nanoparticles and textile substrate however was not offered. Recently, nylon and silk textile fabrics have been coated with silver nanoparticles following a layer-by-layer deposition method¹³⁷. Repeated dipping of the fibres into dilute solutions of poly(diallyldimethylammonium chloride) (PDADMAC) and silver nanoparticles capped with poly(methacrylic acid) (PMA) led to the formation of a film of nanoparticles on the fibre surface possessing antimicrobial properties.

To our knowledge there has been no research undertaken in which silver nanoparticles have been used as multifunctional coatings; whereby the nanoparticles are utilised as both colourants and antimicrobial agents. Hence there is an obvious opportunity gap. The challenge is the control of the colour through the manipulation of the size and shape of the nanoparticles and the subsequent binding to the textile substrates.

1.4 Hypothesis

The aim of the PhD project is to combine the properties of both New Zealand Wool and silver or silver halide nanoparticles, so that the sum of the resulting product is greater than its parts. The silver and silver halide nanoparticles display a spectrum of intense colours and can therefore be utilised as dyes for textiles. In addition, the antimicrobial properties and the intrinsic conductivity of the metal will be transferred. The inherent elasticity, thermal insulation and softness of the woollen substrate will be retained. The combination of New Zealand wool with silver or silver halide nanoparticles will therefore lead to the formation of high value, multifunctional textiles suitable for high quality fashions and interior furnishings.

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2 EXPERIMENTAL METHODS

2.1 Materials

Merino wool and crossbred wool fibres were the two wools used throughout the investigation. 100 % merino wool yarns, in top form, were provided by Ashford Handicrafts, Ashburton, New Zealand. This merino wool has a fibre diameter of 18 to 20 micron, and was processed from fibre to sliver form via a semi-worsted route (refer to section 1.2.3). Crossbred wool was also provided in top form by AgResearch Ltd, Christchurch, New Zealand. The crossbred wool is referred to as mid-micron sized, with a fibre diameter of 32 micron.

All chemicals employed were of analytical grade and used as received unless otherwise stated. Silver nitrate was supplied by Scientific and Chemical Supplies. Sodium chloride and sodium bromide were supplied by Unilab, whereas sodium iodide was supplied by Pure Science. Trisodium citrate was provided by Sigma Aldrich. All other chemicals including ethanol, methanol, hydrochloric acid, acetic acid and potassium hydroxide were obtained from local sources.

2.2 Preparation

2.2.1 Pre-treatments of Textiles

Before preparation of merino wool – silver nanoparticle composites, pre-treatments on the base fibres were undertaken in some cases. Pre-treatments included agitating textile fibres (5 g) in the pre-treatment solution (50 cm³) for 10 minutes with agitation. The pre-treatments typically used were alcoholic potassium hydroxide (0.1 M KOH in methanol) for the preparation of merino wool - silver nanoparticle composites; or hydrochloric acid (0.1 M or 0.001 M HCl) for the preparation of merino wool - silver chloride nanoparticle composites. Following this, textiles were washed thoroughly with distilled water and allowed to air dry before any further treatments with silver-containing solutions were undertaken.

Treatment with alcoholic potassium hydroxide successfully removes lipids and other dirt and contaminants from the surface of merino wool, additionally providing a negative charge at the surface. As mentioned in section 1.2.2, the treatment of wool by potassium *tert*-butoxide removes a significant proportion of the surface lipids, but however also causes some oxidation of the underlying cystine¹. However according to the literature, treatment with potassium hydroxide in methanol equally removes the lipid layer, but causes less sulphur loss and oxidation in the underlying protein. Therefore, this method was viewed superior in terms of washing techniques. As was mentioned above, the alcoholic potassium hydroxide pre-treatment was utilised for the subsequent preparation of merino wool–silver nanoparticle composites. A characterisation of merino wool post treatment with methanolic potassium hydroxide (0.1 M) is provided in section 3.1.2.

The treatment of merino wool with hydrochloric acid allows chloride ions to be absorbed by the fibre therefore becoming doped and additionally providing a protonated surface. This pre-treatment was utilised for the subsequent preparation of merino wool - silver halide nanoparticle composites. Merino wool, after treatment with hydrochloric acid (0.1 M), has been characterised, with the results provided in section 3.1.3. Additional to the mentioned doping with hydrochloric acid, merino wool was also doped with other chloride containing species: sodium chloride, potassium chloride and magnesium chloride (0.1 M NaCl, KCl or MgCl₂ in H₂O), so as to provide comparisons to that of the HCl pre-treatment. A sodium chloride (or potassium chloride or magnesium chloride) solution was pH-adjusted to that comparable to the pH of 0.1 M or 0.001 M hydrochloric acid (pH = 1 or 3) using a non chlorinated acid, typically acetic acid. It should be noted that the pH of the soaking solution could be altered to systematically alter the colour of the resulting silver chloride composite (refer to section 6). Following a relative doping process to the HCl pre-treatment, merino wool was immersed in the chlorinated solution, with agitation, for 10 minutes. Chloride treated merino wool fibres, were then washed thoroughly in distilled water and air dried. The resulting pH of the pre-treated fibres were ~3 and ~5 when immersed in water, for the respective 0.1 M and 0.001 M hydrochloric acid treatments.

For the preparation of alternative silver halide nanoparticle composites, merino wool was doped with sodium fluoride, sodium bromide or sodium iodide (0.1 M NaX in H₂O, where X = F, Br or I), following the same methodology as that outlined above for the doping of merino wool with chloride. The pH of the soaking solution was adjusted to one of 1, 3, 7 or 11 and fibres immersed with agitation for a period of 10 minutes. Similarly, halide-doped fibres were then washed thoroughly with distilled water and air dried before any further treatments with silver-containing solutions were undertaken.

2.2.2 Preparation of Merino Wool - Silver Nanoparticle Composites

The preparation of merino wool - silver nanoparticle or -silver halide nanoparticle composites included two general methods: 1) Preparation of silver nanoparticles in the presence of the merino wool substrate (using external reducing agent) with *in situ* binding; and 2) Preparation of silver nanoparticles in the presence of the merino wool substrate (using reducing nature of wool) with *in situ* binding. Each of the preparation methods will be outlined in further detail as follows.

2.2.2.1 Preparation of Silver Nanoparticles in the Presence of the Merino Wool Substrate, Using an External Reducing Agent, with In Situ Binding

The preparation of merino wool - silver nanoparticle composites was accomplished by the reduction of silver ions to elemental silver, Ag⁺ to Ag⁰, from solution directly onto the fibre surface. The effect of reducing agent concentration, preparation temperature and pre-treatment of the base fibres were the variables of interest. The typical methodology is as follows: merino wool fibres (0.1 g) were heated in silver nitrate AgNO₃ (10cm³, 250 or 500 mg/kg in distilled water) until a constant temperature of 95 °C was obtained. Upon reaching 95 °C, varying quantities of trisodium citrate (TSC) (10, 20, 50 µL, of each 1% w/w or 10% w/w) were added as the reducing agent. Over a 10 minute period silver nanoparticles were generated with simultaneous binding to the surface of the fibres. The resultant composite fibres were washed thoroughly with

distilled water and then subjected to sonication in order to dislodge loosely bound particles.

In order to study the effect of temperature and fibre pre-treatment, each of these components were altered with the effects studied. The temperature was altered from 95 °C to 50 °C. Merino wool pre-treated with KOH and HCl, in addition to no pre-treatment (referred to as untreated) were implemented as the base materials. Colloidal silver particles prepared in the solution phase are predisposed to reduce surface tension by aggregating and thus, in general, it is necessary to protect them using surfactants or polymeric ligands. However, such a protecting agent was not required for this method as, once formed, particles bound to the fibre themselves and consequently became stabilised.

2.2.2.2 Preparation of Silver Nanoparticles in the Presence of the Merino Wool Substrate, Using the Reducing Nature of Wool, with In Situ Binding

It has been established by ourselves that proteins within natural fibres such as merino wool, can in fact act as a reducing agent to facilitate the reduction of silver nitrate to silver nanoparticles with *in situ* binding to the fibre. This is a highly proprietary technology. The preparation of silver textiles when implementing the '*in situ*' method, includes immersing merino wool fibres (0.05 g, untreated or KOH pre-treated (refer to section 2.2.1)) in silver nitrate (5 cm³, 100-500 mg/kg Ag⁺), for up to 72 hours. During this period Ag⁺ ions removed from solution, becoming absorbed onto and within the fibre. Subsequently a reduction of Ag⁺ to Ag⁰ occurs within the fibres, noted by the development of a yellow colour. Following the absorption/reduction period, the resulting silver containing fibres were removed from solution, washed thoroughly with distilled water and allowed to dry at room temperature. The preparation process could be scaled up by a direct scaling of the procedure above.

The temperature at which the reduction reaction was undertaken was altered from room temperature to 50 °C to 80 °C. Elevated temperatures allow for a more rapid uptake of Ag⁺ ions, additionally contributing to an increased rate of reduction of Ag⁺ to Ag⁰. In a

typical reaction, fibres in the silver solution are heated in a water bath set at 50 °C for 24 hours, exhausting silver from solution and giving rise to corn yellow coloured fibres. The typical solution concentration of Ag^+ implemented is between 100-500 mg/kg, depending on the intensity of the colour required.

2.2.3 Preparation of Merino Wool - Silver Halide Nanoparticle Composites

Merino wool - silver halide nanoparticle composites were prepared via the following typical methodology. Merino wool doped with fluoride, chloride, bromide or iodide ions (0.05 g) were immersed and agitated in silver nitrate (5 cm³) for 15 minutes at room temperature. The chloride pre-treatment predominantly used was that of HCl (0.1 or 0.001 M), however NaCl, KCl and MgCl_2 (0.1 M and pH adjusted between 3 and 11, in the final minute), were additionally implemented (refer to section 2.2.1). Fluoride, bromide, and iodide pre-treatments included 0.1 M NaX in H_2O , where X = F, Br or I, similarly pH adjusted to 3, 7 or 11. During the 15 minute soaking period in the silver solution, a micro-precipitation of AgX occurs. Fibres were then removed from solution, washed thoroughly with distilled water and allowed to air dry in natural light. The preparation process could be scaled up by a direct scaling of the procedure above.

When being removed from the silver solution, silver chloride- and silver bromide-textiles are white. A purple colour slowly develops, usually over 24 hours at room temperature, due to the formation of silver nanoparticles within the silver chloride matrix present in the composite. The nanoparticles are formed due to a UV-induced reduction from Ag^+ to Ag^0 and will be discussed in further detail in section 6.8.2. The colour of silver chloride and silver bromide composites can be tuned by altering the pH and concentration of the initial pre-treated fibres. For silver iodide-textiles, a colour change to vibrant yellow occurs almost immediately after I⁻ doped fibres are placed into silver nitrate. Unlike silver chloride and silver bromide no further colour development occurs with silver iodide textiles with exposure to UV light. The reason for this will also be considered in section 6.8.2.

Shorter soaking times in the silver solution, and at room temperature, were the preferred parameters for the preparation of silver halide textiles for crisp clean colours. Increasing the soaking time or temperature allows the competing reduction reaction of silver by merino wool within the textile fibres to additionally take place. This leads to murky greys and browns to form, for the case of silver chloride and bromide, due to the combination of purple and yellow.

2.3 Characterization

2.3.1 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is an important characterisation technique for studying the morphologies the natural fibres and synthetic fabrics alone, and in comparison to their silver or silver halide nanoparticle composite analogues. Individual fibres were mounted on aluminium specimen stubs with double-sided carbon adhesive tape and sputter coated, first with a platinum layer and then carbon in order to reduce a build up of charges on the surface of the sample. The use of a JEOL 6500 F, a field-emission gun scanning electron microscope, enabled the samples to be viewed at sequential magnifications. Images were taken at varying positions so that uniformity within the sample could be determined.

Energy dispersive spectroscopy (EDS) was utilized to study the distribution of certain elements on the surface of the fibre. In addition, end on analyses of silver (halide) nanoparticle–natural fibre composites was undertaken in order to determine the distribution of elements throughout the core of the fibre. Composite fibres were sandwiched between carbon tape, frozen in liquid nitrogen and subsequently sliced with a scalpel, giving a surface of fibre cross sections. For silver nanoparticle-textile composites carbon, nitrogen, oxygen and silver would be mapped for each sample. In the case of the natural fibre composites sulfur would also be mapped. In the case of silver halide composites the concerned halide would additionally be mapped.

2.3.2 Transmission Electron Microscopy

Transmission electron microscopy (TEM) is a complementary characterisation method to SEM as it allows for greater spatial resolution. Thus nanoparticles and nano-structured materials that are too small to be viewed on the SEM may be studied. TEM analyses of merino wool–silver nanoparticle composites were undertaken on a JEOL 2011 high-resolution instrument with a LaB₆ filament operated at 200 kV. Due to the organic nature of merino wool, composites required dehydration and the embedding in resin to allow for TEM analysis. The resin used had a 54:32:12:1 Procure 812:NMA:DDSA:BDMA composition.

Sample preparation of merino wool – nanoparticle composites was undertaken using the following methodology. Merino wool – nanoparticle composites were dehydrated in a series of ethanol solutions, 10 minutes in each (50%, 70%, 90% and 100% consecutively). This was followed by two consecutive 10 minute soak periods in 100% propylene oxide. Composites were then infiltrated with a 1:1 resin:propylene oxide for 1 hour, followed by infiltration with 100% resin overnight. These were then transferred into plastic embedding moulds and cured at 60 °C for 48 hours. Semi-thin (1-2 µm) sections of the embedded composites were undertaken using a glass knife on the Reichert-Jung Ultracut E microtome, so as to identify the area of interest. Ultra-thin (70-90 nm) sections were then cut using a Diatome diamond knife and picked up on copper 200 mesh high transmission grids. The grids were coated with carbon, readied for analysis. Images were taken at varying positions, on various cross sections so that uniformity within the sample could be determined. Elemental analysis and mapping was undertaken on the JEOL 2011 TEM microscope by undertaking Scanning Transmission Electron Microscope (STEM).

2.3.3 UV-Visible Spectroscopy

UV-vis spectroscopy, in reflectance mode, was used as a tool to determine the position of the absorption band in the visible spectrum, thus confirming the presence of silver or silver chloride nanoparticles within the respective merino wool composites and confirming their colour. Composite fibres were stretched across a sample holder

(Fig. 2.1a) and their UV-vis spectra measured in reflectance, due to their opaque nature. Measurements were taken on a Varian Cary 100 Scan UV-vis spectrophotometer using the integrating sphere attachment (Fig. 2.1b). The obtained reflectance spectra were converted to spectra related to the absorbed component of incident light by applying the Kubelka-Munk equation:

$$K / S = (1 - R_{\infty})^2 / 2 R_{\infty}$$

Merino wool fibres are a diffusively scattering medium, and reflectance is affected by both absorption and scattering properties, as described by the Kubelka-Munk equation. R_{∞} stands for the reflectance of an infinitely thick sample, K for the light absorption coefficient and S for the light scattering coefficient.

Figure 2.1: Prepared sample placed in sample holder (a) for UV-vis measurements to be undertaken on the Varian Cary 100 Scan UV-vis spectrophotometer (b).

2.3.4 HunterLab ColourQuest Determination of Colour

Merino wool - silver or silver chloride nanoparticle composites were evaluated with respect to their colour properties by measurements of their spectral reflectance. Measurements were carried out in the visible region using the HunterLab ColourQuest spectrophotometer fitted with a Daylight 65 lamp. Composite fibres were stretched across the light source and the light trap placed behind, so the measurements taken were

for the composite only. CIE L^* , a^* , b^* and 457 nm brightness values were obtained. The L^* coordinate expresses the degree of lightness and darkness (100 = white, 0 = black). The a^* coordinates describes the samples colour between red/magenta (+ve) and green (-ve) and the b^* coordinates describe the colour hue between yellow (+ve) and blue (-ve). The 457 nm value indicates the brightness of the composite (Fig. 2.2).

Figure 2.2: A visual description of L^* , a^* and b^* colour coordinates.

2.3.5 Atomic Absorption Analysis

The quantification of the uptake of silver within the wool fibres for all preparation methods (with and without an external reducing agent) were undertaken by measuring the amount of residual silver in solution following composite preparation, by flame Atomic Absorption (AA). This was carried out on a GBC 906AA spectrometer. Silver solutions were micro-filtered so as to remove any remaining fibres prior to analysis. The analysis methods employed for using the given AA instrument were as recommended by the manufacturer. An air-acetylene flame was used. Calibration of the machine was accomplished using silver standards with the following concentrations: 4, 6, 8, 10 mg/kg Ag^+ .

2.3.6 X-ray Photoelectron Spectroscopy (XPS)

XPS was used in an effort to elucidate the chemical bonding between fibre substrate and silver or silver halide nanoparticles, through the respective bonding energies of the core electrons. XPS utilizes photo-ionization and energy-dispersive analysis of emitted photoelectrons to study the composition and electronic state of the surface region of a sample. In the process a photon is absorbed by an atom in a molecule of a solid, leading to ionization and emission of a core (inner shell) electron. This electron has a defined binding energy that is measured. Because there is a characteristic binding energy associated with each atomic orbital for each and every element, shifts of peak positions in XPS spectra provides information of the nature of chemical bonding.

X-ray photoelectron spectroscopy (XPS) was carried out utilizing the Kratos XSAM800 photoelectron spectrometer at The University of Auckland, New Zealand. Sample preparation included twisting a small number of fibres (up to ~20) and mounting them on a sample bar (Fig. 2.3). The edges of the sample bar were masked so as to reduce charging. The spectra were collected using AlK_{α} radiation, with an overall energy resolution of 15 kV and calibrated to the C 1s line at 285.0 eV. The sample area measured was 300 by 700 μm . The deconvolution of peaks from obtained XPS raw data was accomplished by using either Fityk 0.8.6 or CasaXPS 2.3.13 curve fitting and data analysis programmes. Components present within the peaks of the raw data were assigned using Gaussian/Lorentzian peak fitting.

Figure 2.3: Showing the XPS sample bar, loaded with merino wool - silver nanoparticle composite samples for XPS measurements to be taken.

2.3.7 Synchrotron Radiation X-ray Diffraction (XRD)

X-ray Diffraction (XRD) is an experimental method which studies the scattering of x-rays by crystal atoms which result in a diffraction pattern. By observing the obtained diffraction pattern, information on the structure of the crystal or the identity of a crystalline substance may be acquired. Silver or silver halide nanoparticles attached to the fibre surface of the composite materials are present in very low concentrations. Conventional XRD does not permit silver to be measured at such low concentrations. Synchrotron-based instruments are the only means whereby these limitations can be overcome to give the resolution required to determine and refine precise and accurate structures of the attached nanoparticles.

XRD patterns of textile-silver nanoparticle composites, resulting from each of the methods of preparation, were obtained on the powder diffraction beamline at the Australian Synchrotron. Data were collected in transmission, with a beam size of 5 mm (horizontal) $\times$ 2 mm (vertical) and wavelength 1.0003 Å. Sample preparation included sandwiching composite fibres between two sample holder plates with a hole in the centre with a circular diameter 15 mm. Kapton® tape was utilised as the sample holder windows to ensure fibres were confined to a minimum thickness in the path of the x-ray beam. A photograph of the sample set up is offered in Figure 2.4. Uncoated, pre-treated samples and Kapton® were studied as appropriate reference samples.

The obtained patterns yielded information about the crystallographic structure and chemical composition of silver present on the surface of the textile fibres and as such their relative fractions. In addition, the average crystallite size was able to be calculated by the Scherrer equation from the broadening patterns of the diffraction peaks.

Figure 2.4: Synchrotron XRD sample holder.

2.3.8 Synchrotron Radiation X-ray Absorption Near Edge Structure (XANES)

X-ray Absorption Fine Structure (XAFS), which include Extended X-Ray Absorption Fine Structure (EXAFS) and X-ray Absorption Near Edge Structure (XANES), measures the absorption of x-rays by a sample across the critical energy (the edge) for the photoemission of a core (K or L) electron. XAFS spectra are especially sensitive to the formal oxidation state, coordination chemistry, and the distances, coordination number and species of the atoms immediately surrounding the selected element.

Unlike diffraction-based techniques for studying atomic structure of matter, crystallinity is not required for XAFS measurements, making it one of the few structural probes available for non-crystalline and highly disordered materials. Thus, XAFS, and in particular XANES, provides a complementary way to XPS and XRD in determining the chemical state of silver nanoparticles attached to the fibres surface in addition to suggesting the bonding mechanism between themselves and the fibre substrate.

The XAFS spectrum has three major regions and can be quite complex (Fig. 2.5). The pre-edge region, where the electron has been excited but not emitted, can show features in some elements that can give information on the oxidation state. The XANES region,

up to ~50 eV beyond the edge, where the electron is slow-moving, provides information on the oxidation state of the atom and the local geometry around the atom. In the EXAFS region, up to 1 keV beyond the edge, the electron is fast moving and undergoing single scattering events with neighbouring atoms. It is the EXAFS region that provides detailed information on the local environment of the target atom, in particular co-ordination numbers and bond lengths.

Figure 2.5: X-ray absorption spectrum indicating Extended X-ray Absorption Fine Structure (EXAFS) and X-ray Absorption Near Edge Structure (XANES) regions.

Samples of merino wool coloured by silver nanoparticles of silver chloride nanoparticles were studied by XANES. XANES data was collected by A. Marshall and Prof. R.G. Haverkamp at the Photon Factory (Advanced Ring), Japan, on beamline NW-10A. The ring was operated at 6.5 GeV and approximately 50 mA with the beam monochromated using a Si(311) crystal and focused using a Pt coated mirror. The spot size was approximately 0.5 x 1.1 mm (FWHM) at the sample. Ag K-edge (25.514 keV) XANES were recorded at room temperature in transmission mode with Argon filled ion-chambers.

Merino wool - silver/silver halide composites were pressed into 5 mm thick aluminium holders and sealed with Kapton® adhesive tape. Ag foil (40 micron thick) was used a reference compound in addition to reference compounds of AgNO₃, AgCl, Ag₂O diluted with boron nitride to give a thickness of approximately two absorption lengths. Ag foil was also used as an internal energy calibration standard by measuring its absorption

simultaneously with the sample by placing it between the second and a third ion-chamber. The XANES data were analyzed using the Athena and Artemis software package in the normal manner ².

2.3.9 Colourfastness Testing

Colourfastness measures how permanent the colour of a dyestuff is on fabric. The colour can be adversely affected by a number of factors including exposure to light, to water and to normal wear and tear. Various tests assess how the colour is affected by these different parameters and a numerical value is then established to indicate the degree of colour change. Colourfastness tests to light, washing, rubbing and chlorinated swimming pool water were undertaken on merino wool - silver and merino wool - silver chloride nanoparticle composites in both their top and carpet forms. The merino wool - silver nanoparticle composites tested were loaded with 1.0 wt % silver. Merino wool - silver chloride nanoparticle composites were prepared using 0.1 M HCl pre-treated merino wool with a silver loading of 4.9 wt %. Each of the colourfastness tests are outlined below.

2.3.9.1.1 Colourfastness to Washing

Merino wool coloured by silver or silver chloride nanoparticles in both top and carpet form were tested for their colourfastness to shampooing at AgResearch, Christchurch, using the Australian/NZ Standard 2111.19.2 test. This test evaluates visually and instrumentally the staining of woollen or cotton cloths on textiles. The coloured wool sample (50 mm × 50 mm) was placed in a flat-bottomed dish and covered with two pieces of undyed wool or cotton cloth, then covered with shampoo solution preheated to 40°C. The shampoo consisted of sodium dodecyl benzene sulphonate (1 g/dm⁻³) and lauric monoisopropanolamide (0.2 g/dm⁻³) at pH 7.5. A smooth glass plate was placed on top of the cloths and sample, then a 5 kg weight piece placed on top of this. After 15 minutes, the weight-piece is removed and the dish placed in an oven at 40°C for 1.5 hours. The sample is removed from the dish, hydroextracted, dried and conditioned.

The change of shade in sample colour was monitored, in addition to the degree of staining on the wool or cotton. The samples were evaluated by visual comparison with a set of greyscale fabrics, at 20 °C and 65 % relative humidity, on a scale of 1 to 5. 1 indicates very low colourfastness (maximum colour change), and 5 indicates very high colourfastness (minimum colour change). This is a measure of how much colour is moved from the test sample to pieces of white wool and cotton fabric during the test. According to Australian and New Zealand Standards the pass levels for this test are: change in shade of colour, a minimum of 4; staining on wool and cotton, a minimum of 3.

2.3.9.1.2 Colourfastness to Rubbing

Colourfastness tests to rubbing, in both wet and dry conditions, of prepared merino wool - silver or silver halide carpet samples were also undertaken at AgResearch, Christchurch. The Australian/NZ Standard 2111.19.1 test was implemented on composites in their top and carpet form. The testing device consisted of a rectangular rubbing finger measuring 19 mm × 25 mm, able to be moved in a line along a 103 mm track, with a downward force of 9 N. The finger is mounted with the longer dimension 90 ° to the rubbing direction. The sample (dry or wet) is placed on the base of the device. Ten complete turns of the crank are used to rub the sample. The tested sample is then evaluated for colour change by visual comparison with a set of greyscale fabrics at 20 °C and 65 % relative humidity, on a scale of 1 to 5. According to Australian and New Zealand Standards, for all grades of end use, textiles must show a minimum value of 3 to 4 for dry rubbing and a minimum of 3 for wet rubbing.

2.3.9.1.3 Colourfastness to Chlorinated Swimming Pool Water

Merino wool coloured by silver or silver chloride nanoparticles were tested, via the Australian Standard 2001.4.5 test for their colourfastness to chlorinated swimming pool water. This test includes coloured samples (50 mm × 50 mm) being placed in 300 ml of a solution of sodium hypochlorite with 25 mg/dm⁻³ available chlorine, in a 500 cm³ cylinder. The cylinder is then rotated end over end at 40 revolutions per minute for one hour in a waterbath maintained at 25 °C. The sample is then removed, squeezed, rinsed in cold water, dried, conditioned, and colour changes assessed by comparison with greyscale fabrics ranked on a scale of 1 to 5. The pass level for this test according to Australian standards is 3 or greater

2.3.9.1.4 Colourfastness to Light

Basic colourfastness tests to light were initially undertaken at our home institute. Merino wool coloured by silver or silver halide nanoparticles (0.5 g) were placed in sunlight over periods of up to 3 months, and the colour measured over time by obtaining L*, a*, b* values from the Hunter Lab ColourQuest spectrophotometer. Additionally, 2 g samples of merino wool coloured by silver or silver chloride nanoparticles were prepared (refer to section 6.10.1.2 above) and placed in an envelope. Half of the composite sample was exposed to natural light and half of the sample kept in the dark of the envelope interior. After a period of thirteen weeks the colour of the sample exposed to both light and dark environments were measured by obtaining L*, a*, b* values from the Hunter Lab ColourQuest. Additionally, XPS studies were undertaken in order to determine any change in the chemical species present within the fibres.

Lightfastness tests of merino wool coloured by silver or silver chloride nanoparticles were additionally undertaken at AgResearch, Christchurch, using the ISO test method 105 BO2:1994. In this test, a prepared specimen of fabric is half covered and exposed to Xenon arc lamp operating at 300-400 nm, with a correlated colour temperature of 5500-6000 K, along with a scale of light sensitive blue dyed wool standards designed to fade after different time periods. Only the uncovered part of the test sample will be

subject to any fading. Typical exposure time is 100 hours, which represents approximately four years daylight. The sample temperature is maintained close to 50 °C. The lightfastness is evaluated on a scale of 1 to 8, using the blue dyed wool standards. A score of 1 indicates very low lightfastness (maximum colour change), whereas a score of 8 indicates very high lightfastness (minimum colour change). According to Australian and New Zealand Standards, fabrics should display a minimum rating of 5 to pass this test.

2.3.10 Electrical Conductivity

The DC-conductivity measurements of merino wool - silver nanoparticle composites, prepared using an external reducing agent (refer to section 2.2.2.1), were investigated using the linear four-point probe method (Fig. 2.6). The source potentials are set at 2, 5 and 10 V, with the current being measured at each potential. The thickness (t) of each fibre is measured.

Figure 2.6: The linear four-point probe for measuring electrical conductivity.

The resistivity (R) of the sample is determined using the following formula:

$$R = 2 \times \pi \times t \times P / I$$

Where P is the potential and I is the current. After calculating the resistivity of each fibre sample, via the methods described above, the conductivity (C), recorded in $S\ cm^{-1}$, is determined by taking the reciprocal value of the resistivity.

$$C = 1/R$$

2.3.11 Antimicrobial Testing

In order to characterize the antimicrobial effectiveness of merino wool - silver or silver halide composites, testing at the PTA Microbiology Laboratory of Capital and Coast Health, Wellington Hospital, was undertaken. Composites were predominately tested as individual unspun fibres, however in the case of merino wool - silver nanoparticle composites, prepared using the reducing nature of merino wool, spun yarns were also tested. Samples were placed on agar plates previously inoculated with a bacterial suspension of the pathogen *Staphylococcus aureus* (*S. aureus* ATCC 25923) and incubated for 24hrs to allow for bacterial growth. Merino wool - silver nanoparticle composites, prepared using the reducing nature of merino wool, were additionally tested against *Escherichia coli* (*E. coli* ATCC 25922). All samples were tested against reference samples. These were each of the untreated or pre-treated fibre substrates, fibres treated with reductant only, and silver wire.

Staphylococcus aureus is a Gram-positive spherical bacterium that occurs in microscopic clusters resembling grapes. This type of bacteria was chosen to test against as possible applications of wool fibres exist in garments and dressings and *S. aureus* is a bacterium that is a common coloniser of human skin. Illnesses such as skin and wound infections, urinary tract infections, pneumonia and bacteraemia (blood stream infection) may develop if there is an opportunity for *S. aureus* bacterium to enter the body. *E. coli* is a Gram-negative bacterium, typically found in the lower intestine of warm-blooded organisms (endotherms). Most *E. coli* strains are harmless, but some can cause serious food poisoning in humans. *E. coli* was selected as a representative Gram-negative bacterium so as to express the antimicrobial ability of merino wool - silver nanoparticle composites against both Gram-positive and Gram-negative bacterium.

After incubation, the samples were photographed and analysed visually. Higher magnification images were obtained by optical microscopy using one of either Olympus SZ-ET ($\times 6.7 - \times 40$ magnification), or OL2003-c Metallurgical Microscope with transmitted light illumination ($\times 50 - \times 600$ magnification). Bacterial growth in the vicinity of samples occurred when diffusion of anti-microbial activity from the samples was inadequate to inhibit bacterial replication, or when the pathogen was resistant or not affected by the sample. If anti-microbial activity was sufficient to achieve inhibition, a

circular region of no bacterial growth was noted around the sample. This occurrence is commonly termed a zone of inhibition. The measurements of samples with such areas were noted.

2.4 References

1. Brack, N.; Lamb, R.; Pham, D.; Turner, P. *Surface and Interface Analysis* **1996**, *24*, 704-710.
2. Ravel, B.; Newville, M. *Journal of Synchrotron Radiation* **2005**, *12*, 537-541.

3 CHARACTERISATION OF MERINO WOOL: UNTREATED AND PRE-TREATED

3.1 Untreated Merino

3.1.1 Physical Characterisation and Morphology

When referring to ‘untreated’ merino wool, it indicates that the fibres have had no pre-treatment undertaken on them by myself prior to silver nanoparticle composite preparation. ‘Untreated’ merino wool has however, been scoured to remove non-wool contaminants, carded and processed via the semi-worsted route (refer to section 1.2.3). An image of untreated merino wool is provided in Figure 3.1. The colour of the fibres was measured by obtaining CIE L^* , a^* , b^* values via the Hunterlab ColourQuest instrument. These values are given in Table 3.1. The L^* value refers to the whiteness or blackness of a sample, whereby $L^* = 0$ is pure black and $L^* = 100$ is pure white. The a^* value indicates the samples colour between red/magenta (+ve) and green (-ve). The b^* value indicates the colour of the sample between yellow (+ve) and blue (-ve). Therefore, as the measured a^* and b^* values are very close to zero, 0.29 and 0.30 respectively, and the L^* and 457 nm brightness values are high, 81.32 and 57.96, it confirms the high whiteness of the wool.

Figure 3.1: Untreated merino wool in its a) sliver; and b) fibre form.

Table 3.1: CIE values for untreated merino wool.

L*	a*	b*	457 nm brightness
81.32	0.29	0.30	57.96

From the scanning electron microscopy (SEM) micrographs (Fig. 3.2) of untreated merino wool fibres, the diameter of the fibres can be measured as approximately 18-22 μm . The cuticle plates (scales) of the surface can be clearly distinguished, overlapping one another like tiles on a roof. Increasing the magnification of the image, it is observed that the scales themselves are flat, with minimal deviations. Therefore, the only roughness owing to the surface of the merino wool fibre surface is where cuticle plates overlap. However, given the very fine diameter of the wool this surface roughness does not take away from the softness and handle of the wool fibres.

Figure 3.2: SEM micrographs of untreated merino wool at increasing magnifications.

3.1.2 X-ray Photoelectron Spectroscopy (XPS)

The XPS wide scan spectrum of untreated merino wool is shown in Figure 3.3. Photoelectron peaks at binding energies of 533, 400, 285 and 165 eV are observed. These peaks correspond to the O 1s, N 1s, C 1s and S 2p orbitals respectively, that are to be expected in a spectrum of an α -keratin protein. By measuring the areas under the respective peaks the relative concentrations of the elements present within the untreated merino wool fibres can be calculated. A quantitative elemental analysis of the atomic percentages of carbon, nitrogen, oxygen and sulfur, of which merino wool consists, is provided in Table 3.2. As expected, carbon is the dominant species present comprising approximately 83 atomic % of merino wool. Oxygen, nitrogen and sulfur are shown to make up approximately 11, 4 and 2 atomic % respectively. The carbon to nitrogen

(C : N) ratio is calculated at 20.8 : 1. This C : N ratio will be discussed further in sections 3.2.2. and 3.3.2. when comparisons of KOH with HCl pre-treated merino wool are made.

Figure 3.3: XPS wide scan spectrum of untreated merino wool.

Table 3.2: Elemental composition of untreated merino wool as determined by XPS analysis.

Element	C 1s	N 1s	O 1s	S 2p	C : N ratio
Atomic %	83.1	4.0	10.7	2.2	20.8 : 1

High resolution multiplex spectra of the C 1s, N 1s, O 1s and S 2p peaks are shown in Figures 3.4 to 3.7. Analysis of the high resolution XPS spectra, through the knowledgeable assignment of peaks to the raw data, allows for functional group analysis to be undertaken. The components present within each spectrum were assigned using Gaussian/Lorentzian peak fitting. In the C 1s spectrum, a major peak centred at

285.0 eV is observed with a shoulder present at higher binding energies (Fig. 3.4). The peak at 285.0 eV can be assigned to -C-C, -C-H and -C-S species, corresponding to the hydrocarbon backbone of the covalently bound fatty acids and side groups of the amino acids. Additional to this peak, two other components were fitted to the raw data, centred at both 286.2 and 288.3 eV. The peak at 288.3 eV represents amide species (-NH-CO) and carboxyl groups (-CO-O). The peak present at 286.2 eV corresponds to the presence of -C-O and -C-N which are due to the presence of protein. These assigned peaks are in agreement with XPS studies previously undertaken on wool¹⁻³.

Figure 3.4: XPS spectra of C 1s for raw merino wool.

In the N 1s spectrum a major peak is centred at 400.4 eV with a small shoulder at higher binding energies; 401.9 eV (Fig. 3.5). According to XPS literature pertaining to nitrogen containing species, the peak positioned at 400.4 eV may be assigned to amine, amide and imine (-NH₂, -NH, -N-CO-, =N-) containing species within merino wool, whereas the peak at 401.9 eV can be assigned to oxidised nitrogen⁴⁻⁶. The oxidised nitrogen species are present as an approximate 12 % of the total nitrogen species. The O 1s spectrum similarly consists of a major peak with a small shoulder at higher binding energies (Fig. 3.6). Two components have been assigned, centred at 532.1 and

533.5 eV. The band at 532.1 eV is associated with an average of varied oxygen environments within the proteins of merino wool, whereas the peak at 533.5 eV can be assigned to oxygen with higher oxidation states; notably carboxyl groups (-CO-O). The carboxyl groups make up an approximate 14.5 % of the total oxygen environments present in untreated merino wool.

Figure 3.5: XPS spectra of N 1s for raw merino wool.

Figure 3.6: XPS spectra of O 1s for raw merino wool.

Three components have been assigned to the high resolution S 2p spectrum of untreated merino wool at 163.4, 164.8 and 168.2 eV (Fig. 3.7). The peak centred at 163.4 eV pertains to sulfhydryl (-S-H) functional groups present in the cysteine amino acid. The disulfide (-S-S-) bond of cystine occurs at 164.8 eV. Occurring at higher binding energies, 168.2 eV, is that of oxidised sulfur species and in particular cysteic acid residues (-S-O₃H). The positions of these peaks are in accordance to the literature^{3,7-10}. The predominant sulfur species in untreated merino wool is the disulfide species with untreated merino wool having a ratio of -S-H : -S-S- : -S-O₃H of 1.0 : 2.2 : 0.1.

Figure 3.7: XPS spectra of S 2p for raw merino wool.

3.2 KOH Pre-treated Merino Wool

3.2.1 Physical Characterisation and Morphology

The pre-treatment of merino wool with an alcoholic alkaline solution included soaking untreated merino wool in methanolic potassium hydroxide (0.1 M KOH/MeOH), with agitation, for ten minutes. A visual representation of merino wool pre-treated in this manner is provided in Figure 3.8. The measured CIE L^* , a^* , b^* values, indicate a white fibre with a L^* value of 86.11 and a^* and b^* values very near zero. This is comparable to that of untreated merino wool (Table 3.3). However, it is noted is that the b^* value, which indicates the yellow hues of the fibre, increases from 0.30 to 1.82. When merino wool is subjected to alkaline treatments with extended soaking periods, i.e. thirty minutes, it is noted that the mechanical properties are degraded and the fibres become brittle. An additional yellowing is also observed, with the measured b^* value increasing from 1.82 for a ten minute soaking period to 6.59 for a thirty minute soaking period.

Figure 3.8: Merino wool subjected to immersion in 0.1 M KOH, with soaking periods of:
a) 10 m; b) 30 m.

Table 3.3: CIE values for 0.1 M KOH pre-treated merino wool.

Soaking period in KOH	L*	a*	b*	457 nm brightness
10 minutes	86.11	-0.56	1.82	61.50
30 minutes	79.96	0.01	6.59	54.99

SEM images of merino wool subjected to a ten minute soaking period in methanolic potassium hydroxide, at increasing magnifications, are provided in Figure 3.9. Visually it is observed that the resulting treated fibre is analogous in appearance to that of untreated merino wool (Fig. 3.2). However, when merino wool is subjected to a thirty minute soaking period in potassium hydroxide, SEM micrographs show cuticle damage of the fibre occurs (Fig. 3.9). Bubbling across the cuticle plates is noted (Fig. 3.10a) and plates additionally peel from the fibres surface (Fig. 3.10b). Given the degraded surface and yellowing in colour, this indicates that a soaking period of ten minutes within the alkaline solution is preferable.

Figure 3.9: SEM micrographs, at increasing magnifications, of 0.1 M KOH pre-treated merino wool, with a soaking period of 10 m.

Figure 3.10: SEM micrographs of merino wool pre-treated with a 30 m soaking period in 0.1 M KOH, showing a) fibre surface damage and b) peeling of cuticle plates.

3.2.2 X-ray Photoelectron Spectroscopy (XPS)

The XPS wide scan spectrum of KOH pre-treated merino wool is shown in Figure 3.11. Again, similar to that of untreated merino wool, photoelectron peaks at binding energies of 533, 400, 285 and 165 eV are present, corresponding to the O 1s, N 1s, C 1s and S 2p orbitals respectively. The relative concentrations of elements present within KOH pre-treated merino wool fibres, by measuring the areas under the respective peaks, are offered in Table 3.4. Of particular note, is that the atomic percentage of oxygen within untreated merino wool increases from 10.7 to 13.3 atomic %, post treatment with methanolic potassium hydroxide. The reason for this will be considered further in the following discussion.

The elemental composition of carbon is noted to decrease from 83.1 to 78.8 atomic %. It follows that the C : N ratio is also noted to decrease from 20.8 : 1 to 14.1 : 1. The calculated C/N ratio can be used to indicate the removal of covalently bound surface lipid from the fibre¹. Research has shown that even mild alkaline treatments, especially if carried out in organic solvents such as methanol, leads to a cleavage of the covalently linked fatty acids from the surface of the fibre¹¹:

Therefore, the decrease in the proportion of carbon present and thus the C : N ratio suggests that the majority of hydrocarbon lipids from the surface of the fibre have been removed.

Figure 3.11: XPS wide scan spectrum of KOH pre-treated merino wool.

Table 3.4: Elemental composition of KOH pre-treated merino wool as determined by XPS analysis.

Element	C 1s	N 1s	O 1s	S 2p	C : N ratio
Atomic %	78.8	5.6	13.3	2.3	14.1 : 1

Figures 3.12 to 3.15 show the respective high resolution C 1s, N 1s, O 1s and S 2p spectra for KOH pre-treated merino wool. The C 1s spectrum in Figure 3.12 shows that the proportion of the peak at 285.0 eV, assigned to -C-C-, -C-H and -C-S species decreases substantially from 63.2 % the total carbon species in untreated merino wool, to 34.5 % for KOH pre-treated merino wool. Additionally, the amide (-NH-CO) and carboxyl (-CO-O) carbon contributions for KOH pre-treated merino wool are noted to increase significantly, with the proportion this peak, present at approximately 288.0 eV, increasing from 9.4 to 49.1 %. The amide component at 288.0 eV is associated with the presence of the α -keratin proteins of merino wool, whereas the peak at 285.0 eV is predominantly concerned with the hydrocarbon backbone of the lipid layer. Therefore, additional to the decrease in the C : N ratio as discussed above, these results further indicate that the fatty acid layer originally encapsulating the merino wool fibre has been removed through treatment of KOH.

Figure 3.12: XPS spectra of C 1s for a) untreated merino wool and b) 0.1 M KOH pre-treated merino wool.

All of the spectra relating to N 1s, O 1s and S 2p for KOH pre-treated merino wool show a substantial increase in the shoulder at higher binding energies suggesting an increase in the oxidation state of the respective species (Fig. 13.13 to 3.15). The increase in the oxidised nitrogen, oxygen and sulfur peaks accounts for the increase in the proportion of oxygen as discussed above (Table 3.4). The proportion of the peak owing to oxidised nitrogen within the N 1s spectrum and carboxyl groups within the O 1s spectrum are noted to increase from 12.0 to 28.1 % and 14.4 to 29.4 % respectively (Fig. 3.13 & 3.14). Additionally, a shift in the original positions of these peaks to higher binding energies occurs for KOH pre-treated merino wool when compared to its untreated analogue. The oxidised nitrogen peak is noted to shift from 401.9 to 403.3 eV and the carboxyl group from 533.5 to 535.0 eV. This suggests that merino wool subjected to methanolic potassium hydroxide causes quite a dramatic oxidation of the protein lying under the fatty acid layer, of which merino wool consists.

Figure 3.13: XPS spectra of N 1s for a) untreated merino wool and b) 0.1 M KOH pre-treated merino wool.

Figure 3.14: XPS spectra of O 1s for a) untreated merino wool and b) 0.1 M KOH pre-treated merino wool.

The S 2p spectra for KOH pre-treated merino wool additionally suggests the oxidation of the underlying protein with a significant increase in the proportion of the peak relating to oxidised sulfur, present at higher binding energies (Fig. 3.15). The position of this peak is noted to shift from 168.2 eV in untreated merino wool to 167.6 eV in KOH pre-treated merino wool. However, the full width at half maximum (FWHM) is noted to increase substantially from 1.3 to 4.0. Additional oxidised states of sulfur caused by alkaline treatment may include monoxycystyl (R-SO-S-R) and sulfinic acid (R-SO₂H) and thus their presence would broaden and shift this peak². Unlike in untreated merino wool, the sulfhydryl and oxidised sulfur are the predominant sulfur species rather than the disulphide bond. The ratio of -S-H : -S-S- : -S-O₃H in KOH pre-treated merino wool is calculated at 1.0 : 0.7 : 1.6 compared to that of 1.0 : 2.2 : 0.1 for untreated merino wool. This is likely due to the bond breaking of a large majority of disulfide bonds and their subsequent oxidation.

Figure 3.15: XPS spectra of S 2p for a) untreated merino wool and b) 0.1 M KOH pre-treated merino wool.

3.3 HCl Pre-treated Merino Wool

3.3.1 Physical Characterisation and Morphology

The doping of merino wool with chloride ions included the immersion and agitation of fibres in a hydrochloric acid solution (0.1 M), with a soaking time of ten minutes. Alternatively, merino wool could be soaked in a sodium chloride solution, with an adjusted pH of 3. The resulting chloride doped fibres by treatment with sodium chloride were found to be equivalent to that of the hydrochloric acid treatment. For this reason, only the hydrochloric acid treated merino wool will be discussed in further detail in this section. A visual representation of merino wool pre-treated by hydrochloric acid is provided in Figure 3.16, with the measured CIE L^* , a^* , b^* values

given in Table 3.5. These colour coordinates are once again very similar to that of untreated merino wool (Table 3.1). A high L^* value, and a^* and b^* values very near zero, indicate a fibre white in colour. The whiteness of the fibre however, is not quite as great as that of untreated merino wool. Merino wool pre-treated with HCl has a measured L^* value of 79.34, whereas untreated merino wool is noted to be slightly more; that of 81.32. Additionally, given a negative b^* value, albeit very small, this indicates that the white is a more blue white rather than yellow white. When merino wool is subjected to a thirty minute soaking period in hydrochloric acid the colour is near identical, with all L^* , a^* and b^* values being comparable.

Figure 3.16: Merino wool subjected to immersion in 0.1 M HCl, with soaking periods of:
a) 10 m; b) 30 m.

Table 3.5: CIE values for 0.1 M HCl pre-treated merino wool.

Soaking period in HCl	L^*	a^*	B^*	457 nm brightness
10 minutes	79.34	0.10	-0.50	56.09
30 minutes	79.99	0.23	-0.79	51.06

SEM micrographs of merino wool subjected to ten and thirty minute soaking periods in hydrochloric acid are shown in Figures 3.17 and 3.18 respectively. As with fibres having a ten minute soaking period in potassium hydroxide, fibres soaked in hydrochloric acid for the same length of time (Fig. 3.17), show no discernable differences to that of untreated merino wool (Fig. 3.2). However, after a thirty minute soaking period in hydrochloric acid it is observed that the surface of merino wool fibres becomes eroded by the acid (Fig. 3.18). The areas where cuticle plates overlap are no

longer as clearly defined as the ten minute soaking period, becoming reduced in their height, and the plates themselves are noted to be wrinkled in appearance. This degradation of the fibre surface consequently leads to the fibres no longer feeling as soft to the touch and also appearing slightly crinkled rather than straight. Elemental mapping, undertaken by energy dispersive spectroscopy (EDS), shows that untreated merino wool is successfully doped with chloride ions within a ten minute period soaking in hydrochloric acid (Fig. 3.19). Figure 3.19a provides a secondary electron image (SEI) of a cross section of an HCl pre-treated merino wool fibre, with Figure 3.19b providing the elemental map of that image for chlorine. It is noted that, after the ten minute doping period, chloride is present in even amounts throughout the entire fibre. Therefore, given the above results regarding the successful doping and retention of the fibres original morphology, it follows that untreated merino wool should be subjected to no longer than ten minutes immersion in hydrochloric acid (0.1 M) prior to silver nanoparticle composite preparation.

Figure 3.17: SEM images of raw merino wool after soaking in 0.1 M HCl for 10 m at increasing magnifications.

Figure 3.18: SEM images of raw merino wool after soaking in 0.1 M HCl for 30 m at increasing magnifications.

Figure 3.19: The doping of merino wool with chloride ions following a 10 m soaking period in 0.1 M HCl solution: a) SEI image of a cross section of HCl pre-treated merino wool; b) EDS elemental map of chlorine within the fibre.

3.3.2 X-ray Photoelectron Spectroscopy (XPS)

The XPS wide scan spectrum of HCl pre-treated merino wool is shown in Figure 3.20. Again, the expected photoelectron peaks assigned to O 1s, N 1s, C 1s and S 2p orbitals are noted at binding energies of 533, 400, 285 and 165 eV respectively. Additionally, a very small peak relating to Cl 2p is present at 200 eV due to the doping of merino wool by chloride, through the pre-treatment of merino wool by hydrochloric acid. The relative concentrations of the elements present within such pre-treated fibres are provided in Table 3.6. Apart from the additional presence of chlorine (0.2 atomic %), the elemental composition is noted to be similar to that resulting from the potassium hydroxide pre-treatment process. The atomic percentage of carbon is once more noted to decrease; in this case from 83.1 to 79.7 atomic %. The C : N ratio consequently decreases from 20.8 : 1 to 14.5 : 1. This ratio is comparable to that of KOH pre-treated merino wool which was calculated at 14.1 : 1. The decrease in the C : N ratio indicates that the covalently bound surface lipid is similarly removed from the fibre with hydrochloric acid treatment, but to a slightly lesser extent. There is also an increase in the atomic percentage of oxygen, from 10.7 for untreated merino wool to 12.2 atomic %. Both the removal of the lipid layer and the increase in the proportion of oxygen will be examined in further detail below, when focusing on the high resolution scans of each of the elements present in HCl pre-treated merino wool.

Figure 3.20: XPS wide scan spectrum of HCl pre-treated merino wool.

Table 3.6: Elemental composition of HCl pre-treated merino wool as determined by XPS analysis.

Element	C 1s	N 1s	O 1s	S 2p	Cl 2p	C : N ratio
Atomic %	79.7	5.5	12.2	2.4	0.2	14.5 : 1

The high resolution C 1s, S 2p, N 1s, O 1s and Cl 2p spectra for HCl pre-treated merino wool are provided in Figures 3.21 to 3.25. Much like that observed for the KOH pre-treated counterpart, the C 1s spectrum of HCl pre-treated merino wool sees a decrease in the proportion of the peak at 285.0 eV, assigned to -C-C, -C-H and -C-S species for that of HCl pre-treated merino wool; from 63.2 % to 24.8 %. As was discussed above, this peak is predominantly associated with the hydrocarbon lipid layer on the surface of the fibre. Additionally, both of the peaks at 286.2 and 288.0 eV, related to the protein matrix of merino wool wool below the lipid layer, are noted to increase. The proportion of the peak owing to -NH-CO and -CO-O functional groups, centred at approximately

288.0 eV, increases substantially, from 9.4 to 38.1 %, whereas the peak related to -C-N and -C-O, centred at 286.2 eV, is observed to increase from 27.4 to 37.1 %. The FWHM of the peak is also noted to broaden from 1.8 in untreated merino to 3.3, indicating a greater variety of environments within the HCl pre-treated analogue.

According to the literature wool treated under acidic conditions hydrolyses peptide bonds following the reaction below ¹¹:

This process would therefore contribute to the increase in the proportion of the amide and carboxyl carbon peak with respect to the other carbon peaks owing to HCl pre-treated merino wool. However, the decrease in the C : N ratio mentioned above, together with the decrease in the hydrocarbon component at 285.0 eV and the simultaneous increase in both of the peaks relating to the protein based components of merino wool, centred at 286.2 and 288.0 eV, indicates that the surface fatty acid layer has been completely or partially removed through treatment of HCl.

Figure 3.21: XPS spectra of C 1s for a) untreated merino wool and b) 0.1 M HCl pre-treated merino wool.

The fatty acid lipid layer of merino wool is bound to the wool's surface by a thioester linkage. The literature suggests that after hydrochloric acid treatment on wool, the resultant product has a lipid free (or lipid reduced) hydrophilic surface with the sulfhydryl components (-S-H) oxidised to cysteic acid residues (-S-O₃H), following the reaction below¹¹:

In the S 2p spectrum, an increase in the proportion of the peak owing to oxidised sulfur, present at approximately 168 eV, is noted to increase from 2.7 to 15.1 %, thereby supporting this view (Fig. 3.22). However, instead of the proportion of sulfhydryl groups decreasing, they are noted to increase from 30.2 to 54.2 %. This is likely due to protonation of the fibre under acidic conditions. Again, like KOH pre-treated merino

wool, the sulfhydryl species is the most predominant rather than the disulphide bond, which is the most predominant in untreated merino wool. However, interestingly, despite the literature indicating as such, the sulfur species are not as highly oxidised by hydrochloric acid treatment, in comparison to the KOH pre-treatment. The ratio of -S-H : -S-S- : -S-O₃H in HCl pre-treated merino wool is calculated at 1.0 : 0.6 : 0.3 compared to that of 1.0 : 0.7 : 1.6 for KOH pre-treated merino wool and 1.0 : 2.2 : 0.1 for untreated merino wool.

Figure 3.22: XPS spectra of S 2p for a) untreated merino wool and b) 0.1 M HCl pre-treated merino wool.

The N 1s and O 1s spectra of merino wool pre-treated with hydrochloric acid, both see an increase in the proportion of the peak present at higher binding energies; those species with an increased oxidation state, or those bound to oxygen (Fig. 3.23 & 3.24). Therefore, together with the oxidised sulfur component discussed above, this would account for the increase in the elemental composition of oxygen in chloride doped

merino wool (Table 3.6). The proportion of the peak owing to oxidised nitrogen within the N 1s spectrum and carboxyl groups within the O 1s spectrum is noted to increase from 12.0 to 30.0 % and 14.4 to 31.4 % respectively (Fig. 3.23 & 3.24). This indicates that the treatment of hydrochloric acid to merino wool oxidises the fibre surface, affecting all sulfur, nitrogen and oxygen species.

It is most likely that chloride ions will associate with positively charged entities within merino wool. These would include protonated nitrogen containing species, i.e. protons could protonate -NH_2 groups to form -NH_3^+ in which chloride ions could associate with, much like that of a quaternary amine salt. The position of nitrogen interacting with chloride has been stated to be located at 401.3 eV¹² and thus it is most likely that it would be incorporated within the broad band centred at 400.2 eV (Fig. 3.23). The slight broadening in the peak FWHM from 1.7 to 1.8, from untreated to HCl pre-treated merino wool, may suggest this interaction. A broad peak, centred at 200.2 eV, within the Cl 2p spectrum confirms the presence of chloride within the HCl pre-treated merino wool (Fig. 3.25). According to the literature, the interaction of nitrogen with chloride ions occurs at 197.9 eV and thus would be included in this envelope. However, the broadness of this peak (FWHM of 4.6) indicates that the peak incorporates a number of different interactions and environments, of chloride with positively charged species within merino wool fibres. The raw data owing to the peak in the Cl 2p spectrum is not greatly enough resolved to decipher what other interactions may be taking place.

Figure 3.23: XPS spectra of N 1s for a) untreated merino wool and b) 0.1 M HCl pre-treated merino wool.

Figure 3.24: XPS spectra of O 1s for a) untreated merino wool and b) 0.1 M HCl pre-treated merino wool.

Figure 3.25: XPS spectra of Cl 2p for 0.1 M HCl pre-treated merino wool.

3.4 References

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4 MERINO WOOL - SILVER NANOPARTICLE COMPOSITES: NANOPARTICLES FORMED IN THE PRESENCE OF MERINO WOOL USING AN EXTERNAL REDUCING AGENT

4.1 Physical Characterisation and Morphology

Merino wool - silver nanoparticle composites were prepared by the method outlined in section 2.2.2.1. Silver nanoparticles are formed, using as external reducing agent, in the presence of merino wool and simultaneously become attached. The typical experiment includes the heating of merino wool fibres to 95 °C in a silver nitrate solution, upon which trisodium citrate (TSC) as the reducing agent for the reduction of Ag^+ to Ag^0 and untreated merino wool. Varying quantities of TSC were added as the reducing agent (10, 20, 50 μL , of each 1% w/w or 10% w/w to 10 cm^3 AgNO_3). Over a 10 minute period silver nanoparticles formed, concurrently binding to the surface of the fibres. Untreated merino wool and merino wool, pre-treated with either KOH or HCl, were implemented as the base materials. The physical characterisation and morphology of each of the respective silver nanoparticle composites with each of the substrates will be discussed below.

4.1.1 Untreated Merino Wool

4.1.1.1 Characterisation of Colour

When using untreated merino wool as the base material, the prepared samples range in colour from yellow through to gold, red/brown and finally black/brown (Fig. 4.1). The obtained CIE L^* , a^* , b^* values, representing colour, are additionally offered in Table 4.1. The L^* value expresses the degree of brightness (100 = white, 0 = black). Visually, it is noted that there is a distinct darkening in the colour of the textiles from yellow to brown to black as the volume of reducing agent increases. Therefore the darkening of samples is confirmed by a decrease in the L^* coordinate value with

increasing volumes of TSC. In addition, the 457 Brightness is also noted to decrease from 14.95 to 3.24. The a^* value indicates the sample's colour between red/magenta (+ve) and green (-ve). The reddish tinge in samples appearing red/brown to the eye is confirmed by an increase in the a^* value. The b^* value indicates the colour of the sample between yellow (+ve) and blue (-ve). The b^* value for a yellow sample is measured as 17.08. This value decreases consistently as the change in colour occurs from yellow to brown to black.

Figure 4.1: Untreated merino wool coloured by silver nanoparticles (nanoparticles formed in the presence of merino wool with simultaneous binding).

Table 4.1: CIE L^* , a^* , b^* values of untreated merino wool coloured by silver nanoparticles (nanoparticles formed in the presence of merino wool with simultaneous binding).

Sample	L^*	a^*	b^*	457 nm Brightness
10 μ L, 1 % w/w TSC	54.88	1.47	17.08	14.95
20 μ L, 1 % w/w TSC	41.78	4.56	16.14	7.41
50 μ L, 1 % w/w TSC	32.17	6.19	14.89	6.03
10 μ L, 10 % w/w TSC	29.30	5.49	6.11	4.66
20 μ L, 10 % w/w TSC	25.84	3.57	6.44	3.55
50 μ L, 10 % w/w TSC	24.99	-0.37	3.98	3.24

4.1.1.2 Scanning Electron Microscopy (SEM)

At low magnifications a discernable change in morphology is not readily observed when comparing SEM micrographs of merino wool fibres alone with their silver analogues. However, at increasing magnifications of silver composites it is noted that the nanoparticulate silver coating comprises spheres which wholly encapsulate the fibre (Fig. 4.2 to 4.4). The nanoparticles appear to fuse together to form a coating, which follows the original morphology of the merino wool fibres. As the volume of TSC, used as the reducing agent, increases, the nanoparticulate coating across the merino wool surface becomes less even. This is particularly evident when 50 μL , 10 % w/w TSC is implemented (Fig. 4.4). No longer do silver nanoparticles lie only flush with the merino wool surface. Instead, small areas of agglomerations are noted across the cuticle plates. However, intense sonication did not remove these agglomerations, suggesting particles are strongly bound. At 100,000 times magnification, SEM imaging shows that the size of silver nanoparticles increases with increasing volumes of TSC (Fig. 4.2 to 4.4). An increase in diameter from ~ 15 nm (TSC: 20 μL , 1 % w/w TSC) to ~ 20 nm (TSC: 10 μL , 10 % w/w TSC) to ~ 50 nm (TSC: 50 μL , 10 % w/w TSC) is observed.

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Figure 4.2: SEM images, at increasing magnifications, of a merino wool - silver nanoparticle composite (20 µL, 1 % w/w TSC) indicating the nature of the polymer coating.

Figure 4.3: SEM images, at increasing magnifications, of a merino wool - silver nanoparticle composite (10 µL, 10 % w/w TSC) indicating the nature of the polymer coating.

Figure 4.4: SEM images, at increasing magnifications of a merino wool - silver nanoparticle composite (50 µL, 10 % w/w TSC) indicating the nature of the polymer coating.

4.1.1.3 Transmission Electron Microscopy (TEM)

TEM analysis of cross sections of merino wool - silver nanoparticle composites further confirms the increase in particle size as the volume and concentration of TSC used increases. Figures 4.5 and 4.6 show TEM images of merino wool - silver nanoparticle composites at increasing magnifications, using 20 μL , 1 % w/w TSC and 50 μL , 10 % w/w TSC as the respective amounts of reducing agent. The TEM results are consistent with the average sizes of nanoparticles estimated by SEM. However, TEM provides a more detailed method of measurement, providing precise information on the sizes of individual nanoparticles. When 20 μL , 1 % w/w TSC is used to reduce Ag^+ to Ag^0 , the size of the formed nanoparticle is ~ 10 to ~ 15 nm (Fig. 4.5). The size of nanoparticles prepared by this method is relatively homogeneous. However, when 50 μL , 10 % w/w TSC is used, the nanoparticles formed vary quite considerably in size; from as small as $< \sim 10$ nm, up to ~ 100 nm (Fig. 4.6). The effect the silver nanoparticle size has on the observed colour of merino wool composites will be discussed in detail in section 4.4.

Figure 4.5: TEM images, at increasing magnifications, of a merino wool - silver nanoparticle composite cross section (20 μL , 1 % w/w TSC).

Figure 4.6: TEM images, at increasing magnifications, of a merino wool - silver nanoparticle composite cross section (50 μL , 10 % w/w TSC).

Figure 4.7 provides a TEM image at a lower magnification, expressing again the diversity in silver nanoparticle size when using 50 μL , 10 % w/w TSC as the reducing agent. Larger particles (20-100 nm) are observed on the surface and penetrating up to approximately 200 nm beneath, whereas smaller particles (10-20 nm) are predominantly observed deeper into the fibre. This image shows the overlapping of two cuticle plates. The area in which the cuticle plates meet allows for the ease of infiltration of smaller nanoparticles into the fibre. This area is noted by a more highly populated strip of nanoparticles, extending from the surface of the fibre on the left, horizontally to the right of the image. The number of nanoparticles present in the fibre decreases when moving away from this region and the surface of the composite.

Figure 4.7: TEM image of a merino wool - silver nanoparticle composite cross section (50 μL , 10 % w/w TSC), indicating level of nanoparticle penetration.

When 20 μL , 1 % w/w TSC is utilised as the reducing agent much fewer nanoparticles are formed and thus a reduced amount is observed on the surface of and within the merino wool - silver nanoparticle composite (Fig. 4.8) in comparison to when 50 μL , 10 % w/w TSC is used (Fig. 4.7). Figure 4.8 similarly presents a TEM image whereby two cuticle plates overlap. Nanoparticles, all ~ 10 to ~ 15 nm in size, penetrate up to 150 nm beneath the surface of the fibre, with very few moving deeper within the fibre.

The dark regions along the surface of the composite and where cuticle plates meet indicate higher levels of silver. This is confirmed by elemental analysis by scanning transmission electron microscopy (STEM) (Fig. 4.9). Therefore, as was also seen in Figure 4.7, silver is seen to enter the fibre where cuticle plates meet indicating a facile entry point. However, as quality images at very high magnifications could not be obtained with this sample it cannot be sufficiently concluded whether very small nanoparticles are present in this region or instead exist as unreduced Ag^+ ions. The preparation of merino wool - silver nanoparticle composites, using this method, includes heating merino wool in silver nitrate to 95 °C before adding TSC. Therefore, it is likely that Ag^+ ions were absorbed by the fibre during this period. X-ray photoelectron studies were undertaken in an attempt to distinguish between the ionic and metallic species of silver present within the composites. However, due to the locality of the two species within the Ag 3d spectrum this proved difficult. The XPS studies are outlined in section 4.6.2.

Figure 4.8: TEM image of a merino wool - silver nanoparticle composite cross section (20 μL , 1 % w/w TSC), indicating level of nanoparticle penetration.

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Figure 4.9: A TEM image of the cross section of a wool fibre coloured with silver nanoparticles (20 μL, 1 % w/w TSC), together with the STEM elemental map of Ag.

4.1.2 KOH Pre-Treated Merino Wool

4.1.2.1 Characterisation of Colour

Merino wool - silver nanoparticle composites, prepared using KOH pre-treated merino wool as the substrate, are visually comparable to that of the untreated merino wool - silver nanoparticle composites. The samples range in colour from yellow through to gold, brown and finally black/brown (Fig. 4.10). Yet these colours are not as intensely coloured as untreated merino wool - silver nanoparticle composites. The colour change between samples, with increasing volumes of TSC is also less significant. Table 4.2 provides the CIE L^* , a^* , b^* values representing colour, obtained for merino wool - silver nanoparticle composites using KOH pre-treated merino wool as the base material. When comparing these values to CIE L^* , a^* , b^* values for untreated merino wool - silver nanoparticle composites (Table 4.1), the less apparent colour change for KOH pre-treated merino wool composites is noted. According to L^* values, which express the degree of brightness, with increasing volumes of reducing agent untreated merino wool composites are seen to darken from 54.88 to 24.99 (decrease 29.89), whereas the darkening of KOH pre-treated merino wool composites is from 50.23 to 33.82 only (decrease 16.42). Additionally, when observing the 457 nm brightness value, KOH pre-treated merino wool composites decrease in brightness by a value of 4.81, in comparison to a decrease in brightness of 11.71 for untreated merino wool composites. The reason for which will be discussed further in section 4.4.

Figure 4.10: KOH pre-treated merino wool coloured by silver nanoparticles (nanoparticles formed in the presence of merino wool with simultaneous binding).

Table 4.2: CIE L*, a*, b* values of KOH pre-treated merino wool coloured by silver nanoparticles (nanoparticles formed in the presence of merino wool with simultaneous binding).

Sample	L*	a*	b*	457 nm Brightness
10 μ L, 1 % w/w TSC	50.23	2.35	13.24	12.59
20 μ L, 1 % w/w TSC	48.67	3.04	19.17	10.17
50 μ L, 1 % w/w TSC	37.93	3.71	10.20	7.15
10 μ L, 10 % w/w TSC	34.83	3.77	6.92	6.57
20 μ L, 10 % w/w TSC	34.09	3.24	5.18	6.69
50 μ L, 10 % w/w TSC	33.82	-0.05	0.65	7.78

4.1.2.2 Scanning Electron Microscopy (SEM)

Additional to the colours of merino wool - silver nanoparticle composites resulting from KOH pre-treated merino wool being similar to composites from untreated merino wool, SEM micrograms are also comparable (Fig. 4.11 to 4.13). When low volumes of TSC are used for preparation a fine nanoparticulate coating is observed at high magnifications only (Fig. 4.11). With increasing volumes, this coating becomes more apparent and less even across the fibre surface. As with untreated merino wool - silver nanoparticle analogues the average particle size is observed to increase in size as the volume of reductant increases. However, in comparison to untreated merino wool composites, it appears that fewer particles are generally on the surface and instead of larger particles being spread across the entire surface of the fibre; agglomerations of particles occur predominantly where cuticle plates meet (Fig. 4.12 & 4.13).

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Figure 4.11: SEM images, at increasing magnifications, of a KOH pre-treated merino wool - silver nanoparticle composite (20 µL, 1 % w/w TSC).

Figure 4.12: SEM images, at increasing magnifications, of a KOH pre-treated merino wool - silver nanoparticle composite (10 µL, 10 % w/w TSC).

Figure 4.13: SEM images, at increasing magnifications, of a KOH pre-treated merino wool - silver nanoparticle composite (50 µL, 10 % w/w TSC).

4.1.3 HCl Pre-Treated Merino Wool

4.1.3.1 Characterisation of Colour

When HCl pre-treated merino wool is used for the preparation of merino wool - silver nanoparticle composites, the resulting product is dissimilar to that of composites prepared from untreated merino wool and KOH pre-treated merino wool. Instead of a changing spectrum from yellow to brown to brown/black, the composites vary only slightly in colour, starting from purple/grey and then darkening to purple/grey/brown to purple/black (Fig. 4.14). The corresponding CIE L^* , a^* , b^* values for HCl pre-treated merino wool - silver nanoparticle composites are provided in Table 4.3. With increasing volumes of reductant CIE values relating to a^* remain relatively constant indicating the red hue does not alter dramatically. On the other hand b^* values are noted to increase, indicating a yellow shift. This is visually observed by a shift from purple/grey to purple/grey/brown. The overall slight darkening of the samples is also noted by a decrease in L^* and 457 nm brightness values. When 50 mL, 10% w/w TSC is used as the reductant, in addition to following the decreasing trend for L^* and 457 nm values, both a^* and b^* values change quite significantly. This indicates a change from purple/grey to purple/brown to purple/brown/black.

Figure 4.14: HCl pre-treated merino wool coloured by silver nanoparticles (nanoparticles formed in the presence of merino wool with simultaneous binding).

Table 4.3: CIE L*, a*, b* values of HCl pre-treated merino wool coloured by silver nanoparticles (nanoparticles formed in the presence of merino wool with simultaneous binding).

Sample	L*	a*	b*	457 nm Brightness
10 µL, 1 % w/w TSC	29.77	4.73	4.25	5.17
20 µL, 1 % w/w TSC	29.08	4.06	4.75	5.03
50 µL, 1 % w/w TSC	27.1	4.15	5.15	4.03
10 µL, 10 % w/w TSC	26.03	4.29	5.48	4.13
20 µL, 10 % w/w TSC	25.47	4.48	6.10	3.39
50 µL, 10 % w/w TSC	24.24	1.26	3.00	3.31

4.1.3.2 Scanning Electron Microscopy (SEM)

The SEM images in Figures 4.15 to 4.17 provide visual representations of composites of silver with HCl pre-treated merino wool as the concentration of reducing agent is increased. When low volumes of TSC are used (20 µL, 1 % w/w TSC) for preparation the nanoparticles formed appear to be under, or flush with the fibre surface (Fig. 4.15). Very few aggregates appear on top of the surface of the fibre. When the volume of TSC is increased to 10 µL, 10 % w/w TSC, nanoparticles are observed on the surface itself (Fig. 4.16). Particles are randomly distributed across the fibre surface and are particularly apparent where cuticle plates meet. On the other hand, a complete covering of nanoparticles is evident across the fibre surface when 50 µL, 10 % w/w TSC is used as the reducing agent, entirely encapsulating the fibre (Fig. 4.17).

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Figure 4.15: SEM images, at increasing magnifications, of a HCl pre-treated merino wool - silver nanoparticle composite (20 µL, 1 % w/w TSC).

Figure 4.16: SEM images, at increasing magnifications, of a HCl pre-treated merino wool - silver nanoparticle composite (10 µL, 10 % w/w TSC).

Figure 4.17: SEM images, at increasing magnifications, of a HCl pre-treated merino wool - silver nanoparticle composite (50 µL, 10 % w/w TSC).

4.2 Confirmation of Silver Species

4.2.1 Energy Dispersive Spectroscopy (EDS) and Synchrotron Radiation X-ray Diffraction (XRD)

The confirmation of silver present within merino wool - silver nanoparticle composites was accomplished using elemental analysis by EDS, in addition to synchrotron radiation XRD. EDS elemental analysis of a merino wool - silver nanoparticle composite, using TSC as the reducing agent for preparation, shows the existence of carbon, nitrogen oxygen and sulfur that are present in proteins that form the bulk of wool (Fig. 4.18 & 4.20). The presence of silver within the composites using untreated merino wool as the base material, is confirmed by a peak at 2.98 keV corresponding to Ag L α (Fig. 4.18). Elemental analyses of KOH pre-treated merino wool - silver nanoparticle composites were found to be comparable to untreated merino wool composites. The samples were prepared on aluminium stubs; therefore this element is additionally present. The obtained synchrotron XRD pattern for a merino wool - silver nanoparticle composite confirms the presence silver in its crystalline form (Fig. 4.19). The most intense peak, related to diffraction from the Ag 111 face is centered at 24.4 degrees 2-theta. Peaks relating to diffraction from Ag 200, Ag 220 and Ag 311 faces are observed at 28.3, 40.4 and 47.9 degrees 2-theta respectively.

Figure 4.18: EDS elemental analysis of a merino wool - silver nanoparticle composite (untreated merino wool as base material).

Figure 4.19: Synchrotron radiation XRD for a untreated merino wool - silver nanoparticle composite, prepared with 10 μ L, 10% w/w TSC.

EDS elemental analysis for a merino wool - silver composite, whereby HCl pre-treated merino wool was used as the base material, again shows a peak corresponding to Ag L α at 2.98 keV (Fig. 4.20). However, a peak for chlorine, Cl K α , at 2.62 keV also appears in EDS elemental analysis suggesting the additional presence of silver chloride. Figure 4.21 provides a synchrotron radiation XRD pattern for the said composite. The presence of crystalline silver is confirmed, with the most intense Ag 111 peak centered at 24.4 degrees 2-theta. The presence of silver chloride is additionally confirmed by the presence of peaks relating to diffraction from AgCl 111, AgCl 200, AgCl 220, AgCl 311, AgCl 222 and AgCl 400 faces observed at 17.9, 20.7, 29.5, 34.7, 36.3, 42.2 and 46.2 respectively. The presence of both silver and silver chloride suggests an initial precipitation of Ag⁺ and Cl⁻ upon the initial contact of HCl pre-treated merino wool with silver nitrate solution, which is then followed by a deposition of silver nanoparticles, after reduction with TSC.

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Figure 4.20: EDS elemental analysis of a merino wool - silver nanoparticle composite (HCl pre-treated merino wool as base material).

Figure 4.21: Synchrotron radiation XRD for an HCl pre-treated merino wool - silver nanoparticle composite, prepared with 10 μ L, 10% w/w TSC.

4.3 Extent of Silver Uptake by Merino Wool Fibres

The uptake of silver by merino wool during the preparation of merino wool - silver nanoparticle composites was quantified by atomic absorption (AA) analysis. This was completed by measuring the amount of residual silver in solution after addition of TSC and binding of nanoparticles to merino wool. The results of these studies are logical, showing that increasing the amount of TSC employed as the reducing agent simultaneously increases the amount of silver ions removed from solution.

The uptake of silver from solution during sample preparation by untreated merino wool is provided in Figure 4.22. When comparing the reduction and uptake of silver from two different concentrations of Ag^+ solutions, 250 and 500 mg/kg, the proportional uptake is comparable. However the greater Ag^+ concentration results in a slightly greater uptake. This is likely due to an increased level of Ag^+ present and available for reduction. At low concentrations of reductant (20 μL , 1% w/w TSC) only ~28% of silver from solution is taken up by the merino wool fibres present. When a 500 mg/kg Ag^+ solution is used, this equates to the resulting composite comprising approximately 1.3 wt % of silver to merino wool (Table 4.4). Therefore, it follows that only low levels of silver nanoparticles are noted on the surface of and within merino wool (Fig. 4.2 & 4.5).

Figure 4.22: Percentage uptake of silver by untreated merino wool fibres when reduced with increasing concentrations of TSC.

Table 4.4: Weight percentage loading of silver to untreated merino wool, in composites prepared using a 500 mg/kg Ag⁺ solution.

Sample	Concentration TSC per 10 cm ³ AgNO ₃	Loading of Ag (wt %)
Untreated merino-Ag	10 μL, 1% w/w	1.4
Untreated merino-Ag	20 μL, 1% w/w	1.5
Untreated merino-Ag	50 μL, 1% w/w	1.9
Untreated merino-Ag	10 μL, 10% w/w	2.3
Untreated merino-Ag	20 μL, 10% w/w	3.0
Untreated merino-Ag	50 μL, 10% w/w	4.9

By increasing the concentration of reductant, from 10 μL, 1% w/w TSC to 20 μL, 10% w/w TSC, the uptake of Ag⁺ by merino wool fibres increases gradually from ~25% to ~60% (~3.0 wt % of silver to merino wool). However, when 50 μL, 10% w/w TSC is used an almost full recovery of silver (~95%) is observed (~4.9 wt % of silver to merino wool). The large recovery of silver from solution results in high levels of silver present

on the surface of and within merino wool fibres, both as individual nanoparticles and also aggregates (Fig. 4.4 & 4.6). The increase of silver on the surface and within untreated merino wool fibres was further confirmed by synchrotron radiation XRD. By increasing the volume of reducing agent used, the peak relating to Ag 111 increased in strength (Fig. 4.23). The results contribute to the argument that the colour change of samples from yellow through gold, red/brown to blue/black is related to an increase of the amount of silver nanoparticles on the surface of merino wool.

Figure 4.23: Synchrotron radiation XRD showing the Ag 111 peak for a untreated merino wool - silver nanoparticle composite, using TSC as the reducing agent.

When untreated merino wool is exchanged for 0.1 M methanolic KOH pre-treated merino wool, the relationship for the uptake of Ag^+ from solution is analogous, whereby the amount of Ag^+ ions removed from solution increases as the amount of reductant used is increased (Fig. 4.24). However, the uptake by KOH pre-treated merino wool is comparatively less. For example, when 10 μL , 1% w/w TSC is used as the reducing agent for the preparation of KOH pre-treated merino wool - silver nanoparticle composites, only ~16% of silver from solution is taken up by the fibres. This value is in comparison to untreated merino wool taking up ~25% under the same condition. Additionally, when using 50 μL , 10% w/w TSC as the reducing agent, KOH pre-treated

merino wool removes only ~87% silver from solution, compared to untreated merino wool's uptake of ~95%. Table 4.5 gives the respective weight percentages of silver present within the merino wool composites, prepared using increased concentrations of TSC.

Figure 4.24: Percentage uptake of silver by 0.1 M KOH pre-treated merino wool fibres when reduced with increasing concentrations of TSC.

Table 4.5: Weight percentage loading of silver to KOH pre-treated merino wool, in composites prepared using a 500 mg/kg Ag⁺ solution.

Sample	Concentration TSC per 10 cm ³ AgNO ₃	Loading of Ag (wt %)
KOH pre-treated merino-Ag	10 μL, 1% w/w	0.8
KOH pre-treated merino-Ag	20 μL, 1% w/w	0.9
KOH pre-treated merino-Ag	50 μL, 1% w/w	1.4
KOH pre-treated merino-Ag	10 μL, 10% w/w	2.0
KOH pre-treated merino-Ag	20 μL, 10% w/w	2.8
KOH pre-treated merino-Ag	50 μL, 10% w/w	4.4

These results are interesting as alcoholic alkali treatments to wool have been shown to remove the covalently bound lipid layer on the surface of the fibre. This has been found to reduce the hydrophobic nature of wool, enhancing dye uptake and polymer adhesion (refer to section 1.2.2). Therefore, one may expect the uptake of silver from solution by KOH pre-treated merino wool to be greater than that of untreated merino wool. However, excess hydroxyl ions present during the KOH pre-treatment will deprotonate the surface of the merino wool fibre and induce a negative charge. As silver nanoparticles reduced and stabilised by TSC are also negatively charged it is reasonable to observe the lower % uptake of Ag^+ ions from solution, as like charges will repel each other.

Alternatively, when untreated merino wool is exchanged for 0.1 M HCl pre-treated merino wool the resulting uptake of silver from solution is markedly different to that of when untreated merino wool or KOH pre-treated merino wool are used (Fig. 4.25). When 10 μL , 1% w/w TSC is used as the reducing agent for the preparation of HCl pre-treated merino wool - silver nanoparticle composites, a dramatic increase in the uptake of silver from solution is observed, in comparison to untreated and KOH treated merino wool, with ~75% Ag^+ being removed from solution. As the amount of reducing agent used is increased from 10 μL to 50 μL , 1% w/w TSC, the amount of silver removed from solution increases to ~90% and subsequently to ~97% when 50 μL , 10% w/w TSC is used. The weight percentages of silver to wool present within the composites, prepared using increased concentrations of TSC, are provided in Table 4.6.

The reason for the large initial removal of silver from solution is likely due to a precipitation of Ag^+ ions with Cl^- ions on the surface of merino wool fibres pre-treated with chloride ions, due to its low solubility product. The presence of AgCl is suggested by EDS analysis (Fig. 4.20) and confirmed by synchrotron radiation XRD (Fig. 4.21). With increasing volumes of reducing agent the % uptake of silver from solution increases to ~90% to 97%. Synchrotron radiation XRD shows that as the volume of TSC is increased, the amount of AgCl remains constant as the counts relating to the AgCl 200 peak remain stable (Fig. 4.26). However, there is an increase in the peak relating to Ag 100, suggesting the amount of silver present on the surface of the composites increases as the volume of reductant increases (Fig. 4.27). Thus it can be

concluded that the precipitation of AgCl occurs immediately when Ag^+ and Cl^- are introduced to each other, i.e when HCl pre-treated merino wool fibres are initially submerged in silver nitrate solution. The successive increase in the uptake of silver ions from solution by merino wool fibres, as measured by AA analysis, can be accounted for by the reduction of excess Ag^+ ions present and their subsequent deposition as silver nanoparticles onto the merino wool fibres.

Figure 4.25: Percentage uptake of silver by 0.1 M HCl treated merino wool fibres when reduced with increasing concentrations of TSC.

Table 4.6: Weight percentage loading of silver to HCl pre-treated merino wool, in composites prepared using a 500 mg/kg Ag^+ solution.

Sample	Concentration TSC per 10 cm ³ AgNO ₃	Loading of Ag (wt %)
KOH pre-treated merino-Ag	10 µL, 1% w/w	3.8
KOH pre-treated merino-Ag	20 µL, 1% w/w	4.1
KOH pre-treated merino-Ag	50 µL, 1% w/w	4.5
KOH pre-treated merino-Ag	10 µL, 10% w/w	4.7
KOH pre-treated merino-Ag	20 µL, 10% w/w	4.7
KOH pre-treated merino-Ag	50 µL, 10% w/w	4.9

Figure 4.26: Synchrotron radiation XRD showing the AgCl 200 peak for an HCl pre-treated merino wool - silver nanoparticle composite, using TSC as the reducing agent.

Figure 4.27: Synchrotron radiation XRD showing the Ag 111 peak for an HCl pre-treated merino wool - silver nanoparticle composite, using TSC as the reducing agent.

4.4 Colour

4.4.1 Composites Prepared Using Untreated and KOH Pre-Treated Merino Wool

The increase in average size of silver nanoparticles on the surface of merino wool fibres corresponds to a colour change from gold to brown to brown/black (Fig. 4.28). This suggests that the change in the reflected colour is due to a corresponding change in particle size. As has been outlined above, the larger particles formed, when using increasing volumes of reducing agent, appear to be both independent and consisting of aggregates of particles. As was outlined in section 1.3.1.1 the optical absorption spectra of metal nanoparticles are dominated by surface plasmon resonances (SPR). With increasing particle size, the absorption band is shifted to longer wavelengths. When nanoparticles are sufficiently close together, interactions between neighbouring particles arise, so that models for isolated particles do not hold¹. Thus, the optical absorption of the aggregate will be observed.

Figure 4.28: SEM images of untreated merino wool - silver nanoparticle composites, where scale bar indicates 100 nm.

A) 20 μ L, 1 % w/w TSC; B) 10 μ L, 10 % w/w TSC; C) 50 μ L, 10 % w/w TSC.

The absorption spectra for untreated merino wool - silver nanoparticle composites, obtained via the HunterLab ColourQuest, are presented in Figure 4.29. The y-axis gives an arbitrary value for the intensity of the signal from the machine. The results for KOH pre-treated merino wool are analogous. This instrument takes measurements every 10 nm, thus the spectra are not smooth yet the shape of the curve is apparent. When 20 μ L, 1 % w/w TSC is used as the reducing agent, the resultant textile is gold in

colour. The absorption spectrum of this sample sees the presence of a peak centred at ~430 nm. Absorption is therefore in the blue end of the visible spectrum and thus yellow light is reflected, giving rise to the gold colour observed. Metallic silver is known to have an intense plasmon absorption band in the visible region. It has been reported that the Ag 4d to 5sp interband transition generally occurs around an energy corresponding to 320 nm². However, as mentioned in section 1.3.1.1 the surface plasmon resonances strongly depend on the dielectric functions of surrounding media. The characteristic red shift of the plasmon absorption band observed in the spectra is typical of silver nanoparticles protected by a stabilising agent³.

The full width at half maximum of the plasmon peak depends on the extent of colloid aggregation⁴. The formed silver nanoparticles will possess a negative charge due to adsorbed citrate ions (see section 4.5 for further details), thus a repulsive force will theoretically prevent aggregation. According to TEM and SEM analysis of a merino wool - silver nanoparticle composite, using 20 µL, 1 % w/w TSC as the reducing agent, formed nanoparticles are relatively monodisperse and spread evenly across the surface of the fibre. Therefore, it would be expected to have a narrower peak, than the slightly broadened peak observed. The broadening of this peak may likely be due to an interaction of silver nanoparticles with the surface of the wool fibres.

Figure 4.29: Absorption spectra for merino wool - silver nanoparticle composites prepared by the respective amounts of TSC as the reducing agent: 20 µL, 1 % w/w TSC; 10 µL, 10 % w/w TSC; 50 µL, 10 % w/w TSC.

When 10 μL , 10 % w/w TSC is used as the reducing agent in the preparation of merino wool - silver nanoparticle composites, a further red shift in the plasmon band is observed: from ~ 435 nm to ~ 480 nm. This shift is due to a change in colour from gold to brown. The red shift is also observed by an increase in a^* values (Table 4.1). The broader absorption band, relating to the sample when 10 μL , 10 % w/w TSC is used, is an indication that the sample contains aggregated particles, or particles of larger size. This is confirmed by SEM analysis (Fig. 4.3). It also indicates the absorption of further colours across the visible spectrum and thus the brown colour. When 50 μL , 10 % w/w TSC is used as the reducing agent, the resulting merino wool - silver nanoparticle composite is black. Thus, the sample absorbs all colours in the visible region, resulting in an approximately flat line in the absorption spectrum.

4.4.2 Composites Prepared Using HCl Pre-Treated Merino Wool

Unlike untreated merino- and KOH pre-treated merino wool - silver composites, the change in colour for composites prepared using HCl pre-treated merino wool is somewhat more subtle. With increasing concentrations of TSC, an increased proportion of nanoparticles are seen on top of the fibre surface (Fig. 4.30). The nanoparticles below, or flush with, the surface are likely silver chloride formed by a precipitate on initial contact between Ag^+ and Cl^- . The nanoparticles that aggregate on the surface of the fibre however, are likely silver nanoparticles only. Therefore the change colour is likely due to the combinatory optical effects of both silver chloride and silver nanoparticles.

Figure 4.30: SEM images of untreated merino wool - silver nanoparticle composites, where scale bar indicates 100 nm. A) 20 μL , 1 % w/w TSC; B) 10 μL , 10 % w/w TSC; C) 50 μL , 10 % w/w TSC.

Figure 4.31 provides the absorption spectra for merino wool - silver nanoparticle composites, obtained via the Hunter Colour Quest. As was explained in sections 1.3.2.2.1 and 1.3.2.2.2, AgCl precipitate appears purple due to the formation of photolytic silver through a photoreduction reaction. The purple appearance arises as a result of the silver nanoparticles being formed within a matrix of AgCl, which has a different refractive index to that of TSC or air. The change in the dielectric constant affects the surface plasmon resonance resonance of the material and thus the colour reflected. Silver nanoparticles reduced and stabilised by TSC, on the other hand are yellow. It is for this reason that when low concentrations of TSC are implemented, 20 μL , 1 % w/w, the colour observed is purple grey. The absorption spectrum of this sample is a very broad peak centered at $\sim 500\text{ nm}$. The position and broadness of the peak indicates the absorption of colour over a spectrum ranging green and yellow. The resulting colour reflected is purple/grey.

Figure 4.31: Absorption spectra for HCl pre-treated merino wool - silver composites prepared by the respective amounts of TSC as the reducing agent: 20 μL , 1 % w/w TSC; 10 μL , 10 % w/w TSC; 50 μL , 10 % w/w TSC.

When there is an increase in TSC during preparation, to 10 μL , 10 % w/w, there is an increased amount of silver nanoparticles formed. It is for this reason that there is a shift in colour from purple/grey to purple/grey/brown, as combining both purple and yellow give brown. A shift in the absorption peak maxima is noted from $\sim 500\text{ nm}$ to $\sim 480\text{ nm}$ for a composite prepared by 10 μL , 10 % w/w TSC. This blue shift confirms the additional yellow hues resulting for a greater amount of TSC reduced silver nanoparticles. The peak additionally broadens expressing the incorporation and combination of the absorption spectra of purple silver chloride nanoparticles and yellow silver nanoparticles, present within the composite. When 50 μL , 10 % w/w TSC is used as the reducing agent, the resulting HCl pre-treated merino wool - silver composite is purple/black. Thus, the all colours in the visible region are absorbed by the sample, resulting in an approximately flat line in the absorption spectrum.

4.5 Proposed Mechanisms for Silver Nanoparticle Formation

When Ag^+ ions are reacted with TSC, the TSC first acts as a reducing agent:

Following this, additional negatively-charged citrate ions are adsorbed onto the silver nanoparticles, introducing a surface charge that essentially forms an electrical double layer (Fig. 4.32). As the citrate coated particles are negatively charged on the outside, they repel one another and prevent particle aggregation. In this respect, aggregation to form larger particles should theoretically only occur prior to, or during, the formation of the bilayer. However, the possibility of the potential aggregation after this stage will be examined in the following discussion.

Figure 4.32: Stabilisation of silver nanoparticles by TSC.

Two mechanisms for the formation of silver nanoparticles and the subsequent formation of merino wool - silver nanoparticle composites are proposed. Firstly, the addition of a reductant to the reaction mixture may initially reduce Ag^+ to Ag^0 in solution, forming TSC capped nanoparticles, which then subsequently bind to the fibre. Exactly how particles are bound will be discussed further in section 4.6. At low concentrations of TSC, the number of nanoparticles formed is limited and thus aggregation between particles is minimal. The nanoparticles formed are therefore restricted to a size of ~10-15 nm as seen in Figures 4.2 and 4.5.

However, with increasing concentrations of reducing agent, higher numbers of nanoparticles are able to be formed in solution. Thus, aggregation between particles is more likely to occur prior to, or during, the formation of the bilayer, leading to the formation of larger particles. Aggregation could occur in solution before binding to the fibre. Conversely, small nanoparticles may permeate into the fibre, some penetrating deep. The negative charge on the surface of the nanoparticles may be reduced through TSC binding to positively charged entities in the wool. This would give rise to a more positively charged face allowing for the further deposition and binding of nanoparticles at the surface, consequently leading to an increase in particle size of those on the exterior. The large particles at the surface of the composite, often irregular in shape (Fig. 4.4 & 4.6), indicate that this may well be what is happening. Therefore, indicating that larger particles are agglomerates of smaller particles.

The alternative proposition is that TSC from solution may diffuse into the fibre and reduce absorbed silver on the surface and within the fibre. TSC could enter the fibre permeating through the cuticle surface, or where cuticle plates meet. This proposed mechanism would limit the size of the particle, as the growth of the nanoparticle would be confined within the interior matrix of the fibre. The nanoparticles observed located under the surface and within the fibre, when both 20 μL , 1 % w/w TSC (Fig. 4.4) and 50 μL , 10 % w/w TSC (Fig. 4.6) are implemented as the reducing agent, are noted to be approximately the same size, substantiating this argument. At low concentrations, the depth of penetration within the fibre that TSC could reach before being exhausted is low, i.e. nanoparticles are formed only a short distance from the cuticle surface. However, with increasing concentrations of reducing agent, it is likely that TSC can permeate deeper into the interior of the fibre. This second case however requires the two proposed mechanisms for the formation of merino wool - silver nanoparticle composites to occur simultaneously. In particular, when increasing levels of reducing agent is implemented, for example 50 μL , 10 % w/w TSC. It is most likely that large nanoparticles seen on the surface on the fibres are formed in solution or deposited on top of already bound nanoparticles as outlined by the first mechanism.

4.6 Binding of Nanoparticles to Merino Wool Fibres

Keratin, the main constituent of wool fibres, is made of an abundance of molecular groups. In particular, amino acids containing amine, sulfur, carboxylate and hydroxy functional groups are prevalent. All of mentioned groups have the potential to bind to silver nanoparticles⁵⁻⁷. In order to determine the mode of chemical bonding between molecular groups present in merino wool fibres and the silver nanoparticle surface, scanning transmission electron microscopy (STEM) and x-ray photoelectron spectroscopy (XPS) studies were undertaken.

4.6.1 Scanning Transmission Electron Microscopy (STEM)

Figure 4.33 offers a STEM image of a cross section of a wool fibre coloured with silver nanoparticles, together with the elemental analysis maps of Ag and S and the resultant overlay. The map of Ag shows that silver is predominantly located on the surface, or outer portion of the fibre, with high levels present in the first 500 nm (also refer to Fig. 4.9). However, it is also evident that silver is present throughout the centre of the fibre. As was mentioned in section 1.2.2, the wool fibre has two distinct types of cells, ortho- and paracortical, which make up the orthocortex and the paracortex. The paracortex has characteristically higher levels of sulphur and this area is therefore highlighted in Figure 4.33 on the bottom left of the image by distinct high levels of S. Of particular note is that in such areas with high levels of S, there is corresponding areas with higher levels of Ag. The correlation of Ag with S suggests a chemical association for one another, therefore implying an interaction between the silver nanoparticles and merino wool fibres through one or both of the sulfur containing amino acids, cysteine or cystine.

Figure 4.33: STEM image of a cross section of a wool fibre coloured with silver nanoparticles together with elemental maps of Ag and S and the respective overlay.

4.6.2 X-ray Photoelectron Spectroscopy (XPS)

The XPS results, outlined below, further confirm a relationship between Ag and S suggested by STEM, outlined above. However, instead of a direct Ag-S bond, it is suggested that TSC acts as both stabiliser and linker for the silver nanoparticles. It is indicated that TSC, stabilising silver nanoparticles, binds through carboxylate groups to either sulfur or nitrogen containing groups of proteins comprising the fibre surface (Fig. 4.38). Figure 4.34 presents XPS data for the appropriate Ag 3d of silver nanoparticles alone and the merino wool - silver nanoparticle composite material. XPS O 1s, N 1s and S 2p spectra of untreated merino wool and the merino wool - silver nanoparticle composite material are observed in Figures 4.35, 4.36 and 4.37 respectively. For ease of comparison the vertical scale for some data has been expanded.

The experimental peak envelope of the Ag 3d spectrum (Fig. 4.34) can be assigned to two major components: Ag^0 , due to the reduction of Ag^+ by TSC, and Ag-O-, due to positively charged silver ions on the surface of the nanoparticle bound to an anionic oxygen of the carboxyl group of the citrate. A distinct shift to higher binding energies of peaks relating to Ag^0 (368.3 to 368.7 eV) and Ag-O- (369.3 to 370.1 eV) in the Ag 3d spectrum is observed in the composite material of merino wool - silver nanoparticles (merino-Ag/TSC) when comparing with the nanoparticles alone (Ag/TSC). This in itself implies a chemical interaction between the nanoparticles and the merino wool fibre. Of significance, is the greater shift of the Ag-O- peak of the merino wool - silver composite when compared to Ag^0 . This indicates that the citrate, stabilising the silver nanoparticles, is now bound to a second entity.

Figure 4.34: XPS spectra of Ag 3d for silver nanoparticles alone and merino wool - silver nanoparticle composite.

The interaction of the carboxyl groups from the citrate, in the binding of silver nanoparticles to the merino wool surface is further established by the O 1s spectra (Fig. 4.35). The peak at 532.4 eV is broad and indicates an average of differing oxygen environments in the wool with no shift observed in the merino wool - silver composite. However, the formation of an ancillary peak at higher binding energies (534.1 eV) is noted in the silver composite and can be assigned to a carboxyl group bound to an alternative species.

Figure 4.35: XPS spectra of O 1s for untreated merino wool and merino wool - silver nanoparticle composite.

The XPS spectra of N 1s of the silver composite (Fig. 4.36), when compared to untreated merino wool, shows no change in the peak assigned to amines and imines (400.2 eV), thus it is assumed there is no change in the apparent environments of bulk wool. However, a significant shift in the peak assigned to oxidised nitrogen is noted however (401.2 to 401.7 eV), thus indicating a bond between nitrogen containing amino acids on the surface of the wool with citrate. Much like the N 1s spectrum, an additional peak appears in the S 2p spectrum for the merino wool - silver composite (Fig. 4.37), due to the presence of oxidised sulfur (168.8 eV). This suggests that the citrate stabilising silver nanoparticles may be binding not only to the nitrogen on the surface of the wool but also to sulfur containing amino acids present in the wool. Given the outlined XPS results, a basic schematic of the proposed bonding mechanism of silver nanoparticles through trisodium citrate to nitrogen and sulfur containing functional groups within merino wool is provided in Figure 4.38.

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Figure 4.36: XPS spectra of N 1s for untreated merino wool and merino wool - silver nanoparticle composite.

Figure 4.37: XPS spectra of S 2p for untreated merino wool and merino wool - silver nanoparticle composite.

Figure 4.38: Bonding schematic of silver nanoparticles to the merino wool surface, whereby citrate acts as a linker.

4.7 Electrical Conductivity

The electrical conductivity of merino wool - silver nanoparticle composites was measured using the linear four-point probe method as outlined in section 2.3.10. The calculated results of these measurements, for composites using untreated, KOH pre-treated or HCl pre-treated merino as the base material, are provided in Tables 4.7 to 4.9 respectively. It should be noted that merino wool yarns themselves are non-conducting ($<10^{-10}$ S cm⁻¹). At low concentrations of TSC, for untreated merino wool - silver nanoparticle composites, no apparent increase in conductivity is observed (Table 4.7). This is likely due to the low concentrations of silver on the surface and thus the insufficient contact between particles to allow for an electrical current to flow. However at higher concentrations of TSC conductivities were measured that ranged

from $3.2 \times 10^{-5} \text{ S cm}^{-1}$ to $4.4 \times 10^{-5} \text{ S cm}^{-1}$. Therefore adequate numbers of nanoparticles are present on the surface and the contact between particles is sufficient to allow for the transport of electrons, so as to give an electrical current.

Table 4.7: Calculated electrical conductivities of untreated merino wool - silver nanoparticle composites.

Sample	Concentration TSC per 10 cm ³ AgNO ₃	Loading of Ag (wt %)	Conductivity (S cm ⁻¹)
Untreated merino-Ag	10 µL, 1% w/w	1.4	Non-conducting
Untreated merino-Ag	20 µL, 1% w/w	1.5	Non-conducting
Untreated merino-Ag	50 µL, 1% w/w	1.9	Non-conducting
Untreated merino-Ag	10 µL, 10% w/w	2.3	3.2×10^{-5}
Untreated merino-Ag	20 µL, 10% w/w	3.0	3.7×10^{-5}
Untreated merino-Ag	50 µL, 10% w/w	4.9	4.4×10^{-5}

Similarly, for KOH pre-treated merino wool - silver nanoparticle composites, an increase in conductivity is not observed until greater concentrations of TSC is used as the reducing agent (>20 µL, 10% w/w) (Table 4.8). The conductivities measured for KOH pre-treated merino wool are somewhat lower than the untreated merino wool analogues, ranging from $6.3 \times 10^{-6} \text{ S cm}^{-1}$ to $2.1 \times 10^{-5} \text{ S cm}^{-1}$. The lower conductivities are likely due to the fact that the uptake of silver from solution, and thus the number of nanoparticles on the surface of KOH pre-treated merino wool is less than that of untreated merino wool. However, this increase in electrical conductivity into the weak semi-conducting region for both untreated merino wool and KOH pre-treated merino wool composites is significant and provides opportunities for the development and potential application of conducting or antistatic fabrics that are coloured by silver nanoparticles.

Table 4.8: Calculated electrical conductivities of KOH pre-treated merino wool - silver nanoparticle composites.

Sample	Concentration TSC	Loading of Ag (wt %)	Conductivity (S cm ⁻¹)
KOH pre-treated merino-Ag	10 µL, 1% w/w	0.8	Non-conducting
KOH pre-treated merino-Ag	20 µL, 1% w/w	0.9	Non-conducting
KOH pre-treated merino-Ag	50 µL, 1% w/w	1.4	Non-conducting
KOH pre-treated merino-Ag	10 µL, 10% w/w	2.0	Non-conducting
KOH pre-treated merino-Ag	20 µL, 10% w/w	2.8	6.3×10^{-6}
KOH pre-treated merino-Ag	50 µL, 10% w/w	4.4	2.1×10^{-5}

A significant uptake of Ag⁺ from solution, despite the concentration of TSC used, is observed with HCl pre-treated merino wool - silver composites. Thus, high levels of silver are present on the surface of the composites. However, synchrotron radiation XRD results suggest the major silver species present is silver chloride, which is non-conducting ionic solid. To show electrical conductivity, the ions in ionic solids must be free to move, i.e. by dissolving in water. However, the silver chloride present in the composite is in its solid form, thus ions are fixed in their lattice positions and cannot transport an electrical charge (Table 4.9).

Table 4.9: Calculated conductivities of HCl pre-treated merino wool - silver composites.

Sample	Concentration TSC	Loading of Ag (wt %)	Conductivity (S cm ⁻¹)
HCl pre-treated merino-Ag	10 µL, 1% w/w	3.8	Non-conducting
HCl pre-treated merino-Ag	20 µL, 1% w/w	4.1	Non-conducting
HCl pre-treated merino-Ag	50 µL, 1% w/w	4.5	Non-conducting
HCl pre-treated merino-Ag	10 µL, 10% w/w	4.7	Non-conducting
HCl pre-treated merino-Ag	20 µL, 10% w/w	4.7	Non-conducting
HCl pre-treated merino-Ag	50 µL, 10% w/w	4.9	Non-conducting

4.8 Antimicrobial Testing

Antimicrobial testing for merino wool - silver nanoparticle composites, in which an external reducing agent was used for preparation, was carried out against the bacteria *Staphylococcus aureus* as outlined in section 2.3.11. Depending on the sample's antimicrobial properties different levels of bacterial growth inhibition were observed. Those materials that would test positive for antimicrobial properties would display active hindrance of the growth of bacteria (visible zone of inhibition). Bacterial growth up to but not over the fibres themselves would be observed for materials resistant to microbial attack. A negative test for antimicrobial activity would be noted when bacterial growth occurred over the fibre surfaces themselves.

Figure 4.40 outlines the relevant reference samples for merino wool - silver nanoparticle composites. The base materials, untreated merino wool and KOH and HCl pre-treated merino wool, all do not show any antimicrobial effects (Fig. 4.40: 1-3). Merino wool fibres heated to 95 °C in TSC only, including both 1% and 10% w/w, additionally show no sign of antimicrobial activity (Fig. 4.39: 6 and 7 respectively). However, untreated merino wool and HCl pre-treated merino wool heated to 95 °C in silver nitrate, without an external reducing agent, both show potential as antimicrobial agents (Fig. 4.40: 4 and 5 respectively).

Figure 4.39: Reference materials: 1) untreated merino wool; 2) KOH pre-treated merino wool; 3) HCl pre-treated merino wool; 4) untreated merino wool heated to 95 °C in AgNO₃ only; 5) HCl pre-treated merino wool heated to 95 °C in AgNO₃ only; 6) merino wool heated to 95 °C in 1% w/w TSC only; 7) merino wool heated to 95 °C in 10% w/w TSC only.

Untreated merino wool heated in silver nitrate, with no external reducing agent, results in fibres yellow in colour (Fig. 4.39: 4). This colour is comparable to when the lowest volume of TSC (10 µL, 1% w/w) is used for preparation. This result indicates that a silver species, potentially silver nanoparticles, are formed when merino wool is heated in silver nitrate, without the requirement of an external reducing agent. The development of merino wool - silver composites, prepared in this way, and their subsequent characterisation are discussed in further detail in section 5.

HCl pre-treated merino wool heated in silver nitrate, with no external reducing agent, results in fibres purple/grey in colour (Fig. 4.39: 5). Sections 4.2 and 4.3 imply that silver chloride is present when HCl pre-treated merino wool is used during preparation. The formation of the silver chloride is likely before addition of an external reducing agent and as the colour observed is comparable to that of when 10 µL, 1% w/w TSC is used, the species observed without a reducing agent is also likely silver chloride. The further development of merino wool - silver chloride composites and their characterisations is discussed further detail in section 6, whereby silver halide nanoparticles are formed on the surface of and within merino wool fibres through a nano-precipitation reaction.

Merino wool - silver nanoparticle composites, using untreated merino wool, KOH or HCl pre-treated merino wool (Fig. 4.40 or 4.41 or 4.42), all actively inhibited the growth of microbes and hence tested positive for their anti-microbial activity. This can be observed when comparing reference materials in Figure 4.39 with Figures 4.40 to 4.42. White, hazy areas indicate bacterial growth, whereas the more transparent circles surrounding the merino wool - silver composites, in the agar, indicate bacterial free regions, i.e. zones of inhibition.

Figure 4.40 A - C illustrates antimicrobial ability of untreated merino wool fibres coated in silver nanoparticles. By increasing the volume and concentration of the reducing agent used, from 20 μ L, 1% w/w to 10 μ L, 10% w/w to 50 μ L, 10% w/w TSC, the zones of inhibition simultaneously become larger. The increase in antimicrobial activity is due to increased levels of silver being present on the surface of the fibres. As the concentration of reductant increases AA analysis indicates the amount of silver absorbed by the merino wool fibres also increases (Fig. 4.22). SEM (Fig. 4.2 to 4.4) and TEM analyses (Fig. 4.5 & 4.6) confirm that the increased absorption of silver corresponds to increased numbers of silver nanoparticles on the surface of the composites.

Figure 4.40: Inhibition zones of *Staphylococcus aureus* microbial growth by untreated merino wool - silver nanoparticle composites: A) 20 μL , 1% w/w TSC; B) 10 μL , 10% w/w TSC; C) 50 μL , 10% w/w TSC.

KOH pre-treated merino wool - silver nanoparticle composites also tested positive for antimicrobial properties (Fig. 4.41). As with untreated merino wool composites, it is also observed that as the concentration of TSC increases the number of nanoparticles present on the surface also increases (Fig. 4.11 to 4.13). Due to increased populations of silver, the antimicrobial ability of merino wool - silver nanoparticle composites is also increased. However, KOH pre-treated composites actively inhibit the growth of bacteria to a lesser amount when compared to untreated merino wool composites (Fig. 4.40). This is due to KOH pre-treated merino wool being predominantly negatively charged. Therefore, TSC stabilised silver particles, also negatively charged, do not bind as readily resulting in a lesser uptake of silver from solution and fewer nanoparticles being bound to the surface in comparison to untreated merino wool (Fig. 4.4 vs. Fig. 4.13).

Figure 4.41: Inhibition zones of *Staphylococcus aureus* microbial growth by KOH pre-treated merino wool - silver nanoparticle composites: A) 20 μ L, 1% w/w TSC; B) 10 μ L, 10% w/w TSC; C) 50 μ L, 10% w/w TSC.

Unlike KOH pre-treated merino wool and untreated merino wool composites with silver, in which the amount of silver present in merino wool increased over a large range from ~16 - 25% to ~87 - 95% with increasing levels of TSC (Fig. 4.22 & 4.24), AA analysis of HCl pre-treated merino wool - silver nanoparticle composites indicated a more confined uptake from ~75% to ~97% (Fig. 4.25). Therefore, as the concentration of reducing agent increases during preparation using HCl pre-treated merino wool as the base material, the uptake is rather high for all and not altered as significantly. For this reason the antimicrobial effect of silver composites A-C in Figure 4.42 are comparable. The zones on inhibition noted are approximately one hundred and fifty times that of the fibre diameter. The zones of inhibition observed are equivalent to those seen with untreated merino wool whereby an uptake of a similar value, ~95%, was observed (Fig. 4.40 C).

Figure 4.42: Inhibition zones of *Staphylococcus aureus* microbial growth by HCl pre-treated merino wool - silver nanoparticle composites: A) 20 μ L, 1% w/w TSC; B) 10 μ L, 10% w/w TSC; C) 50 μ L, 10% w/w TSC.

It is generally understood that it is silver ions, and not silver itself, that acts as the anti-microbial agent. As is discussed in section 1.3.3, microbial growth is not possible after the silver cation, released from the composite, binds strongly to electron donor groups containing sulfur, oxygen, or nitrogen within the bacteria. These groups are generally present components in the form of thio, amino, imidazole, carboxylate, and phosphate groups. This binding affects the electron transfer system necessary for basic bacterial functioning and thus halts multiplication.

The zones of inhibition for each of the merino wool - silver composites along with the respective loadings of silver are summarised in Table 4.10. As ionic silver is thought to migrate from the surface of the fibre composite inhibiting the growth of microbes in its path, the silver-induced anti-bacterial hindrance will be directly proportional to amount of silver on the surface of the composite⁸. The migration of silver ions into agar is noted by the zones of microbial inhibition (Fig. 4.41 to 4.43). Hence, given the theory above, the higher the silver concentration, the higher the anti-microbial efficacy will be. This relationship is observed in Figures 4.41 & 4.42 and Table 4.10, where increased

levels of silver are present with increasing concentrations of TSC for untreated merino- and KOH pre-treated merino wool - silver nanoparticle composites. As the formed silver nanoparticles are stabilised by negatively charged TSC, associated silver cations are present at the surface of the particle (Fig. 4.32). It is likely these silver ions that react with the cells of microbes and act in the inhibition of microbial growth. In a similar manner, silver cations present in TSC stabilised silver nanoparticles would migrate in conjunction with silver cations present in silver chloride for HCl pre-treated merino wool - silver composites.

Table 4.10: Inhibition zones of *Staphylococcus aureus* microbial growth by merino wool - silver composites

Code	Sample	Concentration TSC per 10 cm ³ AgNO ₃	Loading of Ag (wt %)	Zone of Inhibition (mm)
n/a	Silver Wire	n/a	n/a	4.0
Fig. 4.40 4	Untreated merino wool heated to 95 °C in AgNO ₃ only	n/a	0.5	0.3
Fig. 4.40 5	HCl pre-treated merino wool heated to 95 °C in AgNO ₃ only	n/a	3.0	1.8
Fig. 4.41 A	Untreated merino-Ag	20 µL, 1% w/w	1.5	1.2
Fig. 4.41 B	Untreated merino-Ag	10 µL, 10% w/w	2.3	2.1
Fig. 4.41 C	Untreated merino-Ag	50 µL, 10% w/w	4.9	2.8
Fig. 4.42 A	KOH pre-treated merino-Ag	20 µL, 1% w/w	0.9	0.6
Fig. 4.42 B	KOH pre-treated merino-Ag	10 µL, 10% w/w	2.0	1.2
Fig. 4.42 C	KOH pre-treated merino-Ag	50 µL, 10% w/w	4.4	1.7
Fig. 4.43 A	HCl pre-treated merino-Ag	20 µL, 1% w/w	4.1	3.0
Fig. 4.43 B	HCl pre-treated merino-Ag	10 µL, 10% w/w	4.7	3.0
Fig. 4.43 C	HCl pre-treated merino-Ag	50 µL, 10% w/w	4.9	3.0

Silver wire itself showed zones of inhibition of up to 3 times the diameter of the wire only. Whereas, the extent in which an individual silver-coated fibre can inhibit the growth of bacteria is up to approximately 150 times the diameter of the fibre. When considering the relative masses of silver present in silver wire, in comparison to the

merino–silver composites, the antimicrobial ability and effect of the composites is even more significant.

4.9 Summary

Merino wool - silver nanoparticle composites were successfully prepared using an external reducing agent, TSC. The preparation method included the heating of merino wool fibres in a silver nitrate solution to 90 °C. When this temperature was reached, TSC was added in increasing concentrations, and the reaction vessel continued to be heated for 10 minutes. As silver is reduced to form silver nanoparticles they simultaneously bind to merino wool and are removed from the solution environment. As the concentration of TSC is increased it follows that greater levels of silver are reduced and removed from solution. The uptake of silver by merino wool fibres was quantified using AA. The uptake by untreated merino wool fibres was noted to be greater than that of KOH pre-treatment on merino wool. This is due to like charges repelling one another, i.e. negatively charged wool surface provided by the KOH pre-treatment and silver nanoparticles being stabilised by negatively charged TSC.

As the concentration of TSC implemented was increased, from 10 µL, 1 w/w % TSC to 50 µL, 10 w/w % TSC, the resulting composites using untreated or KOH pre-treated merino as the substrate are coloured yellow through to gold, red/brown and finally black/brown. EDS and synchrotron radiation XRD confirm the nanoparticles present in merino wool - silver nanoparticle composites using untreated and KOH pre-treated merino are silver metal. On the other hand, when HCl pre-treated merino is used as the substrate the resulting composites are purple/grey in colour, darkening to purple/grey/brown to purple/black as the concentration of TSC is increased. EDS and synchrotron radiation XRD indicate that the nanoparticles are in fact silver chloride. The silver chloride system will be discussed further in section 6.

SEM and TEM studies show that silver nanoparticles the formed silver nanoparticles, when using untreated and KOH pre-treated merino, predominantly bind to the surface of the wool fibres. The nanoparticles of composites yellow in colour are approximately 10

to 15 nm in diameter. The observed colour is due to the surface plasmon resonances; the interaction of the electromagnetic radiation of light interacting with the particle. As the particle or agglomerate size increases to approximately 100 nm in diameter there is a shift in colour from yellow to brown/black, indicating that the change in the reflected colour is due to a corresponding change in particle size.

XPS studies undertaken on merino coloured by silver nanoparticles confirmed the relationship of silver with sulfur as indicated by STEM analysis. However, instead of a direct Ag-S bond, it is suggested that TSC acts as both stabiliser and linker for the silver nanoparticles. It is indicated that TSC, bound to the surface of silver nanoparticles stabilising them, binds through carboxylate groups to either sulfur or nitrogen containing groups of proteins present on the wool fibres surface. This bonding mechanism is implied to be stable the colours of these composites remain constant when being subjected to simulated washability tests.

As was mentioned above, when the concentration of TSC used for the reduction of silver is increased the levels of silver present on the surface simultaneously increases. With high levels of silver - loadings of 2.3 to 4.9 wt % silver per gram of wool - the electrical contact between nanoparticles is sufficient and conductivities of 6.3×10^{-6} to $4.4 \times 10^{-5} \text{ S cm}^{-1}$ were observed. This increase in electrical conductivity, from non-conducting to the weak semi-conducting region provides opportunities for the development and potential application of conducting or antistatic fabrics that are coloured by silver nanoparticles.

Finally, merino wool coloured with silver nanoparticles tested positive for their antimicrobial properties against the microbe *Staphylococcus aureus*. As the loading of silver increased, consequently the zones of inhibited microbial growth also increased. For merino wool - silver nanoparticle composites, zones of inhibition were measured from 0.6 to 2.8 mm for the respective 0.9 to 4.9 wt % silver loadings. This equates to microbial inhibition of up to 150 times the diameter of the fibre. Comparable inhibition zones were measured for merino wool - silver chloride nanoparticle composites. When taking into account that silver wire itself only shows zones of inhibition of up to 3 times the diameter, these results are indeed significant.

4.10 References

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5 MERINO WOOL - SILVER NANOPARTICLE COMPOSITES: NANOPARTICLES FORMED IN THE PRESENCE OF MERINO WOOL USING ITS REDUCING NATURE

5.1 Physical Characterisation and Morphology

5.1.1 Untreated Merino Wool

Merino wool fibres coloured by silver nanoparticles were prepared without an external reducing agent, following the methodology outlined in section 2.2.2.2. Proteins present in merino wool act as the *in situ* reducing agent, facilitating the reduction of silver nitrate to silver nanoparticles with simultaneous binding to the fibre. In a typical reaction, wool fibres (0.1 g) immersed in the silver solution, 50-500 mg/kg Ag^+ (10 cm^3) are heated in a water bath set at 50°C or 80°C for up to 24 hours, giving rise to yellow/gold coloured fibres. The intensity of the colour can be altered by systematically altering the concentration of Ag^+ ions and reaction temperature. An example of this is provided in Figure 5.1.

Figure 5.1: Merino wool coloured by silver nanoparticles, prepared using a) 150 mg/kg Ag^+ and b) 500 mg/kg Ag^+ with a 24 hour soaking period at 50°C .

5.1.1.1 Characterisation of Colour

As mentioned above, by varying the reaction conditions employed the colour of the resultant merino wool - silver fibres can be controlled. Figures 5.2 to 5.4 provide examples of the deviation of colours obtained for untreated merino wool - silver nanoparticle composites by altering the concentration of Ag^+ solution, duration of soaking period and temperature. A comprehensive summary of CIE L^* , a^* , b^* values for the prepared samples are provided in Appendix II. The CIE b^* value indicates the colour of the sample between yellow (+ve) and blue (-ve). The a^* value indicates the samples colour between red/magenta (+ve) and green (-ve). Therefore by monitoring the measured b^* and a^* values of prepared merino wool - silver nanoparticle composites, the colour development observed by the eye, from white to yellow to gold to brown, may be confirmed.

When untreated merino wool is soaked in silver nitrate at room temperature over a period of 72 hours, the colours of the resultant products are comparable to untreated merino wool itself. Even when high concentrations of silver (i.e. 500 mg/kg Ag^+) are employed and for 72 hours, only a very minimal yellowing occurs (Fig. 5.2). CIE values for composites prepared using, show that the b^* value only increases from 3.70, for untreated merino wool alone, to 5.53, 8.74 and 13.12 for 100, 250 and 500 mg/kg Ag^+ respectively. The a^* value shows no relative change. This very nominal increase in b^* values confirms the only very faint yellowing of samples.

When the reaction is undertaken at 50 °C however, a distinct yellowing occurs from very pale yellow, which darkens to gold (Fig. 5.3). The intensity in colour increases with increasing concentrations of silver, i.e. samples prepared with 500 mg/kg Ag^+ have a greater colour than samples prepared with 250 mg/kg Ag^+ , which have a greater colour to samples prepared with 100 mg/kg Ag^+ . This is confirmed by CIE b^* values which determine the yellowness of the sample, with values measured as 21.46, 27.54 and 30.75 for when the respective soaking solutions are used: 100, 250, and 500 mg/kg Ag^+ . No change in a^* value was observed for 100 mg/kg Ag^+ soaking solutions yet when 250 and 500 mg/kg Ag^+ solutions are used the a^* value simultaneously increases with the b^* value, from -0.74 for untreated merino wool to 3.03 and 7.32. This indicates a change from yellow only to a more gold colour.

Compared to those merino wool - silver nanoparticle composites prepared at 50 °C, the colour intensity for those prepared at 80 °C is observed to increase for all concentrations and soaking periods (Fig. 5.4). Over the 72 hour time period, the resulting composites range from yellow, to gold, to brown. Again, for the same time period, samples prepared with 500 mg/kg Ag^+ have a greater colour than samples prepared with 250 mg/kg Ag^+ , which have a greater colour to samples prepared with 100 mg/kg Ag^+ . The increasing colour strength discussed, for 100, 250 and 500 mg/kg Ag^+ soaking solutions, is likely due to increasing amounts of Ag^+ ions available in solution. This will be discussed in further detail in section 5.6. Due to the change in colour from yellow to gold to brown, the a^* values for merino wool - silver nanoparticle composites prepared at 80 °C are seen to increase over the 72 hour time. On the other hand, b^* values peak when gold is observed and then decrease as the sample browns.

Figure 5.2: Merino wool - silver nanoparticle composites prepared using untreated merino wool, at room temperature: a) 500 mg/kg Ag^+ ; b) 250 mg/kg Ag^+ ; c) 100 mg/kg Ag^+ .

Figure 5.3: Merino wool - silver nanoparticle composites prepared using untreated merino wool, at 50 °C: a) 500 mg/kg Ag⁺; b) 250 mg/kg Ag⁺; c) 100 mg/kg Ag⁺.

Figure 5.4: Merino wool - silver nanoparticle composites prepared using untreated merino wool, at 80 °C: a) 500 mg/kg Ag⁺; b) 250 mg/kg Ag⁺; c) 100 mg/kg Ag⁺.

5.1.1.2 Scanning Electron Microscopy (SEM)

The morphology of untreated merino wool - silver nanoparticle composites of various colours was determined by SEM analysis. SEM studies, in secondary electron mode (SEI), show that at low magnifications fibres appear synonymous to the untreated analogue (Fig. 5.5a & 5.5b). With increasing magnifications of a composite prepared using low loadings of silver (100 mg/kg, 16 hour soak period at 50 °C, yellow composite), nanoparticles are not readily evident on the surface of merino wool - silver nanoparticle composites. At 100,000 times magnification, only a very small number of nanoparticles are noted on the surface. These nanoparticles have been indicated

by arrows in Figure 5.5a. Interestingly, when high loadings of silver are implemented (500 mg/kg, 16 hour soak period at 50 °C, gold/brown composite), again nanoparticles are not obvious on the fibre surface (Fig. 5.5b).

Figure 5.5: SEM micrographs (SEI), at increasing magnifications, of untreated merino- silver nanoparticle composites prepared using a soaking period of 16 h at 50 °C in: a) 100 mg/kg Ag^+ ; and b) 500 mg/kg Ag^+ .

It has been shown that similar yellow/gold colours to those above, can also be obtained when an external reducing agent is implemented for the preparation of merino wool - silver nanoparticle composites. The preparation of yellow and gold/brown composites using TSC requires the use of volumes ranging from 10 to 50 μL , 1 w/w % TSC (Fig. 4.1, section 4.1.1.1). When an external reducing agent is used for composite preparation, it is apparent that much greater numbers of nanoparticles are present on the fibre surface. When comparing yellow coloured merino wool - silver composites, prepared by both external and *in situ* reduction, those prepared using TSC (Fig. 5.6b) have a far more textured surface due to a greater number of nanoparticles to that of when the reducing nature of the proteins within merino wool is utilised (Fig. 5.6a). The same statement is valid when comparing gold/brown composites. (Fig. 5.7a & 5.7b).

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Figure 5.6: Yellow coloured merino wool - silver nanoparticle composites prepared using a) reducing nature of merino wool (16 h at 50 °C in 100 mg/kg Ag⁺); and b) TSC as external reductant (10 μL, 1 % w/w TSC).

Figure 5.7: Gold coloured merino wool - silver nanoparticle composites prepared using a) reducing nature of merino wool (16 h at 50 °C in 500 mg/kg Ag⁺); and b) TSC as external reductant (50 μL, 1 % w/w TSC).

5.1.1.3 Transmission Electron Microscopy (TEM)

TEM analysis of untreated merino wool - silver nanoparticle composites, prepared using *in situ* reduction, shows that nanoparticles are present throughout the entire centre of the fibre instead of the majority being present at the surface. Figure 5.8 provides a TEM image of a cross section of a merino wool - silver nanoparticle composite. The method of preparation included soaking in 500 mg/kg Ag^+ solution for 24 hours at 50 °C. The fibre embedded within the resin is somewhat difficult to distinguish in this image. It is positioned in the bottom left of the image and for ease of location it is indicated by arrows on the left and right sides of the image. Silver nanoparticles, observed as small black dots, are observed to be regularly distributed throughout the entire fibre. At higher magnifications the nanoparticles are noted to be relatively homogenous in size, ranging from ~4-7 nm (Fig. 5.9).

Figure 5.8: TEM image of a untreated merino wool - silver nanoparticle composite (16 h at 50 °C in 100 mg/kg Ag^+), indicating nanoparticle distribution within merino wool fibre.

Figure 5.9: TEM image of a untreated merino wool - silver nanoparticle composite (16 h at 50 °C in 100 mg/kg Ag⁺) at increasing magnifications indicating size of nanoparticles.

The size and distribution of silver nanoparticles observed for merino wool - silver nanoparticle composites, prepared using in situ reduction within the fibre, is quite dissimilar to when an external reducing agent is used for composite preparation. When comparing gold coloured samples of both methods, in general, the size of smaller nanoparticles using an external reducing agent for sample preparation ranged between ~10-15 nm (Fig. 4.5, section 4.1.1.3). The smaller nanoparticles penetrated the surface of the fibre by up to ~150 nm only. In addition, small aggregates of nanoparticles were also noted at the surface. No agglomerates are observed when the reducing nature of merino wool is implemented. The intensity and comparability of colour for merino wool - silver nanoparticle composites, prepared using in situ reduction and binding within the fibre or an external reducing agent, is therefore likely due to a large number of small nanoparticles evenly distributed throughout the fibre, rather than an equivalent amount of nanoparticles being localised within a small distance from the fibre surface.

5.1.2 KOH Pre-Treated Merino Wool

5.1.2.1 Physical Characterisation of Colour

When 0.1 M KOH pre-treated merino wool was alternatively used as the base material for silver nanoparticle composite formation, comparable colours to that of when untreated merino wool were obtained (Fig. 5.10 to 5.12). However, the resulting colours for KOH pre-treated merino wool composites were somewhat more intense in colour than their untreated merino wool analogues. Similar to untreated merino wool composites (Fig. 5.2), when prepared at room temperature, only a minimal yellowing occurs even when high concentrations of silver (i.e. 500 mg/kg Ag⁺) are employed for 72 hours (Fig. 5.10). However, the KOH pre-treated merino wool composites are notably more yellow in comparison to untreated merino wool composites.

The increased yellowing of KOH pre-treated merino wool - silver nanoparticle composites is confirmed when comparing ColourQuest CIE L*, a*, b* measurements of these composites to their untreated merino wool analogues (Appendix III). The b* value indicates the colour of the sample between yellow (+ve) and blue (-ve), therefore the greater the b* value the more yellow the sample is. Table 5.1 compares b* values for untreated merino wool and KOH pre-treated merino wool composites with silver nanoparticles at varying temperatures, after a 16 hour soaking period. The b* value for a untreated merino wool sample emerged in silver nitrate for such a time period is measured at 9.81, whereas a KOH pre-treated sample under the same conditions has a greater measured b* value, at 10.63. The relationship, whereby a greater b* value is obtained by the composite is prepared using KOH pre-treated merino wool, is again observed at 50 °C and 80 °C. These results conclude that KOH pre-treated merino wool samples prepared at room temperature are more yellow than the untreated merino wool composite analogues.

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Figure 5.10: Merino- silver nanoparticle composites prepared using KOH pre-treated merino wool, at room temperature: a) 500 mg/kg Ag^+ ; b) 250 mg/kg Ag^+ ; c) 100 mg/kg Ag^+ .

Figure 5.11: Merino- silver nanoparticle composites prepared using KOH pre-treated, at 50 °C: a) 500 mg/kg Ag^+ ; b) 250 mg/kg Ag^+ ; c) 100 mg/kg Ag^+ .

Figure 5.12: Merino- silver nanoparticle composites prepared using KOH pre-treated, at 80 °C: a) 500 mg/kg Ag^+ ; b) 250 mg/kg Ag^+ ; c) 100 mg/kg Ag^+ .

Table 5.1: CIE b* values comparing of untreated merino- and KOH pre-treated merino wool - silver nanoparticle composites, prepared using a soak time of 16 hours in Ag⁺ solution.

Base Material	Temperature	Ag ⁺ Concentration	b*
Untreated merino wool	Room temp.	500 mg/kg	9.81
KOH pre-treated merino wool	Room temp.	500 mg/kg	10.63
Untreated merino wool	50 °C	500 mg/kg	20.18
KOH pre-treated merino wool	50 °C	500 mg/kg	27.22
Untreated merino wool	80 °C	500 mg/kg	29.50
KOH pre-treated merino wool	80 °C	500 mg/kg	29.66

In comparison to untreated merino wool composites, the reason for the greater intensity in colour, is likely due to deprotonation of functional groups at the surface by the hydroxyl ions of KOH, providing a negatively charged surface. The creation of a negatively charged surface creates a greater attraction for positively charged silver ions in solution. In addition, the alcoholic base treatment removes the lipid layer from the surface of the merino wool allowing for greater ease of penetration of silver ions into the fibre. Thus, it follows that the combination of both these reasons would allow for greater numbers of silver ions to enter the fibre for KOH pre-treated merino wool thus resulting in a greater intensity in colour. The uptake of silver ions from solution by untreated merino wool and KOH pre-treated merino wool will be discussed in further detail in section 5.3. Proposed mechanisms of nanoparticle formation will be outlined in section 5.5.

5.1.2.2 Scanning Electron Microscopy (SEM)

SEM studies of KOH pre-treated merino wool - silver nanoparticle composites, in secondary electron mode (SEI), once again show that at low magnifications the composite appears equivalent to untreated merino wool (Fig. 5.13). However, with increasing magnifications, nanoparticles of silver become evident across the fibre surface. Unlike what was seen when TSC was used as a reducing agent for preparation of merino wool - silver nanoparticle composites, a full and even coverage of the surface

by nanoparticles is not observed. Instead, the nanoparticles at the surface are present in small numbers and appear to be grouped together at random across the fibre. However, when comparing KOH pre-treated merino wool - silver nanoparticle composites with to their untreated merino wool analogues it becomes evident that the nanoparticles noted at the surface of composites are present in much greater numbers (Fig. 5.14).

Figure 5.13: SEM micrographs (SEI), at increasing magnifications, of KOH pre-treated merino-silver nanoparticle composites prepared using a soaking period of 16 h at 50 °C in 500 mg/kg Ag⁺.

Figure 5.14: Merino wool - silver nanoparticle composites prepared using a soaking period of 16 h at 50 °C in 500 mg/kg Ag⁺: a) untreated merino wool; b) KOH pre-treated merino wool.

5.1.2.3 Transmission Electron Microscopy (TEM)

TEM analysis of a KOH pre-treated merino wool - silver nanoparticle composite (Fig. 5.15) shows that like their untreated merino wool analogues (Fig. 5.8), silver nanoparticles are present throughout the centre of the fibre. Additionally, agglomerates of nanoparticles are also noted at the surface of the fibre. Figure 5.16 provides higher magnification images of agglomerates at the composite surface, which are approximately 25 to 75 nm in size (Fig. 5.16a), in addition to the nanoparticles present throughout the centre of the fibre (Fig. 5.16b). The nanoparticles throughout the fibre appear to be slightly larger in size to those of untreated merino wool, measuring approximately 5-12 nm in diameter, compared with 4-7 nm. It is also indicated that such nanoparticles may have a higher distribution number to those of the untreated merino wool composites. This may account for the greater intensity in colour and will be discussed further in section 5.6.

Figure 5.15: TEM image of a KOH pre-treated merino wool - silver nanoparticle composite (16 h at 50 °C in 100 mg/kg Ag⁺), indicating nanoparticle distribution within merino wool fibre and larger agglomerates at the fibre surface.

Figure 5.16: TEM images of a KOH pre-treated merino wool - silver nanoparticle composite cross section (16 h at 50 °C in 100 mg/kg Ag⁺) indicating: a) larger agglomerates present at the fibre surface; and b) smaller nanoparticles present within the composite.

5.2 Confirmation of Silver Species

5.2.1 Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS)

The presence of silver species within merino wool composites, prepared using the reducing nature of proteins within the fibre, was first suggested by SEM backscatter and subsequently confirmed using EDS and synchrotron radiation XRD. Figure 5.17 presents SEM images in backscatter mode of a merino wool - silver nanoparticle composite prepared using 500 mg/kg Ag⁺ and a soaking period of 16 hours. The intensity of the signal of a backscattered SEM image is strongly related to the atomic number of the specimen. Therefore, the greater the atomic number of the element, the whiter that element will appear in the resulting image. As silver is a much heavier element, in comparison to C, N, O, S that make up merino wool, it will appear whiter in the image. Areas of higher silver concentrations will consequently appear brighter white. The merino wool - silver nanoparticle composite fibre in Figure 5.17 is displayed as being much lighter in shade in comparison to that of the carbon tape background indicating the presence of a heavier element, in this case silver. At 10,000 times magnification, individual silver nanoparticles start to become apparent as bright

white dots. These nanoparticles are particularly evident within the circled area of the image. Additional particles have been highlighted with arrows.

Figure 5.17: SEM micrographs (backscatter), at increasing magnification, of a untreated merino-silver nanoparticle composite prepared using 500 mg/kg Ag^+ with a 16 h soaking period.

The presence of silver, as suggested by backscattered SEM analysis above was verified by EDS elemental analysis and mapping. When comparing two methods of preparation: a) 16 hour soaking in 500 mg/kg Ag^+ at 50 °C (yellow/gold) and b) 24 h soaking in 500 mg/kg Ag^+ at 80 °C (gold/brown); peaks relating to carbon, nitrogen, oxygen and sulphur are observed by EDS elemental analysis (Fig. 5.18a & 5.18b). These elements are present as the various proteins that make up the composition of wool. The presence of silver within both composites is confirmed by a peak at 2.98 keV corresponding to $\text{Ag L}\alpha$. As samples were prepared on aluminium stubs this element is additionally present. The ratios of S to Ag for both untreated and KOH pre-treated merino wool composites are comparable.

Figure 5.18: EDS elemental analyses of merino wool - silver nanoparticle composites prepared by the following methods: a) 16 h soaking in 500 mg/kg Ag^+ at 50 °C; b) 24 h soaking in 500 mg/kg Ag^+ at 80 °C.

Figure 5.19 provides a secondary electron SEM image of a merino wool - silver nanoparticle composite together with the elemental map of silver. This image is representative of when both 16 hour soaking periods in 500 mg/kg Ag^+ at 50 °C and 24 hour soaking periods in 500 mg/kg Ag^+ at 80 °C is used for preparation. The composite present in the image has been sliced through the centre and viewed end-on so as to obtain elemental analysis through the centre of the fibre. The elemental map for silver expresses that silver is present not only on the surface of the fibre but additionally throughout the centre. This adds further weight to the results obtained by TEM analysis (Fig. 5.8 & 5.15).

Figure 5.19: A SEM image together with EDS elemental analysis of a cross section of a wool fibre coloured with silver nanoparticles, representative of all methods of preparation.

5.2.2 Synchrotron Radiation X-Ray Diffraction (XRD)

The obtained synchrotron XRD pattern for a yellow/gold merino wool - silver nanoparticle composite, prepared using a 16 hour soaking period in 500 mg/kg Ag^+ at 50 °C, confirms the presence of crystalline silver (Fig. 5.20). The most intense Ag 111 peak is centred at 24.6 degrees 2-theta. Peaks relating to diffraction from Ag 200, Ag 220 and Ag 311 faces are observed at 28.5, 40.6 and 48.1 degrees 2-theta respectively. However, when the reaction is undertaken at 80 °C, with a 24 hour soaking periods in 500 mg/kg Ag^+ , the composite product is brown and crystalline silver is no longer observed (Fig. 5.21). As silver is still present in EDS elemental analysis (Fig.

5.18b), this result implies a transition from crystalline Ag^0 to an amorphous form of silver, likely Ag_2O .

Figure 5.20: Synchrotron Radiation XRD pattern for a merino wool - silver nanoparticle composite prepared using a 16 h soaking period in 500 mg/kg Ag^+ at 50 °C.

Figure 5.21: Synchrotron Radiation XRD patterns, focusing on the Ag 111 peak, for merino wool - silver nanoparticle composites prepared by the following methods: a) 16 h soaking in 500 mg/kg Ag^+ at 50 °C; b) 24 h soaking in 500 mg/kg Ag^+ at 80 °C.

5.3 Extent of Silver Uptake by Merino Wool Fibres

The uptake of silver ions from solution by untreated merino wool and KOH pre-treated merino wool was quantified by atomic absorption (AA) analysis. The effect of concentration and temperature of the silver solution, in addition to the duration of soaking within the solution were studied. Three concentrations (100, 250, 500 mg/kg Ag^+), and three temperatures (room temperature, 50 °C, 80 °C) were applied. Figures 5.22 to 5.24 show the uptake of silver ions from solution by untreated merino wool compared to KOH pre-treated merino wool for 100, 250 and 500 mg/kg Ag^+ solutions respectively. The raw data for these graphs can be found in Appendix V. In addition, the physical characterisations of both untreated merino wool and KOH pre-treated merino wool composites, altering the said conditions, have been outlined above in sections 5.1.1 and 5.1.2.

Figure 5.22: Following the uptake of Ag^+ ions from a 100 mg/kg solution over a 72h soaking period using the following reaction conditions: a) untreated merino wool, room temperature; b) untreated merino wool, 50 °C; c) untreated merino wool, 80 °C; d) KOH pre-treated merino wool, room temperature; e) KOH pre-treated merino wool, 50 °C; f) KOH pre-treated merino wool, 80 °C.

Figure 5.23: Following the uptake of Ag^+ ions from a 250 mg/kg solution over a 72h soaking period using the following reaction conditions: a) untreated merino wool, room temperature; b) untreated merino wool, 50 °C; c) untreated merino wool, 80 °C; d) KOH pre-treated merino wool, room temperature; e) KOH pre-treated merino wool, 50 °C; f) KOH pre-treated merino wool, 80 °C.

Figure 5.24: Following the uptake of Ag^+ ions from a 500 mg/kg solution over a 72h soaking period using the following reaction conditions: a) untreated merino wool, room temperature; b) untreated merino wool, 50 °C; c) untreated merino wool, 80 °C; d) KOH pre-treated merino wool, room temperature; e) KOH pre-treated merino wool, 50 °C; f) KOH pre-treated merino wool, 80 °C.

For all concentrations of silver, 100, 250 and 500 mg/kg Ag^+ , a number of distinct trends are observed. Firstly, the amount of silver taken up by merino wool, for both untreated and KOH pre-treated fibres, is seen to increase with an increase in temperature from room temperature to 50 °C to 80 °C. As the temperature increases so will the speed of motion of molecules within the solution. Therefore, as the temperature is raised from room temperature to 50 °C to 80 °C, collisions between silver ions and merino wool fibres will become increasingly more frequent, and at greater speeds. The diffusion into the wool fibre, away from the surface, will also be greater leaving more surface capacity to absorb more Ag^+ ions. Subsequently, greater numbers of silver ions will be able to penetrate the fibre, resulting in a greater uptake of ions.

Secondly, for each individual sample, the majority of the total amount of silver that is taken up by merino wool over of the 72 hour time period occurs in the first 2-24 hours, depending on the concentration of the silver solution. That is to say, that there is a large initial uptake of silver ions, the rate of which then slows down dramatically. The greater the concentration of the silver solution, the more extended the majority uptake period becomes. For example, the large initial uptake by merino wool for a 100 mg/kg

Ag^+ solution occurs in the first 2-5 hours. When 250 mg/kg Ag^+ and 500 mg/kg Ag^+ solutions are used the majority uptake increases to 5-16 hours and 16-24 hours respectively. Tables 5.2 to 5.4 offer the % total uptake of silver ions from solution for untreated and KOH pre-treated merino wool for the said time periods. The uptake of silver ions by merino wool using either 100, 250 or 500 mg/kg Ag^+ solutions resulted in approximately 83.0-99.8 % of the total sorption occurring within 5, 16 or 24 hours respectively.

Table 5.2: Percentage total silver ion uptake by merino wool after 5 hours, using a 100 mg/kg Ag^+ solution.

Base Material	Temperature	Uptake Ag^+ After 5 hours	Total Uptake Ag^+ (mg/kg)	% Total Uptake
Untreated merino wool	Room Temp.	68.5	79.2	86.5
KOH pre-treated merino wool	Room Temp.	76.6	88.3	86.7
Untreated merino wool	50 °C	81.9	92.4	88.6
KOH pre-treated merino wool	50 °C	88.5	94.6	93.6
Untreated merino wool	80 °C	99.7	100.0	99.7
KOH pre-treated merino wool	80 °C	99.8	100.0	99.8

Table 5.3: Percentage total silver ion uptake by merino wool after 16 hours, using a 250 mg/kg Ag^+ solution.

Base Material	Temperature	Uptake After 16 hours	Total Uptake Ag^+ (mg/kg)	% Total Uptake
Untreated merino wool	Room Temp.	112.6	134.8	83.5
KOH pre-treated merino wool	Room Temp.	124.2	146.4	84.8
Untreated merino wool	50 °C	158.8	183.9	86.4
KOH pre-treated merino wool	50 °C	169.4	186.5	90.8
Untreated merino wool	80 °C	235.3	249.9	94.2
KOH pre-treated merino wool	80 °C	249.3	249.9	99.8

Table 5.4: Percentage total silver ion uptake by merino wool after 24 hours using a 500 mg/kg Ag⁺ solution.

Base Material	Temperature	Uptake After 24 hours	Total Uptake Ag ⁺ (mg/kg)	% Total Uptake
Untreated merino wool	Room Temp.	129.7	152.7	84.9
KOH pre-treated merino wool	Room Temp.	161.0	194.0	83.0
Untreated merino wool	50 °C	367.9	388.8	94.6
KOH pre-treated merino wool	50 °C	401.4	412.3	97.4
Untreated merino wool	80 °C	412.4	451.9	91.3
KOH pre-treated merino wool	80 °C	435.9	498.4	87.5

Thirdly, despite following the same general trend, the amount of silver taken up by KOH pre-treated merino wool (curves d-f in Fig. 5.22 to 5.24) is always somewhat greater to that of untreated merino wool (curves a-c in Fig. 5.22 to 5.24). This is also emphasised in Tables 5.2 to 5.4. For example, when merino wool is soaked in a 500 mg/kg Ag⁺ solution at 50 °C for 72 hours, the total uptake is 412.3 mg/kg Ag⁺ for KOH pre-treated merino wool in comparison to an uptake of 388.8 mg/kg Ag⁺ for untreated merino wool. The likely reason for the increased uptake by KOH pre-treated merino wool fibres is due to the alcoholic base treatment removing the lipid layer from the surface. The removal of hydrophobic lipids at the surface consequently allows for a greater ease of penetration of silver ions into the fibre. Furthermore, hydroxyl ions present during the methanolic KOH pre-treatment deprotonate functional groups at the surface of the fibre providing an overall negative charge that will attract positively charged silver ions.

What is additionally made evident by Tables 5.2 to 5.4 is that for the same temperatures, when the concentration of silver solution is increased the uptake of silver ions by merino wool is simultaneously seen to increase. That is to say, when a higher concentration of silver is implemented a greater total uptake is observed. For example, when a 100 mg/kg Ag⁺ solution is used, the uptake of silver from solution by KOH pre-treated merino wool after 72 hours at room temperature is 88.3 mg/kg Ag⁺, whereas the uptake from 250 and 500 mg/kg Ag⁺ solutions is 146.4 and 194.0 mg/kg Ag⁺ respectively. Similarly, at 80 °C the uptake by KOH pre-treated merino wool increases from 100.0 to 249.9 to 498.4 mg/kg Ag⁺ when the concentration of silver solution is

increased from 100 to 250 to 500 mg/kg Ag^+ . This is a very interesting result as, in addition to the temperature, the saturation point of merino wool by silver appears to be due to the availability of silver ions in solution. As the availability of silver ions increases so does the apparent saturation point.

Figure 5.25 compares the uptake of silver ions by untreated merino wool and KOH pre-treated merino wool, from silver solutions of increasing concentrations. The temperature in which the reaction was undertaken was 80 °C. When considering the absorption of silver ions by merino wool fibres, the diffusion of ions can be assumed to proceed according to Fick's law ¹. The rate of transport, P , across a unit area of the layer is given by:

$$P = D \cdot \Delta c / \sigma$$

where D is the diffusion coefficient, and Δc the change in concentration across the layer of width σ . The diffusion of silver ions into a merino wool fibre is a function of concentration ($D \propto \Delta c / \sigma$). Therefore, as the concentration of silver ions increases so does the driving force of diffusion.

Figure 5.25: Following the uptake of Ag^+ ions at 80 °C over a 72h soaking period using the following reaction conditions: a) untreated merino wool, 100 mg/kg Ag^+ solution; b) untreated merino wool, 250 mg/kg Ag^+ solution; c) untreated merino wool, 500 mg/kg Ag^+ solution; d) KOH pre-treated merino wool, 100 mg/kg Ag^+ solution; e) KOH pre-treated merino wool, 250 mg/kg Ag^+ solution; f) KOH pre-treated merino wool, 500 mg/kg Ag^+ solution.

The difference in Ag^+ concentration present in solution compared to that within the fibre, i.e. nil, accounts for the large initial uptake. When a large proportion of the silver ions are absorbed by the fibre, the concentration of silver ions remaining in solution is dramatically decreased and thus the driving force of diffusion simultaneously decreases. This occurrence leads to a saturation point, whereby merino wool cannot absorb any further silver ions. At a given temperature, as the specific silver concentration increases the saturation points of merino wool are simultaneously observed to increase. At room temperature this saturation point appears to be a ~85 % uptake of the silver content from solution. Whereas at 50 °C or 80 °C the saturation points appears to be a ~90 or 95 % uptake of the silver content from solution respectively.

5.4 Scale Up

When thinking towards the future commercialisation of the product, the preparation methods for merino wool - silver nanoparticle composites required scaling up. The initial consideration was to move from untreated merino wool fibres in the top form to merino wool fabric. In trialling the use of merino wool fabric as the base material, samples 2×2 cm and 3×8 cm in size were used. However, the colours of the resulting products were found to be uneven (Fig. 5.26). The unevenness in colour is not particularly evident in the smaller 2×2 cm samples (Fig. 5.26a-c) but is especially apparent in the larger 3×8 cm sample (Fig. 5.26d). The likely explanation for this is that Ag^+ ions are not able to diffuse into the fibres of the merino wool fabric evenly, due to the woven nature of the material. Additionally, a grease or wax from the mechanical process of weaving may interfere with the diffusion process of Ag^+ ions. Contributing to this argument is the observed slight darkening around the edges of merino wool squares, where Ag^+ ions can more readily enter the fibres.

Figure 5.26: Merino wool fabric coloured by silver nanoparticles: a) 100 mg/kg Ag^+ ; b) 250 mg/kg Ag^+ ; c) 500 mg/kg Ag^+ ; d) 500 mg/kg Ag^+ .

Due to the uneven colouring of merino wool fabric by silver nanoparticles, this scale up option was deemed inadequate. Therefore, due to the clean yellow colours available when merino wool is used in its top form, this method of preparation was deemed preferable. Subsequent spinning and weaving of the top after completion of the colouring process would be required. However, in order to make the colouring process commercially viable, it is imperative that the amount of silver is kept to a minimum and that there is a complete uptake of silver ions from solution whilst also gaining the desired yellow colour. A complete uptake of silver ions from solution also provides a very highly environmentally friendly process. The product would therefore consist of only merino wool and silver, with the waste solution containing no heavy metals but consisting of a very dilute solution of nitric acid (pH ~5.9).

Therefore, the uptake of silver ions from solution was followed using lower concentrations, notably 50, 100 and 150 mg/kg Ag^+ , and at elevated temperatures, 50 °C and 80 °C. This was done in order to determine the required concentration of silver and soaking period to gain a 100% Ag^+ uptake, whilst also providing a suitable colour. Figures 5.27, 5.29 and 5.31 provide a visual representation of the resulting merino wool - silver nanoparticle composites over time. Both untreated merino wool and KOH pre-treated merino wool were used for comparison as the base materials. The corresponding graphs showing the percentage uptake of silver ions from solution are offered in Figures 5.28, 5.30 and 5.32. The raw data for these graphs is offered in Appendices VI and VII.

When merino wool, untreated or KOH pre-treated, is soaked in a 50 mg/kg Ag^+ solution over a 72 hour time period, an almost complete uptake of silver from solution (>99 %) generally occurs in the first 30 minutes at both 50 °C and 80 °C (Figure 5.28). With a 100% uptake of silver by merino wool from a 50 mg/kg Ag^+ solution, the resulting

composite material consists of 0.05 weight percent (wt %) in silver. However, only a very minimal yellowing occurs when the preparation is undertaken at 50 °C and the colour is not readily observed until after 5-16 hours of soaking has occurred.

The yellowing of KOH pre-treated merino wool is greater than that of untreated merino wool (Figure 5.27a & 5.27b). On the other hand, when the preparation is undertaken at 80 °C, the fibres are already a distinct yellow colour after the said 5-16 hour period (Figure 5.27c). With extension of the soaking time, this colour darkens to brown (Figure 5.27d). The obtained colours after 5 hours however are dirty in their appearance, not having the bright colour desired. Therefore, due to aesthetics, a soaking time of 5 hours for the preparation of merino wool - silver nanoparticle composites consisting of 0.5 wt % Ag^+ is recommended.

Figure 5.27: Merino- silver nanoparticle composites prepared by soaking untreated merino wool (a & c) or KOH pre-treated merino wool (b & d) in 50 mg/kg Ag^+ over 72 h at 50 or 80°C.

Figure 5.28: Percentage uptake of Ag⁺ ions by merino wool from a 50 mg/kg Ag⁺ solution using the following reaction conditions: a) untreated merino wool, 50 °C; b) untreated merino wool, 80 °C; c) KOH pre-treated merino wool, 50 °C; d) KOH pre-treated merino wool, 80 °C.

Alternatively, the colours of merino wool-silver nanoparticle composites, when a 100 mg/kg Ag⁺ solution is implemented, are more intense in yellow colour, at both 50 °C and 80 °C (Fig. 5.29), in comparison to when a 50 mg/kg Ag⁺ solution is used (Fig. 5.27). The increased colour is due to greater levels of reduced silver being present within the fibres. The colours are additionally much cleaner and clearer in their appearance. With a 100% uptake of silver by merino wool from a 100 mg/kg Ag⁺ solution, the resulting composite material consists of 1.0 wt % in silver.

At 50 °C, untreated merino wool is seen to take greater than 24 hours to completely remove silver ions from solution (Fig. 5.30). At 80 °C however, this time is reduced to 5 hours. This is compared to a complete uptake of silver ions from solution for the same time period at 50 °C when is used as the base material. When the preparation is undertaken at 80 °C, using KOH pre-treated merino wool, an almost complete uptake (99.4 %) is noted after only 30 minutes. The most desirable colours of merino wool - silver nanoparticle composites that consist of 1.0 wt % in silver are obtained through the soaking of untreated or KOH pre-treated merino wool in a 100 mg/kg Ag⁺ solution for 16 hours.

Figure 5.29: Merino- silver nanoparticle composites prepared by soaking untreated merino wool (a & c) or KOH pre-treated merino wool (b & d) in 100 mg/kg Ag^+ over 72 h at 50 or 80 °C.

Figure 5.30: Percentage uptake of Ag^+ ions by merino wool from a 100 mg/kg Ag^+ solution using the following reaction conditions: a) untreated merino wool, 50 °C; b) untreated merino wool, 80 °C; c) KOH pre-treated merino wool, 50 °C; d) KOH pre-treated merino wool, 80 °C.

Finally, when a 150 mg/kg Ag^+ solution is used for the preparation of merino wool - silver nanoparticle composites (Fig. 5.31), the obtained colours are again a slight degree

darker to that of when a 100 mg/kg Ag^+ solution is implemented (Fig. 5.29). With a 100% uptake of silver by merino wool from a 150 mg/kg Ag^+ solution, the resulting composite material consists of 1.5 wt % in silver. At 50 °C a complete uptake is accomplished after 72 hours for untreated merino wool (Fig. 5.32). However, when composite preparation is being undertaken at 80 °C, this time period is reduced to 16 hours. Similarly, the soaking period of merino wool in silver solution for a complete uptake is reduced from 16 to 5 hours when KOH pre-treated merino wool is used. The most desirable colours obtained, whereby all silver ions have been completely removed from solution, requires the soaking of either untreated merino wool or KOH pre-treated merino wool for a period of 16 hours at 80 °C.

Figure 5.31: Merino- silver nanoparticle composites prepared by soaking untreated merino wool (a & c) or KOH pre-treated merino wool (b & d) in 150 mg/kg Ag^+ over 72 h at 50 or 80°C.

Figure 5.32: Percentage uptake of Ag^+ ions by merino wool from a 150 mg/kg Ag^+ solution using the following reaction conditions: a) untreated merino wool, 50 °C; b) untreated merino wool, 80 °C; c) KOH pre-treated merino wool, 50 °C; d) KOH pre-treated merino wool, 80 °C.

According to the above results, the most desirable colours for the complete uptake of silver by merino wool from 50, 100 or 150 mg/kg Ag^+ solutions are obtained when the temperature of the silver solution is set at 80 °C. When a 50 mg/kg Ag^+ solution is implemented the soaking period required is 5 hours. Whereas, when using either 100 or 150 mg/kg Ag^+ solutions, a 16 hour soaking period is required. The defined soaking periods were determined by the results from preliminary tests, as outlined above. A complete uptake of silver from solution is required whilst also resulting in an attractive, clean and crisp yellow or gold colour.

Figure 5.33 offers an image showing 2 g samples of merino wool - silver nanoparticle composites consisting of 0.5, 1.0 and 1.5 wt % silver respectively. The sample preparation was a direct scale up from the small scale initial tests previously discussed (method outlined in section 2.2.1.4). The method included soaking 2 g merino wool in 200 cm³ of one of either: 50, 100 or 150 mg/kg Ag^+ solutions. This increase in sample size was undertaken in order to determine the feasibility of upscale, i.e. whether increasing the sample size will affect the silver uptake and resulting colour. The process was deemed successful as post-preparation residual silver in solution as tested by atomic absorption (AA) was nil and the resulting colours were those required.

Figure 5.33: Merino wool - silver nanoparticle composites consisting of: a) 0.5 wt % Ag^+ ; b) 1.0 wt % Ag^+ ; c) 1.5 wt % Ag^+ .

Consequently, the processes for the preparation of merino wool - silver nanoparticle composites consisting of 1.0 wt % silver have been scaled for larger scale production. A direct upscale of the method outlined in section 2.2.1.4 was again employed: 100 g of fibres in $10,000 \text{ cm}^3$ silver nitrate. Fine merino wool and cross bred wool were both used. Figure 5.34a and 5.34c provides images of the respective merino- or crossbred wool-silver nanoparticle composites in their top and spun forms. The silver nanoparticle-dyed fine merino wool top was spun and then woven, providing the world's first fine merino wool scarf coloured by silver nanoparticles (Fig. 5.34b). The silver nanoparticle-dyed crossbred wool yarns, spun at AgResearch, Christchurch, New Zealand, were provided to Wools of NZ Ltd, Ilkley, United Kingdom, who subsequently prepared a large carpet sample, $750 \times 750 \text{ cm}$ in size (Fig. 5.34d). This sample has been showcased by Wools of NZ Ltd as part of their international marketing operation. It should be noted that, despite merino wool coloured with silver nanoparticles not having a measurable conductivity, a build up of static electricity was not observed during spinning from fibre to yarn. This simplifies greatly the spinning process which traditionally experiences problems due to the build up of static electricity and is a particularly important trait to have for application in aircraft and motorvehicle interiors.

Figure 5.34: Wool coloured by silver nanoparticles: Fine merino wool in its a) dyed top and spun forms; b) woven into a scarf; Crossbred wool in its c) dyed top and spun forms; d) woven into a carpet sample.

5.5 Silver Nanoparticles: Proposed Mechanism of Formation and Binding to Merino Wool

The formation of silver nanoparticles within wool fibres and the nature of the bond between the two were studied using EDS and XPS analysis. A secondary electron SEM image of a cross section of a wool fibre coloured with silver nanoparticles, together with the EDS elemental analysis maps of Ag and S is shown in Figure 5.35. The elemental

map of Ag shows that silver nanoparticles are present not only on the surface but also throughout the centre of the fibre. A distinct correlation of silver with sulfur is observed. This chemical association for one another suggests an interaction between the nanoparticles and merino fibres through one or both of the sulfur containing amino acids, cysteine or cystine.

Figure 5.35: A SEM image of the cross section of a merino wool fibre coloured with silver nanoparticles together with the individual EDS maps of S and Ag and the respective overlay.

The chemical association of silver with sulphur is further implied by XPS studies and will presently be discussed in detail. Figure 5.36, provides the S 2p spectra relating to a merino wool - silver nanoparticle sample, in comparison to merino wool alone as a reference. Both spectra are of the KOH pre-treated analogues. In the spectrum for merino wool alone, three peaks positioned at 163.9, 165.2 and 167.7 eV are present. The positions of these peaks are in accordance with the literature. Previous XPS studies of wool suggest that the peak at ~164 eV is due to –S–H present in cysteine; the peak at ~165 eV is due to the disulfide linkage –S–S– present in cystine; and the peak at ~168 eV is due to –SO₃H present in cysteic acid ².

The positions of the peaks relating to –S–H and –S–S– in the S 2p spectrum of merino wool - silver nanoparticle composite remain stable when comparing to merino wool alone. However, the formation of a new peak at 162.1 eV appears, indicating an interaction of silver with sulfur moieties present within the wool. The position of this peak is at a higher position to that of a direct –S–Ag linkage, stated in the literature to occur at 160.9 eV ³. The shift to a higher binding energy of this peak may be attributed

to silver being present in its nanoparticulate form. Alternatively, the interaction between sulfur and silver may be a stabilising interaction only, rather than a direct bond.

Figure 5.36: XPS spectra of S 2p for a) merino wool - silver nanoparticle composite and b) untreated merino wool.

Studies undertaken by Hadad et al. suggest a similar situation to that described above⁴. In the said study, silver nanoparticles were deposited on the surface of natural wool with the aid of powered ultrasound. A peak, positioned at 161.7 eV is observed in the XPS S 2p spectrum of their resulting composite. This peak has similarly been attributed to an ‘interaction’ of sulfur with silver. Additionally, it has been suggested that the reason the band arises is due to a disconnection of the -S-S- bond, present in cystine.

The breaking of the disulfide bond is also suggested in our own system, whereby the ratio of $-S-S-$ to $-S-H$ for merino wool alone to the merino wool - silver nanoparticle composite changes from 0.8:1 to 0.6:1 respectively. The reduction in the amount of cystine present in the composite indicates that the two sulfur entities of the broken disulfide bond subsequently interacting with silver ions on the surface of the nanoparticle. A very basic schematic of this is provided in Figure 5.37, whereby 'x' indicates the wool matrix. As there is no change in the oxidation state of sulfur through this process, in addition to the fact that the peak relating to oxidised sulfur does not increase, it is unlikely that the breaking of the disulphide bond is involved in the reduction and formation of silver nanoparticles.

Figure 5.37: Diagram showing the breaking of the cystine disulphide bond and the subsequent interaction of S^- with Ag^+ ions at the silver nanoparticle surface.

The relationship of silver with sulfur, and in particular the binding of silver to cystine through the breaking of the disulfide bond, was studied further by an initial reduction of the disulfide bond, prior to treatment with silver nitrate. Garlick et al. has proven that tris(2-carboxyethyl)phosphine (TCEP) successfully reduces the disulfide bond within wool, giving rise to two cysteine entities, containing only thiol groups (Fig. 5.38) ⁵. This process was undertaken on merino wool fibres and the uptake of silver ions by TCEP pre-treated merino wool was monitored over time at room temperature, 50 °C and 80 °C. The results of the percentage uptake of silver ions by TCEP pre-treated merino wool from a 500 mg/kg Ag^+ solution are compared to those for KOH pre-treated merino wool in Figure 5.39.

It is noted that the silver uptake by reduced merino wool, i.e. that containing no disulphide bonds, takes up far less than that of KOH pre-treated merino wool, despite the relative fraction of sulfur remaining within the wool remaining constant (Fig. 5.39). The reactivity of thiol groups is analogous to the hydroxyl anion⁶. However, the results of the uptake of silver by merino wool over time, together with XPS results suggest that the association and bond breaking of the disulfide bond, with subsequent bond making of sulfur with silver, must be preferable to the attraction of silver to thiols. In addition, as an important biological feature, thiols are readily involved in redox processes. Among the most prominent oxidation products of thiols in wool are cystine (-S-S-) or cysteic acid (-SO₃H). Although again the XPS results above suggest that sulfur containing amino acids are not involved in the reduction of Ag⁺ to Ag⁰.

Figure 5.38: Reduction of the disulphide bond present in cystine to by tris(2-carboxyethyl)phosphine (TCEP).

Figure 5.39: Percentage uptake of Ag⁺ ions by merino wool from a 500 mg/kg Ag⁺ solution using the following reaction conditions: a) KOH pre-treated merino wool, room temperature; b) KOH pre-treated merino wool, 50 °C; c) KOH pre-treated merino wool, 80 °C; d) TCEP pre-treated merino wool, room temperature; e) TCEP pre-treated merino wool, 50 °C; f) TCEP pre-treated merino wool, 80 °C.

The final observation when comparing the S 2p spectra of merino wool alone to that of the merino wool - silver nanoparticle composite is that a distinct shift in the peak relating to cysteic acid and other oxidised species of silver, from 167.7 to 168.9 eV, occurs (Fig. 5.36). The shift to higher binding energies suggests a change in the environment of the oxidised form of sulfur. This could be the formation of a more oxidised species of sulfur, or more likely, an interaction of lone pairs of electrons on carboxyl groups interacting with the surface of formed silver nanoparticles through weak electrostatic interactions (Fig. 5.40).

Figure 5.40: Possible interaction of cysteic acid with silver nanoparticles.

The comparison of N 1s XPS spectra for merino wool alone and its silver nanoparticle analogue is provided in Figure 5.41. In the spectrum for merino wool alone (Fig. 5.41b), a single peak is assigned for amine, amide and imine groups at 400.2 eV. A band for oxidised nitrogen species is located at a binding energy of 401.6 eV. In the spectrum for the merino wool - silver nanoparticle composite an insignificant shift is observed for the encompassing amino peak. However, a distinct shift and broadening is noted for the peak relating to oxidised nitrogen. The noted shift is from 401.6 to 402.9 eV, with the full width at half maximum (FWHM) correspondingly increasing from 1.7 to 3.0. Additionally, there is a considerable increase in the proportion of oxidised nitrogen (from 17.7 to 42.17 %) present in the composite when compared to merino wool alone.

The significant increase in oxidised nitrogen in the composite implies that the nitrogen containing amino acids present in merino wool are primarily involved in the reduction of Ag^+ to Ag^0 . Additionally, the shift in this peak suggests an interaction of oxidised nitrogen with silver. The broadening of the band relating to oxidised nitrogen indicates

greater deviations in the nature of the oxidised species, in addition to changes in the surrounding environment. That is to say that the introduction of silver ions, and the subsequent reduction of (and potential binding to) a proportion of these ions by nitrogen containing functional groups, changes the environment dramatically, from being somewhat regulated to much less defined. The limits of the fitted broad peak represent the end members of the continuum of the environments. Figure 5.42 gives a basic visual representation of the size of nanoparticles formed, in comparison to that of the protein structure that constitutes merino wool. This gives an idea as to the varied environment the formed silver nanoparticles would be exposed to.

Figure 5.41: XPS spectra of N 1s for a) merino wool - silver nanoparticle composite and b) untreated merino wool.

Figure 5.42: A comparison of the size of a 4 nm sized nanoparticle with the protein structure within wool.

The comparison of N 1s spectra between merino wool alone and the composite (Fig. 5.41) indicated the role nitrogen containing moieties within the wool have in the reduction and formation of silver nanoparticles. However, the deconvolution of peaks owing to amine, amide and imine groups and those of the oxidised species poses too subjective a task to be able to confidently determine which N-containing groups, or if all groups, contribute to the reduction and/or bonding.

The XPS C 1s spectrum for the merino wool - silver nanoparticle composite sees a large increase in the band present at ~288 eV. The proportion of this peak increases from 14.3 in merino wool alone to 49.1 % in the silver nanoparticle composite (Fig. 5.43a & 5.43b). This occurrence indicates an increase in the presence of amide and carboxyl groups present in the composite. An increase in carboxyl groups in the merino wool - silver nanoparticle composite is additionally confirmed in the O 1s spectra, whereby an increase in the peak owing to the carboxyl functional group increases from 25.0 to 61.7 % (Fig. 5.43c & 5.43d). The peak additionally becomes very broad, with the FWHM increasing from 1.9 to 3.5. Again this indicates a large variety in the environments surrounding this functionality. These results indicate that the carboxyl-amine bond present in both of aspartic and glutamic acid (Fig. 5.44) may be broken with treatment of silver. The amine is oxidised, simultaneously reducing silver. Meanwhile, the carboxylic acid is formed.

5 - MERINO WOOL - SILVER NANOPARTICLE COMPOSITES: NANOPARTICLES FORMED IN THE PRESENCE OF MERINO WOOL USING ITS REDUCING NATURE

Figure 5.43: XPS spectra of a) C 1s for merino wool - silver nanoparticle composite; b) C 1s for untreated merino wool; c) O 1s for merino wool - silver nanoparticle composite; b) O 1s for untreated merino wool.

Figure 5.44: Protein structure of merino wool.

Finally, the Ag 3d spectra for silver metal alone the merino wool - silver nanoparticle composite are offered in Figure 5.45. The peak for silver metal alone relating to Ag^0 ($3d_{5/2}$) occurs at 368.2 eV. The position of this peak is accordance with the literature for Ag^0 , which is recorded to be typically located between 368.0 to 368.3 eV^{7,8}. The peak is narrow, with a FWHM of 0.68, indicating regulated domains of silver within the metal. In comparison, the peak position of silver within the composite is observed at a higher binding energy to that of silver metal alone, at 368.6 eV. This shift could be associated to the nanoparticulate size of the silver present; in addition to the interaction silver has with the fibre. The said peak is approximately twice as broad as the peak relating to Ag^0 of the silver metal sample, with a FWHM of 1.44.

The broadening of this peak is likely for two reasons. Firstly, because the silver nanoparticles are exposed to varied environments within the fibre, no longer within a highly regulated system as with silver metal. Secondly, it is likely that the association of silver with sulfur is also enveloped within this peak, as a peak relating to an Ag-S-bond occurs at equivalent binding energies to that of Ag^0 ⁹⁻¹². The peak positioned at 369.7 eV in the Ag 3d spectrum of the merino wool - silver nanoparticle composite may be assigned to the association of silver with oxygen. This interaction may be with either an oxidised form of sulfur or nitrogen, as was indicated by both S 2p and N 1s spectra for the composites, i.e. $\text{Ag}^+ - \text{O-S-}$ or $\text{Ag}^+ - \text{O-N-}$.

Figure 5.45: XPS spectra of Ag 3d for a) silver metal and b) merino wool - silver nanoparticle composite.

Therefore, from the XPS results discussed, the following is suggested for the mechanism of formation of silver nanoparticles within merino wool fibres. Silver ions are firstly absorbed by the fibre. Due to the favourable interaction between silver and sulfur the silver ions associate with cysteine and cystine amino acids. The formation of an Ag-S bond occurs over an Ag-N bond as the stability constant of an Ag-S bond is almost twice that of an Ag-N bond¹³. Nitrogen containing functional groups are in close vicinity and act as the reducing agent, effectively reducing Ag^+ to Ag^0 . The increased temperature additionally increases reaction kinetics and hence the rate of reduction, from Ag^+ to Ag^0 . Therefore more highly coloured fibres are obtained in a shorter period of time.

5.6 Colour of Merino Wool - Silver Nanoparticle Composites

5.6.1 UV-Visible Spectroscopy

The colour of yellow-coloured merino wool - silver nanoparticle composites is due to the interaction of light with silver nanoparticles formed within the fibre. As was discussed in section 4.4, Henglein has previously reported that the Ag 4d to 5sp interband transition of silver generally occurs at an energy corresponding to 320 nm¹⁴. However, the surface plasmon resonance visible in the UV-vis spectrum depends strongly on not only the size and shape of the nanoparticle, but also the dielectric function of surrounding medium. According to TEM analysis, nanoparticles are spherical in shape (Fig. 5.9 & 5.16). The light absorbed from spherical silver nanoparticles is typically in the blue region of the visible spectrum; 400-490 nm¹⁵. The reflected light that is visible to the eye is thus yellow. The characteristic red shift of the plasmon absorption band from 320 to the 400 nm region observed by silver nanoparticles in UV-vis spectra is characteristic of silver nanoparticles protected by, and interacting with, a stabilising agent¹⁶.

A similar yellow colour of the merino wool - silver nanoparticle composite was achieved when an external reducing agent was alternatively used during preparation (see sections 4.1.1.1 & 4.1.2.1). When 20 μ L, 1 % w/w TSC was utilised as the reductant the formed spherical nanoparticles present in the composite are approximately 10-15 nm in diameter. The plasmon absorption band for this sample is observed at ~430 nm in the UV-vis (Fig. 4.29). The peak shift from 320 to 430 nm is therefore due to the interaction of silver nanoparticles with TSC, as the stabiliser, which has a refractive index of 1.3. The size of spherical nanoparticles formed within wool, using the reducing nature of proteins, is comparable; with diameters measuring from 4-12 nm. In this case, wool is the medium which acts as the stabilising agent. Wool becomes transparent in methyl salicylate and dichlorobenzene indicating that its refractive index lies somewhere between 1.539 and 1.549¹⁷. Therefore, as both the size of the spherical-shaped nanoparticles and the refractive index of surrounding medium are

similar to that of the external reducing agent example, one would expect the peak of the plasmon absorption band for this system to be similarly in the 400-450 nm region.

The UV-vis spectrum for a KOH pre-treated merino wool - silver nanoparticle composites is offered in Figure 5.46b below. The merino wool - silver nanoparticle composite was initially measured in reflectance mode and then converted to spectra related to the absorbed component of incident light by applying the Kubelka-Munk equation (refer to section 2.3.3). The result for an untreated merino wool - silver nanoparticle composite, measured in the same manner, is analogous to that of the KOH pre-treated merino wool composite. A single peak is observed at ~320 nm in the UV-vis. The position of this peak could well be due to the Ag 4d to 5sp interband transition of silver. However, interestingly, the UV-vis is very similar to that of the spectrum for the merino wool - silver nanoparticle composite (Fig. 5.46a). Again a single peak is located at 316 nm. Although no peaks are present in the visible region for either, the composite absorbs much greater amounts in the blue region, between 400 and 500 nm, therefore reflecting yellow light. The composite thus appears yellow to the eye.

When the reducing nature of proteins within wool is exploited for the preparation of merino wool - silver nanoparticle composites, the nanoparticles are formed within the fibre itself and are typically not present at the surface. The particles are only present in low quantities, typically 0.5-1.5 wt %. Additionally, the UV-vis spectra for merino wool - silver nanoparticle composites, in addition to untreated merino wool, are originally measured in reflectance before conversion to an absorption spectrum. Therefore it is possible that the nanoparticles are being masked by the bulk fibre and therefore a peak itself is not observed in the spectra.

Figure 5.46: UV-vis spectra for: a) untreated merino wool and b) a merino wool - silver nanoparticle composite.

5.6.2 Colourfastness Testing

5.6.2.1 Colourfastness to Washing

In order to determine the robustness of the colour of merino wool - silver nanoparticle composites, colour fastness tests to washing and rubbing were undertaken. Colourfastness tests of merino wool - silver nanoparticle composites to shampooing were undertaken at AgResearch, Christchurch, using the Australian/NZ Standard 2111.19.2 test was used, as outlined in section 2.3.9.1.1. The composites studied were loaded with 1.0 wt % silver. This test ranks the shampooing colourfastness of tested composites on a scale of 1 to 5, where 1 indicates maximum colour change and thus very poor light fastness, and 5 indicates the minimum colour change and thus excellent light fastness. The change in the shade of colour of the tested composite is monitored, in addition to the degree of staining on both wool and cotton surfaces that are used to rub the sample. Table 5.5 shows that merino wool - silver nanoparticle composites, in both top and carpet forms, score up to the maximum value obtainable (4 to 5) for

colourfastness to shampooing. These results reach the pass level for the change in shade of colour and surpass that for staining on wool and cotton. As the colour remains stable to shampooing it implies that the nanoparticles are strongly bound throughout the fibre. The nature of this bond was discussed in detail in section 5.5.

Table 5.5: Results from colourfastness testing on merino wool - silver nanoparticle composites to shampooing.

Sample Form	Test	Score	Pass Level
Top	AS/NZS 2111.19.2 Change of shade	4-5	4
Top	AS/NZS 2111.19.2 Staining on wool	5	3
Top	AS/NZS 2111.19.2 Staining on cotton	5	3
Carpet	AS/NZS 2111.19.2 Change of shade	4-5	4
Carpet	AS/NZS 2111.19.2 Staining on wool	5	3
Carpet	AS/NZS 2111.19.2 Staining on cotton	5	3

5.6.2.2 Colourfastness to Rubbing

As with the colourfastness tests of merino wool - silver nanoparticle composites to shampooing, colourfastness tests on samples to rubbing, were undertaken at AgResearch, Christchurch, using the Australian/NZ Standard 2111.19.1 test (refer to section 2.3.9.1.2). The test monitors the transfer of colour from the coloured material being analysed, to a cotton fabric which is rubbed upon the sample. The cotton rubbing fabric is used either dry or wet, with both conditions studied. The amount of staining of the rubbing fabric is evaluated on a scale of 1 to 5, whereby 1 signifies maximum staining and 5, no staining. Textiles must score a minimum value of 3 to 4 for dry rubbing and a minimum of 3 for wet rubbing to pass this test. Table 5.6 provides the results for merino wool - silver nanoparticle composites, in both top and carpet form, tested for colourfastness to rubbing. It is observed that samples exceed the pass level for the test, scoring 4 to 5 in both wet and dry conditions. An image showing the pieces of the rubbed cotton fabrics, after colourfastness to rubbing tests have been undertaken is given in Figure 5.49. No apparent colour transfer is noted on the cotton squares and thus the high score obtained.

Table 5.6: Results from colourfastness testing on merino wool - silver nanoparticle composites to rubbing in both wet and dry conditions.

Sample Form	Test	Score	Pass Level
Top	AS/NZS 2111.19.1 Wet	4-5	3
Top	AS/NZS 2111.19.1 Dry	4-5	3-4
Carpet	AS/NZS 2111.19.1 Wet	4-5	3
Carpet	AS/NZS 2111.19.1 Dry	4-5	3-4

Figure 5.47: Cotton fabric implemented for colourfastness to rubbing tests (AS/NZS 2111.19.1), undertaken in: a) wet conditions and b) dry conditions.

5.6.2.3 Colourfastness to Chlorinated Swimming Pool Water

Colourfastness tests for the colour stability of merino wool - silver nanoparticle composites to chlorinated swimming pool water were again undertaken at AgResearch, Christchurch. The method implemented for this test was the Australian Standard 2001.4.5 whereby coloured samples are rotated in a solution containing sodium hypochlorite in a water bath held at 25 °C, for one hour (refer to section 2.3.9.1.3). A score of 1 implies a severe change in colour or staining and 5, that of no change in colour or staining. The results in Table 5.7 show that for the staining of wool and cotton, the maximum or close to maximum values are obtained, with scores of 4 to 5 and 5 respectively. The score for the change of shade for merino wool - silver nanoparticle composites is slightly lower than that for the staining, measured at 3 to 4. However, this value is still greater than 3, which is required to pass this test.

Table 5.7: Results from colourfastness testing on merino wool - silver nanoparticle composites to chlorinated swimming pool water.

Sample Form	Test	Score	Pass Level	
Top	AS 2001.4.5	Change of shade	3-4	3
Top	AS 2001.4.5	Staining on wool	4-5	3
Top	AS 2001.4.5	Staining on cotton	5	3
Carpet	AS 2001.4.5	Change of shade	3-4	3
Carpet	AS 2001.4.5	Staining on wool	4-5	3
Carpet	AS 2001.4.5	Staining on cotton	5	3

5.7 Stability of the Colour of Merino Wool - Silver Nanoparticle Composites

5.7.1 Stability of Colour to Time and Temperature

Despite the stability of colour observed for merino wool - silver nanoparticle composites to washing and rubbing the same cannot be said for the stability of composites over periods of time, both at ambient and elevated temperatures. When merino wool fibres are soaked in silver nitrate at an elevated temperature for an extended period, i.e. 24 hour soaking period at 80 °C, a change in colour from yellow to brown is noted. Synchrotron radiation XRD indicates that a consequent change in the form of silver, from crystalline silver to an amorphous state occurs with the change in colour (refer to Fig. 5.21, section 5.2.2). A colour change is also observed, from yellow to yellow/grey/brown, when merino wool - silver nanoparticle composites are exposed to air for extended periods of time (Fig. 5.50). However, the colour is not as significant a change as the example with extended heating in solution.

The change in colour over time, with exposure to air, was monitored by UV-vis spectroscopy (Fig. 5.51). The peak originally present at 316 nm shifts to higher wavelengths: 321 nm after 2 weeks exposure, and 332 nm after 3 months exposure. The peaks are also noted to broaden with subsequent exposure times. The browning of the sample is implied by the red shift in conjunction with the peak broadening, i.e. more

light is absorbed throughout the visible region contributing to the ‘dirty’ appearance of the sample.

Figure 5.48: Expressing the visual colour change of merino wool - silver nanoparticle composites over a period of three months: a) 1 day; b) 2 weeks; c) 3 months following preparation.

Figure 5.49: UV-vis absorption spectra of merino wool - silver nanoparticle composites over a period of three months: a) 1 day; b) 2 weeks; c) 3 months following preparation.

As with the extended heating of merino wool in silver nitrate solution example that is discussed above, a change in the form of silver simultaneously occurs with the change of colour from yellow to brown with long periods of exposure to light. Synchrotron radiation XRD again confirms this as a change from crystalline silver to a non-crystalline form, indistinguishable by XRD. The crystalline silver Ag 111 peak, due to the presence of crystalline silver nanoparticles, is present one day following the

preparation of the composite. However, two weeks following composite preparation, the crystalline Ag 111 peak is no longer observed indicating that silver in its crystalline form is no longer present (Fig. 5.52).

Figure 5.50: Synchrotron Radiation XRD patterns, focusing on the Ag 111 peak, for merino wool - silver nanoparticle composites showing the conversion of metallic silver to an amorphous form of silver: a) 1 day; b) 2 weeks; c) 3 months following preparation.

Therefore, it may be concluded that the yellow colour of merino wool - silver nanoparticle composites is due to crystalline silver nanoparticles, whereas the brown colour is due to an oxidised form. This oxidised form of silver could be due to a chemical reaction with free oxygen, to form silver oxide (Ag_2O)¹⁸.

Alternatively, it could be due to the reaction of silver with sulfur-containing substances in the air to form disilver sulphide (Ag_2S). According to Graedel, the sulfidation mechanisms of silver are dependent on the humidity¹⁹. At low relative humidity, H_2S gas reacts with silver metal directly, but at high relative humidity, dissolved species (HS^- , S^{2-}) from H_2S gas reacted with silver.

Alternatively, Volpe and Peterson exposed silver to dry air containing H₂S (100 ppb~400 ppb) in flowing gas and proposed the following reaction ²⁰:

It is typically a combination of silver oxide and silver sulfide that makes up the black tarnish found on silver jewellery and ornaments.

In an attempt to determine which species of silver, either silver oxide or silver sulfide or both, causes the darkening of merino wool - silver nanoparticle composites, XPS studies were undertaken. The composites were studied one day after preparation (yellow), and 3 months after preparation (yellow/grey/brown) (Fig. 5.33 to 5.35). The results of the XPS spectra obtained from these samples indicate that silver is oxidised, likely forming both silver oxide and silver sulfide. However, in addition, oxidation of sulfur and nitrogen containing species also occurs. Noteworthy shifts of peaks present in each of the Ag 3d, S 2p and N 1s spectra are provided in Table 5.8. A distinct increase in the proportion of oxidised species is observed for the spectra Ag 3d, S 2p and N 1s and will be discussed in further detail below.

Figure 5.51: XPS Ag 3d spectra of merino wool - silver nanoparticle composites: a) 3 months; b) 1 day following preparation.

Figure 5.52: XPS S 2p spectra of merino wool - silver nanoparticle composites: a) 3 months; b) 1 day following preparation.

N 1s/26

Figure 5.53: XPS N 1s spectra of merino wool - silver nanoparticle composites: a) 3 months; b) 1 day following preparation.

Table 5.8: Changes in the proportions of peaks present in the XPS spectra of merino wool - silver nanoparticle composites: 1 day and 3 months following preparation.

XPS Spectrum	Position of peak (eV)	Peak Relating to	% Peak Area 1 Day Following Preparation	% Peak Area 3 Months Following Preparation
Ag 3d	~370	Ag-O-	26	35
S 2p	~162	-S-Ag	8	15
	~168	-S(ox)	23	39
		-SO-Ag		
N 1s	~ 401	-N(ox)	18	43
		-NO-Ag		

From the Ag 3d spectrum, the percentage value relating to silver bound to oxygen increases from 26 % to 35 % after 3 months (Fig. 5.53, Table 5.8). This relates to an increase in the ratio of Ag-O- : Ag⁰/Ag-S- from 0.4 : 1 to 0.7 : 1. This result suggests the formation of Ag₂O on the surface of the nanoparticles, darkening them. The standard state enthalpy ($\Delta H^\circ_{\text{rxn}}$) and entropy ($\Delta S^\circ_{\text{rxn}}$) changes for the formation of silver oxide, as calculated from the thermodynamic data, are -62.2 kJ and -0.133 kJ/K respectively (Table 5.9). These values tell us that the reaction is exothermic and that the entropy of the reaction is negative. However, these terms are in conflict. The enthalpy term favours the reaction being spontaneous, but the entropy term favours the reaction being non-spontaneous. When the terms conflict in such a manner, the temperature at which the reaction occurs will determine the spontaneity. Standard Gibb's free energy ($\Delta G^\circ_{\text{rxn}} = \Delta H^\circ_{\text{rxn}} - T \Delta S^\circ_{\text{rxn}}$) of the reaction to be calculated.

Table 5.9: Standard states enthalpy, entropy and Gibb's free energy of silver oxide ¹³.

Compound	$\Delta H^\circ_{\text{rxn}}$ (kJ)	S°_{rxn} (kJ/K)	$\Delta G^\circ_{\text{rxn}}$ (kJ)
Ag ₂ O (s)	-62.2	-0.133	-22.6

When the enthalpy and entropy terms conflict in such a manner, the temperature at which the reaction occurs will determine the spontaneity. The standard Gibb's free energy ($\Delta G^\circ_{\text{rxn}} = \Delta H^\circ_{\text{rxn}} - T \Delta S^\circ_{\text{rxn}}$) is calculated at -22.6 kJ. Since $\Delta G^\circ_{\text{rxn}} < 0$, the reaction is spontaneous at room temperature. This agrees with our experience that silver does spontaneously tarnish as it sits in air. By rearranging the standard Gibb's free energy equation we may determine at what temperature the reaction would be at equilibrium ($\Delta G^\circ_{\text{rxn}} = 0$, therefore $T = \Delta H^\circ_{\text{rxn}} / \Delta S^\circ_{\text{rxn}}$). It should be noted that it is not entirely accurate to use standard state thermodynamic quantities away from 298 K, as the values are temperature dependent. However, an acceptably small error in the resulting calculations is introduced and an idea of the equilibrium temperature can be gauged.

The equilibrium temperature for the reaction of the formation of silver oxide is calculated at 468 K, or 195 °C. This means that for temperatures below 195 °C the forward reaction is spontaneous. However, for temperatures above 195 °C the reaction would be non-spontaneous and the reverse reaction would occur.

Therefore, a way of removing silver oxide formed on the merino-nanoparticle composite would be to increase the temperature to above 195 °C. This method is not deemed appropriate however. Wool does not burn until a much greater temperature is reached, 570-600 °C. Although at 195 °C or above the high temperature would degrade the nature of the chemical nature of the wool, becoming brittle and losing mechanical strength²¹.

The spectrum owing to S 2p indicates an increase in the peak relating to Ag-S-, from 8 % in the initial sample to 15 % after 3 months (Fig. 5.54, Table 5.8). This greater proportion of Ag associating with S suggests that the formed silver nanoparticles may be reacting with H₂S in the air, forming Ag₂S on the surface. In an additional attempt to visually determine whether disilver sulphide is present, a simple experiment was undertaken on darkened merino wool - silver nanoparticle samples in an attempt to convert any silver sulfide present back into silver. The experiment is a common household method for successfully cleaning tarnished silver ornaments. In the typical reaction a silver object is placed into an aluminium lined vessel, making sure there is sufficient contact between silver and aluminium. A sodium bicarbonate solution (0.1 M, 80 °C) is then poured over the object so as to completely immerse it. Sulfur atoms are transferred from silver to aluminium during the reaction, freeing the silver metal and forming aluminium sulfide. The sodium bicarbonate solution acts as a carrier of the sulfur from the silver to the aluminium.

The above procedure was undertaken using merino wool - silver nanoparticle composites wrapped in aluminium foil and placed in an aluminium foil lined beaker. However, as the results show in Figure 5.56, no change in colour was observed and the colours remain darkened. This indicates one of two things. Firstly, the darkening of fibres is not due to the formation of disilver sulfide on the surface of the nanoparticles, or secondly because the contact between the fibres and aluminium is insufficient. The latter is plausible as nanoparticles are generally formed below the fibre surface and thus it is questionable whether adequate contact between silver species and aluminium would occur.

Figure 5.54: Merino wool - silver nanoparticle composites 3 months following preparation, initially prepared using: a) 50 mg/kg; b) 100 mg/kg; c) 150 mg/kg. The resulting fibres after S-removal treatment with aluminium: d)-f).

The S 2p spectrum for the merino wool - silver nanoparticle composite over time also indicates a significant increase in the peak area relating to sulfur bound to oxygen (Fig.5.54, Table 5.8). Shortly after preparation the area under this peak is 23 %. An increase to 39% is observed after 3 months. The N 1s spectrum also sees an increase in the oxidised nitrogen species, from 18 to 43 % (Fig. 5.55, Table 5.8). It may not be that the nitrogen of sulfur species are oxidised, the greater proportion of -N-O and -S-O may be due to the greater numbers of oxidised silver nanoparticles and the interaction of nitrogen and sulfur with the oxide layer at the surface. The literature also indicates that silver can react with nitrates in the air forming a surface layer of silver nitrate²². However, this is not the case with merino wool - silver nanoparticle composites as the peak for nitrates, typically present at ~406 eV, is not observed in the N 1s spectrum.

5.7.2 Stability of Colour to Light

In addition to the colour of merino wool - silver nanoparticle composites being unstable over time; colour stability issues for the composites are also evident with regard to direct exposure to light. Lightfastness tests, using the ISO test method 105-BO2:1994, were undertaken at AgResearch, Christchurch as outlined in section 2.3.9.1.4. The tested samples are scaled from 1 to 8, whereby a score of 1 indicates poor colourfastness with light exposure and 8 indicates excellent lightfastness. An image of the change in colour of the merino wool - silver nanoparticle composite, in its top form, is provided in Figure 5.57. The composite achieved the lowest possible grade, of 1 out of 8, in both the top and carpet forms (Table 5.10).. Considering, the pass level for this test is considered a score of 5, this indicates further work is required to halt the change of the colour of merino wool - silver nanoparticle composites when exposed to light.

Figure 5.55: The resulting colour change of a merino wool - silver nanoparticle composite following lightfastness testing (ISO 105-BO2:1994).

Table 5.10: Results from lightfastness tests on merino wool - silver nanoparticle composites.

Sample Form	Test	Score	Pass Level
Top	ISO 105-BO2:1994	1	5
Carpet	ISO 105-BO2:1994	1	5

In an attempt to further understand the discolouration process of merino wool coloured by silver nanoparticles, a study was undertaken at our home institute. Composites were placed in an envelope with half the sample exposed to natural light and half of the sample kept in the dark of the envelope interior (Fig. 5.58a). After a period of thirteen weeks a distinct change in colour was observed. To the eye, the portion exposed to natural light lightened and whitened in colour considerably, whereas the change in colour to the portion kept in the dark was insignificant (Fig. 5.58b).

Figure 5.56: Stability of merino wool - silver nanoparticle composites to light and dark: a) experimental setup and b) resulting colour of composite exposed to light (upper portion) and no light (lower portion).

The CIE L*, a*, b* values for merino wool - silver nanoparticle composites exposed to light or kept in the dark, together with the values for the reference sample, are provided in Table 5.11. As is noted from these results, when compared to the reference sample, only a very minimal darkening and reddening of the sample occurs when kept in the dark. This darkening of the sample is indicated by a small decrease in L* and 457 nm Brightness values from 56.65 to 52.99 and 13.48 to 11.69 respectively. The increase of red hues present in the composite is indicated by a small increase in a* values from 5.71 to 10.35. Conversely, the significant lightening of the merino wool - silver nanoparticle composite, when exposed to natural light, is confirmed by a large increase in the L* and 457 nm Brightness values, from 56.65 to 72.25 and 13.48 to 26.18 respectively. A reduction in the red hues of the sample is also observed by a decrease in the b* values, from 23.95 to -0.01. This is seen visually as the apparently whitening of the sample.

Table 5.11: CIE L*, a*, b* values of a merino wool - silver nanoparticle composite kept in the dark or exposed to natural light.

Merino wool - silver nanoparticle composite exposed to:	L*	a*	b*	457 nm Brightness
Reference	56.65	5.71	23.95	13.48
Dark	52.99	10.35	28.20	11.69
Light	72.25	-0.01	26.46	26.18

XPS studies of merino wool - silver nanoparticle composites, either kept in the dark or exposed to natural light, were undertaken in order to determine the chemical cause for the colour change. From these studies theories have been proposed, yet additional studies are required to further characterise and understand the processes that occur during exposure of composites to natural light which cause the observed colour change. The obtained XPS spectra for Ag 3d, N 1s and S 2p are provided in Figures 5.59, 5.60 and 5.61 respectively. For ease of comparison, Tables 5.12, 5.13 and 5.14 provide a summary of the peaks present in that spectrum. The XPS results, comparing peaks present within the Ag 3d spectrum show that the positions remain stable, as do the relative proportions of the peaks (Fig. 5.59, Table 5.12). For example, the ratio of Ag-O⁰ : Ag-S- remains approximately 1 : 3 for both composites. Similarly, the positions and relative proportions of peak present in the N 1s are comparable for both of merino wool - silver nanoparticle composites kept in the dark or exposed to natural light

(Fig. 5.60, Table 5.13). This suggests that neither sulfur nor nitrogen play a significant role in the distinct lightening of colour observed for the silver nanoparticle composites when exposed to natural light.

In contrast to the analogous Ag 3d and N 1s spectra for merino wool - silver nanoparticle composites the S 2p spectra of the composites kept in the dark compared to that exposed to natural light, are very dissimilar (Fig. 5.61). The composite kept in the dark has the expected peaks of a merino wool - silver nanoparticle composite (Fig. 5.61a). Observed are the bands associated with -S-Ag, -S-H, -S-S- and -S-O₃H- / -S-O-Ag at 162.3, 163.8, 165.1 and 168.6 eV respectively. These peak positions are in agreement to those discussed in section 4.6.2. There is no change to the positions of those peaks relating to S-H, -S-S- and -S-O₃H- / -S-O-Ag for the composite exposed to natural light (Fig. 5.61b). However, the ratio of S-H : -S-S- : -S-O₃H- / -S-O-Ag is noted to change from 1 : 0.9 : 3.7 for the sample kept in the dark, to 1 : 1.3 : 5.8 for that in the sunlight. That is to say, the proportion of oxidised silver bound to silver increases substantially. A new broad band is also noted to appear at 170.5 eV, indicating a more highly oxidised sulfur species. The proportion of -S-S- also increases to greater than that of -S-H, likely due to an oxidation of cysteine residues (-S-H) within the wool to form the disulfide bond in cystine (-S-S-).

When exposed to UV light, the chemical composition wool itself is known to degrade. The photodegradation of wool by sunlight has been extensively studied, but the complex chemical processes involved are not fully understood²³. However what has been noted from XPS studies in this field is a large increase in the oxidised species of sulfur within wool, from the +1 (-S-H) and +2 (-S-S-) states to the +6 state (-SO₃H)²⁴. Wool is observed to yellow as a consequence of the photooxidation process. Merino wool - silver nanoparticle composites similarly see an increase in the oxidation states of sulfur species when subjected to natural light. In particular, the significant increase in the proportion of the peak related to oxidised sulfur (-S-O₃H- / -S-O-Ag), in addition to a more highly oxidised form of sulfur, suggests that the wool coloured by silver nanoparticles may also be degraded by light in the same manner as that outlined above. Given that the chemistry of silver is not changed, there is also the possibility that the silver nanoparticles act as a photocatalyst for the oxidation of wool, increasing its rate

of degradation. It is proposed that the photodegraded wool could have an altered refractive index to that of the original wool matrix. Given the dielectric constant of the surrounding environment of silver nanoparticles present within the wool would be different, the surface plasmon resonance effects and thus the reflected colour would consequently be affected.

Another interesting attribute to the S 2p spectrum of the merino wool - silver nanoparticle composite exposed to natural light is that the peak relating to sulfur bound to silver, typically present at ~162 eV, is no longer observed (Fig. 5.61b). In addition to the oxidation of this bond through the photooxidation processes mentioned above, an alternative reason for the loss of the Ag-S- bond may be due to the formation of a thin oxide layer on the surface on the silver nanoparticles which disrupts this bond. The surface plasmon resonance scattering by silver nanoparticles on the metallic surface would be reduced by this oxide layer and thus a lightening in the shade of the yellow colour would be observed. This is in comparison to a potentially much thicker oxide layer being formed and thus a darkening of silver nanoparticle composites occurring. However in saying this, a change in the proportion of Ag-O- is not observed in the Ag 3d spectrum for merino wool - silver nanoparticle composites when exposed to natural light. Therefore, the argument for the observed colour change being due to the photodegradation of wool, and its change in dielectric constant, as discussed above, is the most likely.

The instability of the colour of merino wool - silver nanoparticle composites to UV light over time poses problems for the real life application in fashion or interior furnishing markets. As was mentioned above further research is required to understand the colour degradation processes so that it may be reduced or halted. An alternative option would be to use the merino wool - silver nanoparticle composites as antistatic and antimicrobial agents but over dye the resulting woollen textiles, or blend with other fibres, so that the change in colour is not apparent to the consumer.

5 - MERINO WOOL - SILVER NANOPARTICLE COMPOSITES: NANOPARTICLES FORMED IN THE PRESENCE OF MERINO WOOL USING ITS REDUCING NATURE

Figure 5.57: XPS Ag 3d spectra of merino wool - silver nanoparticle composite kept in: a) dark; b) natural light for 13 weeks.

Table 5.12: Positions of peaks present in the Ag 3d spectrum.

Merino wool nanoparticle exposed to:	- silver composite	Position of peak (eV)	Peak Relating to	% Peak Area
Dark		368.8	Ag ⁰	72
			Ag-S-	
		370.2	Ag-O-	28
Light		368.4	Ag ⁰	75
			Ag-S-	
		370.3	Ag-O-	25

5 - MERINO WOOL - SILVER NANOPARTICLE COMPOSITES: NANOPARTICLES FORMED IN THE PRESENCE OF MERINO WOOL USING ITS REDUCING NATURE

Figure 5.58: XPS N 1s spectra of merino wool - silver nanoparticle composite kept in: a) dark; b) natural light for 13 weeks.

Table 5.13: Positions of peaks present in the N 1s spectrum.

Merino wool - silver nanoparticle composite exposed to:	Position of peak (eV)	Peak Relating to	% Peak Area
Dark	400.3	Amino groups	79
	402.0	-N(ox) -NO-Ag	21
Light	400.2	Amino groups	73
	402.2	-N(ox) -NO-Ag	27

Figure 5.59: XPS S 2p spectra of merino wool - silver nanoparticle composite kept in: a) dark; b) natural light for 13 weeks.

Table 5.14: Positions of peaks present in the S 2p spectrum

Merino wool - silver nanoparticle composite exposed to:	Position of peak (eV)	Peak Relating to	% Peak Area
Dark	162.3	-S-Ag	7
	163.8	-S-H	17
	165.1	-S-S-	14
	168.6	-SO ₃ H	62
		-SO-Ag	
Light	n/a	-S-Ag	n/a
	163.6	-S-H	8
	165.1	-S-S-	10
	168.5	-SO ₃ H	44
		-SO-Ag	
	170.5	-S(ox)-?	39

5.8 Leaching of silver

There is currently a lot of fear regarding the use of silver nanoparticles for antibacterial applications. At present, there are numerous products on the market that have silver species incorporated into fabrics in order to prevent the bacterial build-up that causes odour. The viable concern is that during washing nanosilver could be leached and, due to its antibacterial properties, could interrupt delicate ecosystems or municipal waste water systems that depend on bacteria. Thus it is very important that it is ensured that leached silver is halted or kept to an absolute minimum. At intervals, over a cumulative 72 hour period, samples were analysed using atomic absorption (AA) so as to assess the amount of silver leached (Fig. 5.62).

Figure 5.60: Percentage silver released from merino wool - silver nanoparticle composites with increasing silver loadings.

An insignificant percentage value of silver is leached from merino wool - silver composites after 72 hours of washing (Table 5.15), with negligible amounts of silver released following 24 hours. The leaching of silver during the initial washing stages is likely due to loosely bound nanoparticles on the surface of the fibre becoming dislodged. The subsequent stability of the composites to washing suggests silver-based nanoparticles are bound throughout merino wool with a strong bond.

When comparing the amounts of silver released by merino wool - silver based nanoparticle materials, prepared by ourselves, to studies undertaken by Benn *et al*²⁵ on commercially available nanosilver sock products, the results are significant indeed. Three of four samples studied by Benn *et al* released greater than 95% of the silver impregnated in the fabric of the sock (Table 5.15). Only one of the samples studied by Benn *et al*, the Fox River nanosilver sock, had a leaching value comparable to our own merino wool - silver based nanoparticle composites. However, this value is almost double that what is leached using our novel and proprietary method of preparation.

Table 5.15: Comparison of the release of silver species from merino wool - silver nanoparticle composites with commercially available nano-silver socks.

Reference	Sample Type	% Ag Released
Merino wool - silver composite (0.5 wt % Ag)	Fibres	0.28
Merino wool - silver composite (1.0 wt % Ag)	Fibres	0.22
Merino wool - silver composite (1.5 wt % Ag)	Fibres	0.18
Sharper Image a)	Nanosilver socks ²⁵	100.00
Sharper Image a)	Nanosilver socks ²⁵	100.00
Fox River	Nanosilver socks ²⁵	0.53
AgActive London	Nanosilver socks ²⁵	95.00

5.9 Antimicrobial Testing

Antimicrobial testing of merino wool - silver nanoparticle composites, prepared using the reducing nature of merino wool, was undertaken against both Gram-positive *Staphylococcus aureus* bacterium (ATCC 25923) and Gram-negative *E. coli* bacterium (ATCC 25922) with an incubation time of 24 hrs (refer to section 2.3.11). Merino wool - silver nanoparticle composites in their fibre form, with loadings of 0.5, 1.0 and 1.5 wt % Ag, were tested. For each loading of silver, the composites were studied in its as prepared form, in addition to the same composite after three 24 hour washing periods and after 13 weeks exposure to natural light. Appendix VIII provides a visual representation of the respective samples mounted on bacterium loaded plates after testing.

Unlike the merino wool - silver nanoparticle composites prepared using an external reducing agent (Fig. 4.41 & 4.42, section 4.9), the antimicrobial properties for all composites prepared using the reducing nature of merino wool, in fibre form and loaded with 0.5, 1.0 or 1.5 wt % silver, are not evident to the eye. Figures 5.63 and 5.64 provide images taken under the optical microscope of merino wool - silver nanoparticle composites loaded with 0.5 and 1.5 wt % silver respectively and tested against *Staphylococcus aureus*. At this magnification, zones of microbial inhibition are also not apparent. When increasing the magnification further still, it is observed that with loadings of 0.5 wt % silver, microbial growth occurs up until the fibre but does not grow on the fibre itself (Fig. 5.65).

However, when the fibre is loaded with 1.5 wt % silver a very small zone of inhibition is noted, approximately 0.01 mm in size (Fig. 5.66). This equates to roughly 50 % the fibre diameter. A comprehensive list of the results from the antimicrobial testing of merino wool - silver nanoparticle composites against *Staphylococcus aureus* and *E. coli* are additionally provided in Appendix VIII. These results show that the same antimicrobial properties exist for composites both pre- and post-washing. For a composite loaded with 1.0 wt % silver, the zone of inhibition for both composites is approximately 0.005 mm; approximately 30 % the fibre diameter. However, after 13 weeks exposure to light, the antimicrobial properties decrease to a non measurable amount. Such findings will be considered further in the discussion below on the spun forms of merino wool - silver nanoparticle composites prepared using the reducing nature of merino wool.

Figure 5.61: Antimicrobial testing of merino wool - silver nanoparticle composite fibres, loaded with 0.5 wt % Ag, against *Staphylococcus aureus*.

Figure 5.62: Antimicrobial testing of merino wool - silver nanoparticle composite fibres, loaded with 1.5 wt % Ag, against *Staphylococcus aureus*.

Figure 5.63: Antimicrobial testing of a merino wool - silver nanoparticle composite fibre, loaded with 0.5 wt % Ag, against *Staphylococcus aureus*.

Figure 5.64: Antimicrobial testing of a merino wool - silver nanoparticle composite fibre, loaded with 1.5 wt % Ag, against *Staphylococcus aureus*.

When merino wool - silver nanoparticle composites loaded with 1.0 wt % silver, are spun into a yarn form the antimicrobial ability is noted to substantially increase. Figures 5.67 to 5.70 provide images relating to the antimicrobial properties of spun composites tested against *Staphylococcus aureus*. The images provided in Figures 5.71 to 5.74 relating to the same composites against *E. coli*. Tables 5.16 and 5.17 summarise the zones of microbial inhibition for the composites pre- and post-washing and for that left in natural light for thirteen weeks. As was indicated above, the antimicrobial properties for composites pre- and post-washing are the same or very similar. Given that insignificant levels of silver are released during the washing process (refer to section 5.8) this result is to be expected. The growth of *Staphylococcus aureus* bacteria is inhibited by 1.7 mm for both composites; approximately 85 % the width of the yarn. The inhibition of *E. coli* growth was slightly less, being 1.5 mm and 1.2 mm for the respective pre- and post-washed composites. This corresponds to approximately 75 % and 60 % the width of the fibre. For individual fibres also loaded with 1.0 wt % silver, the growth of bacteria was around 30 % the diameter of the fibre for both *Staphylococcus aureus* and *E. coli*, therefore this increase in antimicrobial activity by at least 200 % is impressive.

However, the antimicrobial activity of merino wool - silver nanoparticle composites prepared using the reducing nature of merino wool still remains dramatically less than that of those composites prepared using an external reducing agent. For these composites it was noted that bacterial growth could be inhibited by up to approximately 100 times the diameter of the fibre. Composites prepared using an external reducing agent, are loaded with up to 5.0 wt % silver, in comparison to the 1.0 wt % silver discussed above. Therefore the apparent difference in microbial inhibition is due to an increase in silver concentration. In theory it however should only be at variance by a factor of five. The causative factor for the increased antimicrobial action of composites prepared using an external reducing agent is likely the fact that nanoparticles are bound immediately above and below the surface of the fibre and thus become in contact with microbes more effectively. On the other hand, when merino wool is used as the reducing agent for silver nanoparticle composite preparation, nanoparticles are not predominantly present at the surface. Instead, they are strongly bound throughout the centre of the fibre.

Figure 5.65: Antimicrobial testing of spun merino wool - silver nanoparticle composites, loaded with 1.0 wt % Ag, against *Staphylococcus aureus*: a) prior to washing; b) post 3×24 h washing periods; c) after 13 weeks exposure to natural light.

Figure 5.66: Zone of microbial inhibition by a spun merino wool - silver nanoparticle composite, loaded with 1.0 wt % Ag, against *Staphylococcus aureus* prior to washing.

Figure 5.67: Zone of microbial inhibition by a spun merino wool - silver nanoparticle composite, loaded with 1.0 wt % Ag, against *Staphylococcus aureus* post 3×24 h washing periods.

Figure 5.68: Zone of microbial inhibition by a spun merino wool - silver nanoparticle composite, loaded with 1.0 wt % Ag, against *Staphylococcus aureus* after 13 weeks exposure to natural light.

Figure 5.69: Antimicrobial testing of spun merino wool - silver nanoparticle composites, loaded with 1.0 wt % Ag, against *E. Coli*: a) merino-Ag, prior to washing; b) merino-Ag, post 3×24 h washing periods; c) crossbred-Ag, prior to washing.

Figure 5.70: Zone of microbial inhibition by a spun merino wool - silver nanoparticle composite, loaded with 1.0 wt % Ag, against *E. coli* prior to washing.

Figure 5.71: Zone of microbial inhibition by a spun merino wool - silver nanoparticle composite, loaded with 1.0 wt % Ag, against *E. coli* post 3×24 h washing periods.

Figure 5.72: Zone of microbial inhibition by a spun merino wool - silver nanoparticle composite, loaded with 1.0 wt % Ag, against *E. coli* after 13 weeks exposure to natural light.

Table 5.16: Zones of microbial inhibition by a spun merino wool - silver nanoparticle composite, loaded with 1.0 wt % Ag, against *Staphylococcus aureus*.

Code	Sample	Bacteria	Zone of Inhibition (mm)
Fig. 5.68	Prior to washing	<i>S. aureus</i>	1.7
Fig. 5.69	Post 3 × 24 h washing periods	<i>S. aureus</i>	1.7
Fig. 5.70	After 13 weeks exposure to natural light	<i>S. aureus</i>	0.5

Table 5.17: Zones of microbial inhibition by a spun merino wool - silver nanoparticle composite, loaded with 1.0 wt % Ag, against *E. coli*.

Code	Sample	Bacteria	Zone of Inhibition (mm)
Fig. 5.72	Prior to washing	<i>E. coli</i>	1.5
Fig. 5.73	Post 3 × 24 h washing periods	<i>E. coli</i>	1.2
Fig. 5.74	After 13 weeks exposure to natural light	<i>E. coli</i>	0.7

5.10 Summary

Merino wool and crossbred wools have been successfully implemented as *in situ* reducing agents for the preparation of wool - silver nanoparticle composites. The preferred preparation method for yellow/gold coloured composites includes soaking merino wool fibres in silver nitrate for a period of 24 hours at 50 °C. After which, a complete uptake of silver ions by the fibres has been accomplished and absorbed silver has been reduced to silver nanoparticles. As silver is removed from solution in its entirety during the colouring process it is considered environmentally friendly, providing a substantial improvement to the current environmentally problematic dyeing processes. The product consists of only merino wool and silver, with the waste solution containing no heavy metals but instead consisting of a very dilute solution of nitric acid (pH ~5.9). Further steps for the removal of heavy metals are not required.

SEM and TEM studies indicate that, unlike silver nanoparticle composites that are prepared using an external reducing agent, whereby nanoparticles were predominantly on the fibres exterior, nanoparticles reduced by merino wool are not typically present on the surface of the fibres. Instead the nanoparticles are regularly distributed throughout the entire centre of the fibre. The nanoparticle diameters for composites of similar colour are comparable to those composites prepared with TSC, measuring approximately 4 to 12 nm in comparison to 10 to 15 nm. Similarly, the colour of the composites is due to surface plasmon resonances.

The intensity of the colour of silver nanoparticle composites can be altered by systematically altering the concentration of silver solution, soaking time of fibres in solution and the reaction temperature for preparation. Colours range from very pale yellow to gold to brown. EDS elemental analysis confirms the presence of silver within the composite fibres and synchrotron radiation XRD indicates that when the sample colour is yellow the silver is in its crystalline form. However when the composite is brown in colour XRD shows no crystalline forms of silver are present and that silver has converted to an oxidised form, most likely silver oxide.

XPS studies of merino coloured by silver nanoparticles, using the reducing nature of wool as the reductant for preparation, suggest that silver ions are absorbed by the fibre and firstly associate with cysteine and cystine amino acids owing to the favourable interaction between silver and sulfur. The formation of an Ag-S bond occurs over an Ag-N bond due to bond stability constants. It is thought that nitrogen containing functional groups in close vicinity then act as the reducing agent, effectively reducing Ag^+ to Ag^0 . The increased temperature additionally increases reaction kinetics and hence the rate of reduction, from Ag^+ to Ag^0 . Therefore more highly coloured fibres are obtained in a shorter period of time.

The Ag-S bond stabilising the nanoparticles within the merino wool fibres is a strong and stable bond and therefore the colour of silver nanoparticle composites passes tests relating to shampooing and rubbing, and to tests against chlorinated swimming pool water. When undergoing simulated washability tests, the leaching of silver is also noted to be insignificant, thereby reducing reservations regarding the potential environmental

impact of textiles containing silver. On the other hand, the colour of merino wool - silver nanoparticle composites are not stable when exposed to direct natural light for long periods of time. It has been proposed that this lightening may be due to changes in surface plasmon resonance effects from a change in the dielectric constant of merino due to photooxidation processes caused by UV light, or the formation of an oxide layer on the surface of the silver nanoparticles. Further studies are required however, in order to gain a greater understanding of the colour degradation processes.

Additionally, when composites are exposed to the air only, the composites are noted to darken, becoming more brown/grey in colour. As was mentioned above, XRD data of composites this colour shows no indication of silver in its crystalline form. XPS results indicate that silver is oxidised, likely forming both amorphous silver oxide and silver sulphide, both of which are black in colour. The thicker oxide or sulphide layer, when compared to exposure to direct light, thus provides the darkened colour of the composite. The discolouration of woollen textiles coloured by silver is not a desirable trait for application in the apparel or interior furnishing industries and thus further research is required in an attempt to stop this from happening. An alternative option is to over dye the merino wool -silver nanoparticle textiles, thereby retaining the antistatic and antimicrobial properties owing to silver yet removing the colour change problem.

The prepared silver nanoparticle composites tested positive for both their antistatic properties, and their antimicrobial activity. Despite not having a measurable conductivity, antistatic properties were exhibited during spinning from fibre to yarn form. This greatly simplifies the spinning process which is traditionally known to have issues relating to the build up of static electricity. When is their spun form merino wool - silver nanoparticle composites inhibited the growth of both the Gram positive bacterium *Staphylococcus aureus* and the Gram negative bacterium *E. coli*. The measured zones of inhibition were however much less compared to that noted for silver nanoparticle composites, prepared using an external reducing agent. For such composites, individual fibres coloured with silver nanoparticles saw inhibition zones of up to 150 times the fibre diameter, whereas when using merino as the reducing agent, the spun yarn inhibits only up to 85 % of its diameter. Comparatively speaking the loading of silver in composites prepared using the reducing nature of wool is

approximately one fifth that when an external reducing agent. The strong bond between silver and sulfur which exists in the composites will additionally limit the transport of silver ions.

5.11 References

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6 MERINO WOOL - SILVER HALIDE NANOPARTICLE COMPOSITES: NANOPARTICLES FORMED IN THE PRESENCE OF MERINO WOOL

6.1 Physical Characterisation and Morphology

Merino wool - silver chloride nanoparticle composites were prepared following the method outlined in section 2.2.3. The typical methodology included initially doping merino wool fibres with chloride ions (via soaking in a chloride source: typically 0.1 M HCl or 0.001 M HCl (or 0.1 M NaCl, pH adjusted to either 1 or 3). The chloride doped fibres, with the resulting fibre pHs of ~3 and ~5, were air-dried and then agitated in silver nitrate for 10 minutes at room temperature, during which a precipitation of silver chloride nanoparticles occurred. The colour of merino wool - silver chloride nanoparticle composites develops over a 24 hour period when exposed to natural light. The range of colours spans dark purple, through purple greys to pink and peach (Fig. 6.1).

Figure 6.1: Merino wool coloured by silver chloride nanoparticles.

The shade of the colour can be tuned by systematically altering the pH of the chloride pre-treatment. This may be achieved by either controlling the concentration of hydrochloric acid, or adjusting the pH of a chloride-containing solution using a non

chloride containing acid (typically acetic acid). An example of prepared samples using the latter method is offered in Figure 6.2. Altering the pH of the doping solution simultaneously adjusts the pH of the fibres which are then reacted with silver nitrate. As the pH becomes more alkaline the ability of silver chloride to form is reduced and thus the resulting composite is likely a mixture of silver chloride and silver nanoparticles. Under highly alkaline conditions ($\text{pH} > 11$) silver chloride will not form and thus silver nanoparticles, or silver oxide, only will form. The effect of pH will be considered further in section 6.5 on the confirmation of silver species present in the prepared composites.

Figure 6.2: Change in colour of merino wool - silver chloride nanoparticle or merino wool - silver nanoparticle composites by altering pH of the fibre prior to preparation.

Additionally, the intensity of colour of merino wool - silver chloride nanoparticle composites can be controlled by altering the concentration of Ag^+ ions. The temperature of the reaction, as well as the soaking period of merino wool in silver nitrate solution also contributes to the resultant colour. The physical characterisation and morphology of two specific composites have been studied in detail and will be further discussed in this section: those prepared using merino wool fibres initially doped with either 0.1 M or 0.001 M HCl.

6.1.1 Merino Wool - Silver Chloride Nanoparticle Composites Prepared Using 0.1 M HCl Pre-treated Merino Wool

6.1.1.1 Characterisation of Colour

When 0.1 M HCl is used as the chloride source to dope merino wool, the pH of the resulting fibres is approximately 3. After the subsequent treatment with silver nitrate, followed by washing with distilled water and then placement in natural light, the colour of the composite develops to purple. The same colour result may be obtained by

soaking merino wool in 0.1 M NaCl and adjusting the pH of the solution to 1. Following an analogous reaction to that discussed for merino wool - silver nanoparticle composites in section 5, a series of preparations were undertaken, altering silver solution concentration, temperature and soaking time in the attempt to develop a greater range of colours. The visual results of such preparations are offered in Figures 6.3 to 6.5. A summary of CIE L*, a*, b* values for the prepared samples using a 500 mg/kg Ag⁺ solution are provided in Appendix IX.

When 0.1 M HCl pre-treated merino wool is soaked in silver nitrate at room temperature for 0.25 hours (15 minutes), the colour which develops is purple (Fig. 6.3). The intensity of this purple colour simultaneously decreases as the concentration of silver decreases. As the soaking time, of merino wool fibres in silver nitrate, progresses from 0.25 hours to 72 hours a greying/browning of samples is observed by the eye. This is confirmed by both an increase in all of L* and 475 nm brightness values and a decrease of a* values for those composites prepared using 500 mg/kg Ag⁺. The increase of L* and 475 nm brightness values, from 35.79 to 48.58 and 6.23 to 15.22 respectively, indicates a lightening of the samples colour. The decrease in the a* values from 13.33 to 6.57 indicate a decrease in the red hues of the sample. The b* values remain relatively constant, i.e. yellow hues remain steady. The colour is therefore that of a developing purple/grey/brown that becomes dirtier in appearance with longer soaking periods. A greying/browning is also observed with extended soaking periods of merino wool in silver nitrate at 50 °C, however becoming more pronounced in the colour change (Fig. 6.4).

Figure 6.3: Merino wool - silver chloride composites prepared, using 0.1 M HCl pre-treated merino wool, at room temperature: a) 500 mg/kg Ag^+ ; b) 250 mg/kg Ag^+ ; c) 100 mg/kg Ag^+ .

Figure 6.4: Merino wool- silver chloride composites prepared, using 0.1 M HCl pre-treated merino wool, at 50 °C: a) 500 mg/kg Ag^+ ; b) 250 mg/kg Ag^+ ; c) 100 mg/kg Ag^+ .

On the other hand, when the preparation of merino wool - silver chloride nanoparticle composites is undertaken at 80 °C, the resulting products are noted to range in colour from purple/grey to gold/brown (Fig. 6.5). The distinct yellowing of samples prepared using a 500 mg/kg Ag^+ solution is shown by an increase in b^* values from 3.13 to 13.84. All of L^* , a^* and 475 nm brightness remain stable. The reason for the greying/browning which occurs to merino wool - silver chloride nanoparticle composites prepared at room temperature and 50 °C, and the yellowing of samples that occurs at 80 °C, is likely due to the competing reaction to the nano-precipitation of silver chloride: that of the reduction reaction of Ag^+ to form silver nanoparticles. This will be discussed in further detail in section 6.5.

Figure 6.5: Merino wool- silver chloride composites prepared, using 0.1 M HCl pre-treated merino wool, at 80 °C: a) 500 mg/kg Ag⁺; b) 250 mg/kg Ag⁺; c) 100 mg/kg Ag⁺.

The above results imply that the cleanest, most attractive colours of merino wool - silver chloride nanoparticle composites, using 0.1 M HCl pre-treated merino wool, are obtained with shorter soaking periods. Therefore, the times in which merino wool remained in solution were further reduced; soaking for 2, 10 and 30 minute durations only. The visual results from this procedure are offered in Figure 6.6, with Appendix X providing the corresponding CIE L*, a*, b* values for samples prepared using both 500 and 100 mg/kg Ag⁺. At room temperature the resulting composites are purple after 2 minutes soaking. Increasing the soaking period from 2 to 10 to 30 minutes increases the redness of the composite, as observed by an increase in the a* value from 5.19 to 5.52, for samples prepared using 500 mg/kg Ag⁺. As the reduction of the concentration of silver occurs, so does the intensity of the colour. Once again, as the temperature is increased the composites are noted to become greyer due to the competing reaction of silver nanoparticle formation by the *in situ* reduction by merino wool. This indicates that purples can be successfully prepared at room temperature, whereas purple/greys require heating at 80 °C.

Figure 6.6: Merino wool - silver chloride composites prepared, using 0.1 M HCl pre-treated merino wool: a) 500 mg/kg Ag^+ ; b) 250 mg/kg Ag^+ ; c) 100 mg/kg Ag^+ .

6.1.1.2 Scanning Electron Microscopy (SEM)

Characterisation of the morphology of merino wool - silver chloride nanoparticle composites was determined by SEM analysis. When viewed in SEI mode, nanoparticles present in a merino wool - silver chloride nanoparticle composite (prepared using 0.1 M HCl pre-treated merino wool as the base material) appear as bright white dots (Fig. 6.7). The nanoparticles are present in what appear to be isolated aggregates across the fibre. These aggregates are larger in size, and have a greater population density, where cuticle plates meet. It is observed that the size and number of nanoparticles decrease towards the outer limits of each cuticle plate. The visibility of nanoparticles within merino wool - silver chloride nanoparticle composites via SEM imaging is quite unlike the merino wool - silver nanoparticle composites, whereby nanoparticles were not readily evident (refer to Fig. 5.5, section 5.1.1.2).

Figure 6.7: SEM micrographs (SEI), at increasing magnifications, of a merino wool- silver chloride nanoparticle composite (HCl pre-treated merino wool) prepared using a soaking period of 10 min at room temperature.

Figure 6.8, provides an image of a merino wool - silver chloride nanoparticle composite at 50,000 times magnification. At this higher magnification, the surface of the composite fibre is smooth indicating nanoparticles are typically present under the surface of the fibre and not above the surface itself. The proposed mechanism for the formation of silver chloride nanoparticles within merino wool will be discussed in further detail in section 6.6. A small number of larger aggregates are also noted however above the fibres surface (Fig. 6.7). These are generally present where cuticle plates meet. The aggregates attached to the fibre above the surface are likely formed due to residual chloride ions remaining in the crevasses of meeting cuticles after the doping of merino wool process.

Figure 6.8: SEM micrograph of a merino wool - silver chloride nanoparticle composite, prepared using 0.1 M HCl pre-treated merino wool, at 50,000 times magnification.

6.1.1.3 Transmission Electron Microscopy (TEM)

Unlike merino wool - silver nanoparticle composites, in which nanoparticles are present throughout the entire fibre, TEM analyses of merino wool - silver chloride nanoparticle composites, prepared using 0.1 M HCl pre-treated merino wool, show that the formed nanoparticles are predominantly present just under the surface of the fibre (Fig. 6.9). The fibre itself is indicated by arrows within the image, for ease of location. The nanoparticles are varied in size from approximately 10 to 100 nm. Again this is quite dissimilar from the silver nanoparticle analogues, whereby nanoparticles showed monodispersity in size, having a narrow range from 4-7 nm. The white dots along the surface of the silver chloride nanoparticle composite are where nanoparticles have become dislodged from the resin section during preparation. The dark line through the centre of the fibre composite is where the resin section has likely become creased in the transfer from cutting with the diamond knife to placement on the carbon grid.

Figure 6.9: TEM micrographs of a cross section of a merino wool - silver chloride nanoparticle composite, prepared using 0.1 M HCl pre-treated merino, at increasing magnifications.

Elemental mapping of nanoparticles within merino wool - silver chloride nanoparticle composites was accomplished using scanning TEM (STEM). Results from these studies are offered in Figure 6.10. A distinct relationship is observed between silver and chlorine. Where nanoparticles are present, high levels of silver correspond to high levels of chlorine confirming that nanoparticles are that of silver chloride. The observed

elemental mapping suggests that silver is present in a greater amount due to a greater intensity in colour for that element. However, this is likely not the case. Silver is a heavier element than that of chlorine and therefore will have a stronger elemental signal due to a greater production of x-rays and the lesser absorption of the silver x-rays by the wool matrix.

Figure 6.10: STEM elemental mapping of merino wool - silver chloride nanoparticle composites, prepared using 0.1 M HCl pre-treated merino, confirming that nanoparticles are in the form of silver chloride.

When TEM imaging is undertaken at higher magnifications, lattice fringes are observed (Fig. 6.11). Lattice fringes are caused by the diffraction of the incident electrons by periodic lattice planes within the specimen and appear as intermittent light and dark bands in the image. Crossed lattice fringes are formed by the intersection of two or more sets of lattice fringes. By noting such lattice fringes, the crystallinity of the silver chloride nanoparticles is confirmed. Nanoparticles appear spherical when TEM imaging of composites is undertaken at low magnifications (Fig. 6.11a). By increasing the magnification it becomes evident that nanoparticles are present as both spherical and non-spherical (Fig. 6.11b).

Silver chloride is part of the cubic family. Silver halide crystals can be formed that are octahedral in shape, or in the form of tabular hexagonal plates, which when analysed by TEM microscopy may appear spherical. The non-spherical nature of selected nanoparticles is suggested by straight edges of particles (Fig. 6.12a) or twinning planes (Fig. 6.12b) observed in the obtained micrographs. Twinned crystals are two or more inter-grown crystals are formed in a symmetrical fashion. With respect to the mechanisms of twinning of silver chloride nanoparticles, there are two theories: one based on the coalescence of particles^{1,2} and the other on the formation of stacking faults during growth^{3,4}. Growth studies of the silver halide nanoparticles formed within merino wool were outside the scope of the project and therefore specific details on the growth of the non-spherical nanoparticles observed will not be discussed in any further detail.

Figure 6.11: High resolution TEM images of a) a smaller sized silver chloride nanoparticle and b) a larger sized nanoparticle, prepared using 0.1 M HCl pre-treated merino, both showing lattice fringes.

Figure 6.12: a) TEM micrographs of non-spherical silver chloride nanoparticles, prepared using 0.1 M HCl pre-treated merino; expressing twinned planes.

Figure 6.12: b) TEM micrographs of non-spherical silver chloride nanoparticles, prepared using 0.1 M HCl pre-treated merino; expressing twinned planes.

Figure 6.13: Silver chloride crystal shapes ⁵.

6.1.2 Merino Wool - Silver Chloride Nanoparticle Composites Prepared Using 0.001 M HCl Pre-treated Merino Wool

6.1.2.1 Physical Characterisation of Colour

Alternatively, when merino wool is pre-treated with 0.001 M HCl (or similarly, with 0.1 M NaCl and pH adjusted to 5), the colour of the resulting merino wool - silver chloride nanoparticle composites develop to peach/pink over 24 hours. As with 0.1 M HCl pre-treated merino wool composites, a series of preparations were undertaken: altering silver solution concentration, temperature and soaking time. The visual results of such preparations are offered in Figures 6.14 to 6.16. The corresponding summary of CIE L*, a*, b* values for samples prepared using a 500 mg/kg Ag⁺ solution provided in Appendix XI.

When 0.001 M HCl pre-treated merino wool is soaked in silver nitrate at room temperature for 0.25 hours (15 minutes), the colour develops to pink (Fig. 6.14). As the soaking time of merino wool in silver solution increases to 72 hours the colour becomes pink/grey. Over this time period, L* values are observed to decrease from 54.43 to 47.39, indicating a darkening of the sample. Additionally, both a* and b* values are noted to decrease, from 16.21 to 9.62 and 19.88 to 12.00 respectively; indicating a

decrease in red and yellow hues and a simultaneous an increase in green and blue. These combined changes result in the visual greying of the sample.

Figure 6.14: Merino wool- silver chloride composites prepared, using 0.001 M HCl pre-treated merino wool, at room temperature: a) 500 mg/kg Ag^+ ; b) 250 mg/kg Ag^+ ; c) 100 mg/kg Ag^+ .

When the preparation of merino wool - silver chloride nanoparticle composites is undertaken at 50 °C, after 0.25 hours the resulting colour is the same as that prepared at room temperature (refer to Appendices XI & XII). However, as time progresses over the 72 hour period, instead of samples becoming grey, a browning is observed (Fig. 6.15). The obtained a^* values are noted to decrease from 15.56 to 7.24, indicating a decrease in the pink colour and a subsequent increase in green tones. The yellow hues on the other hand, as suggested by b^* values, remain stable.

At 80 °C the prepared composites range in colour from a dirty pink/brown to dark yellow/brown (Fig. 6.16). The increased yellowing is noted by an increase in b^* values from 10.25 to 23.75. Yet again, the likely reason for the browning/yellowing which occurs to merino wool - silver chloride nanoparticle composites prepared at 50 °C, and increasingly more so at 80 °C, is due to that of the competing reaction of the reduction reaction of Ag^+ by merino wool to form silver nanoparticles. In fact, after 1 hour soaking in silver nitrate at 80 °C, pink hues owing to silver chloride are not observed. This indicates that the predominant species is silver rather than silver chloride. A further discussion of this will be provided in section 6.5.

Figure 6.15: Merino wool- silver chloride composites prepared, using 0.001 M HCl pre-treated merino wool, at 50 °C: a) 500 mg/kg Ag⁺; b) 250 mg/kg Ag⁺; c) 100 mg/kg Ag⁺.

Figure 6.16: Merino wool- silver chloride composites prepared, using 0.001 M HCl pre-treated merino wool, at 80 °C: a) 500 mg/kg Ag⁺; b) 250 mg/kg Ag⁺; c) 100 mg/kg Ag⁺.

As with when 0.1 M HCl pre-treated merino wool is used for composite preparation, the most desirable colours of merino wool - silver chloride nanoparticle composites, using 0.001 M HCl pre-treated merino wool, are obtained with shorter soaking periods. The visual results from soaking for 2, 10 and 30 minutes only at room temperature, 50 and 80 °C are provided in Figure 6.17. Appendix XII offers the corresponding CIE L*, a*, b* values for the prepared samples using either 100 or 500 mg/kg Ag⁺. Again it is observed that the preparation of composites is preferred at room temperature so as to obtain the cleanest, clearest colours.

Figure 6.17: Merino wool - silver chloride composites prepared, using 0.001 M HCl pre-treated merino wool: a) 500 mg/kg Ag⁺; b) 250 mg/kg Ag⁺; c) 100 mg/kg Ag⁺.

When prepared at room temperature, the resulting composites are pink after 2 minutes soaking. All of L*, a* and 475 nm brightness values remain constant when increasing the soaking period to 10 or 30 minutes. The b* value sees a minimal increase from 18.98 to 20.35, indicating a slight increase in the yellowness of the sample. Increasing the preparation temperature to 50 or 80 °C corresponds to a yellowing/browning of the resulting composites. For example, when comparing the colour of composites prepared using a 10 minute soak period, at room temperature, 50 and 80 °C, a decrease in the a* is noted from 15.16 to 12.97 to 11.58 respectively, indicating a decrease in the pinkness of the sample. Additionally, an increase in the b* value is observed from 19.87 to 22.14 to 24.01 representing the increase in the yellow hues. The 475 nm value decreases from 12.19 to 11.64 to 10.57 following a darkening of the prepared samples with increasing preparation temperatures.

6.1.2.2 Scanning Electron Microscopy (SEM)

The morphological characterisation of merino wool - silver chloride nanoparticle composites (prepared using 0.001 M HCl pre-treated merino wool) was determined by SEM analysis. Figure 6.18 offers images of such composites in secondary electron (SEI) mode at increasing magnifications. In comparison to those composites prepared using 0.1 M HCl pre-treated merino wool (Fig. 6.7), the population density of nanoparticles is notably less. The isolated aggregates of nanoparticles present in composites, prepared using 0.001 M HCl pre-treated merino wool, appear smaller and more similar in size in contrast to 0.1 M HCl composites. Additionally, As was observed in composites prepared using 0.1 M HCl pre-treated merino wool, larger quantities of aggregates are not observed where cuticle plates meet, reducing in quantity moving towards the edges of cuticle plates. Instead, nanoparticles appear to be more evenly distributed across each individual cuticle plate of the fibre.

Figure 6.18: SEM micrographs (SEI), at increasing magnifications, of a merino wool- silver chloride nanoparticle composite, prepared using 0.001 M HCl pre-treated merino, with a soaking period of 10 m at room temperature in 500 mg/kg Ag⁺ solution.

At 150,000 times magnification the surface of a merino wool - silver chloride nanoparticle composite is noted to be smooth (Fig. 6.19). Once more this suggests that the nanoparticles are present beneath the surface of the fibre. Unlike composites prepared using 0.1 M HCl pre-treated merino wool, negligible nanoparticle aggregates are noted above the fibres surface. This is likely because at lower concentrations of HCl (0.001 M versus 0.1 M HCl) the levels of doping of merino wool by chloride will be less. The presence of excess chloride ions on the surface will therefore be less likely.

Figure 6.19: SEM micrograph at 150,000 times magnification of a merino wool- silver chloride nanoparticle composite, prepared using 0.001 M HCl pre-treated merino, with a soaking period of 10 m at room temperature in 500 mg/kg Ag^+ solution.

6.1.2.3 Transmission Electron Microscopy (TEM)

As was initially indicated by SEM analyses, TEM microscopy confirms that the number of silver chloride nanoparticles present within composites prepared using 0.001 M HCl pre-treated merino wool (Fig. 6.20), is much fewer than that of analogues using 0.1 M HCl pre-treated merino wool (Fig. 6.9). This is a direct result of both a lesser availability of chloride ions and slightly higher pH (ability to form silver chloride). Again it is observed that the formed nanoparticles are predominantly present just under the surface of the fibre. The nanoparticles present in composites prepared with 0.001 M HCl pre-treated merino wool have a much closer size distribution in comparison to composites prepared using 0.1 M HCl pre-treated merino wool; ranging from approximately 10 to 25 nm. Elemental mapping of nanoparticles within merino wool - silver chloride nanoparticle composites, using scanning TEM (STEM), substantiates that nanoparticles are that of silver chloride (Fig. 6.21). This is confirmed by the distinct relationship between silver and chlorine; whereby high levels of silver corresponds to high levels of chlorine

Figure 6.20: TEM micrographs of a cross section of a merino wool - silver chloride nanoparticle composite, prepared using 0.001 M HCl pre-treated merino, at increasing magnifications.

Figure 6.21: STEM elemental mapping of merino wool - silver chloride nanoparticle composites, prepared using 0.001 M HCl pre-treated merino, confirming that nanoparticles are in the form of silver chloride.

As with merino wool - silver chloride nanoparticle composites prepared using 0.1 M HCl pre-treated merino wool, when composites prepared using 0.001 M HCl pre-treated merino wool are imaged at low magnifications under the TEM, the nanoparticles appear spherical in shape (Fig. 6.20 & 6.22). When TEM imaging is undertaken at higher magnifications however, twinning planes are observed, indicating that particles are in fact non-spherical (Fig. 6.23). The shape of the nanoparticles may be one of a number, as outlined in Figure 6.13 above. Further electron microscopy studies, will be required in order to determine the actual shape of the particles. At high magnification lattice fringes are also noted, confirming the crystallinity of the silver chloride nanoparticles (Fig. 6.24).

Figure 6.22: TEM micrograph of silver chloride nanoparticles within a merino wool - silver chloride nanoparticle composite, prepared using 0.001 M HCl pre-treated merino.

Figure 6.23: TEM micrograph of a non-spherical silver chloride nanoparticle, prepared using 0.001 M HCl pre-treated merino, expressing twinned planes.

Figure 6.24: High resolution TEM images of a silver chloride nanoparticle, prepared using 0.001 M HCl pre-treated merino, showing lattice fringes.

6.1.3 The Doping of Merino Wool with Alternative Chlorine Containing Species and the Effect of pH on the Preparation of Merino Wool - Silver Chloride Nanoparticle Composites

Following a comparative doping process to that of the 0.1 M HCl pre-treatment, merino wool was immersed in a 0.1 M NaCl solution, with the pH adjusted to that comparable to the pH of hydrochloric acid (2.8-3.0) using a non chlorinated acid, typically acetic acid (refer to section 2.2.1). The alternative chloride providing agents, potassium chloride and magnesium chloride, were similarly used for the doping process. Washed and air dried chloride-doped merino wool fibres were then placed in a silver containing solution and agitated for 10 minutes. The resultant merino wool - silver chloride composites developed to become purple in colour over a 24 hour period. This colour is comparable to when 0.1 M HCl is used as the dopant. The visual results from preparations, using sodium chloride, potassium chloride and magnesium chloride doped merino wool fibres and 100, 250 and 500 mg/kg Ag^+ solutions, are offered in Figure 6.25. Table 6.1 provides CIE L^* , a^* , b^* values for samples prepared using a 500 mg/kg Ag^+ solution.

Figure 6.25: Merino wool - silver chloride nanoparticle composites prepared using merino wool doped with: a) NaCl; b) KCl; c) MgCl_2 , and adjusted to pH = 3 after exposure to light.

Table 6.1: CIE L*, a*, b* values for merino wool - silver chloride nanoparticle composites prepared using different chlorine containing dopants for fibre pre-treatment and a 500 mg/kg Ag⁺ solution.

Merino wool doped with:	L*	a*	b*	475 nm brightness
NaCl	38.66	10.19	5.02	8.98
KCl	39.32	10.78	4.92	9.15
MgCl ₂	36.87	11.14	4.33	7.22

Although it may not be particularly evident from Figure 6.25 (due to variations in light levels etc, when samples were being imaged), the obtained CIE values indicate that synonymous colours are achieved when both sodium chloride and potassium chloride are used as the doping agents. When magnesium chloride is used as the chloride-containing dopant a more intense purple is observed. This is confirmed by magnesium chloride pre-treated composites, when compared to sodium chloride and potassium chloride analogues, having an increased a* and a decreased b* value, indicating an increase in red and blue hues, i.e. an increase in purple colour. The increased intensity in colour is likely due to one mole of magnesium chloride having twice the amount of available chloride ions to that of sodium or potassium chloride. The ability of magnesium chloride to dope merino wool will be greater and thus a greater amount of chloride ions will be available to form silver chloride nanoparticles. Hence, a greater number of silver chloride nanoparticles will be present in the consequential composites.

When altering the pH of the chloride-containing solution for the doping of merino wool, and thus the resulting pH of the fibre, prior to treatment with silver solution, the colour of the formed composite can be further tuned (Fig.6.26). As was also mentioned above, at pH = 3 the resulting composite is purple. By altering the pH of the fibre to 6, 9 and 12, the colour is simultaneously altered to pink, peach and yellow/gold respectively. A complete record of CIE values for all samples prepared using sodium, potassium or magnesium chloride doped merino wool, at the four different pHs is provided in Appendix XVI. As the pH of the fibre becomes more alkaline the ability of silver to precipitate silver chloride decreases. Therefore, at pH = 12 it is likely that the composite will contain silver nanoparticles and not silver chloride nanoparticles. The presence of silver nanoparticles solely, under highly alkaline condition, is additionally suggested by the yellow/gold colour of the composite. The pH of the fibre prior to

submersion in silver nitrate solution and the subsequent silver or silver halide product will be discussed further in section 6.5.

Figure 6.26: Merino wool - silver chloride nanoparticle composites, prepared using different Cl^- dopants: a) 0.1 M NaCl; b) 0.1 M KCl; c) 0.1 M MgCl_2 , and altering the pH of the fibre.

6.2 Extent of Silver Uptake by Chloride Doped Merino Wool Fibres

The uptake of silver ions from solution by merino wool doped with chloride ions (0.1 M or 0.001 M HCl) was quantified by atomic absorption (AA) analysis. Following the same method discussed in section 5.3 pertaining to the uptake by untreated and KOH pre-treated merino wool, the effect of concentration and temperature of the silver solution was studied, in addition to the duration of soaking within the solution. Three concentrations (100, 250, 500 mg/kg Ag^+), and three temperatures (room temperature, 50 °C, 80 °C) were employed. Figures 6.27 to 6.29 show the uptake curves of silver ions from 100, 250 and 500 mg/kg Ag^+ solutions by 0.1 M HCl pre-treated merino wool compared to 0.001 M HCl pre-treated merino wool. The untreated data for these graphs can be found in Appendix XIV. The resulting colours of both 0.1 M and 0.001 M HCl pre-treated merino wool composites, altering the said conditions, are offered in Figures 6.3 to 6.5 in section 6.1.1.1.1 and Figures 6.14 to 6.16 in section 6.1.1.2.1 respectively.

Figure 6.27: Following the uptake of Ag^+ ions from a 100 mg/kg solution over a 72h soaking period using the following reaction conditions: 0.1 M HCl pre-treated merino wool: a) room temperature; b) 50 °C; c) 80 °C; 0.001 M HCl pre-treated merino wool: d) room temperature; e) 50 °C; f) 80 °C.

Figure 6.28: Following the uptake of Ag^+ ions from a 250 mg/kg solution over a 72h soaking period using the following reaction conditions: 0.1 M HCl pre-treated merino wool: a) room temperature; b) 50 °C; c) 80 °C; 0.001 M HCl pre-treated merino wool: d) room temperature; e) 50 °C; f) 80 °C.

Figure 6.29: Following the uptake of Ag^+ ions from a 500 mg/kg solution over a 72h soaking period using the following reaction conditions: 0.1 M HCl pre-treated merino wool: a) room temperature; b) 50 °C; c) 80 °C; 0.001 M HCl pre-treated merino wool: d) room temperature; e) 50 °C; f) 80 °C.

When 0.1 M HCl pre-treated merino wool is implemented for the preparation of merino wool - silver chloride nanoparticle composites a distinct trend in the uptake of silver ions from solution is noted for all concentrations and reaction temperatures. Within the

first few minutes of soaking, the majority of silver ions are removed from solution by merino wool. In fact, after only 10 minutes an almost complete uptake (>97 %) is observed for 100 and 250 mg/kg Ag⁺ solutions at all temperatures (Tables 6.2 & 6.3). When the concentration of silver solution is increased to 500 mg/kg Ag⁺ the uptake over the same time period decreases to approximately 80-90 % (Table 6.4).

On the other hand, the uptake of silver ions from solution, after a 10 minute soaking period, is significantly less when a merino wool - silver chloride nanoparticle composite is prepared using 0.001 M HCl pre-treated merino wool as the base material. These samples follow a similar trend to that of merino wool - silver nanoparticle composites discussed in section 5.3. The rate of uptake is likely due to the kinetics of diffusion of silver into the fibres in addition to the kinetics of silver formation. Therefore, due to thermal kinetics, as the temperature increases so does the amount of silver removed from solution. Additionally, as the concentration of silver increases, the quantity of removed silver simultaneously increases. This is similarly due to the increased driving force of diffusion with increased concentrations.

Table 6.2: Percentage total silver ion uptake by merino wool after 10 minutes using a 100 mg/kg Ag⁺ solution.

Merino wool pre-treated with:	Temperature	Uptake Ag ⁺ (mg/kg)	% Ag ⁺ Uptake
0.1 M HCl	Room Temp.	97.4	97.4
0.1 M HCl	50 °C	98.4	98.4
0.1 M HCl	80 °C	99.9	99.9
0.001 M HCl	Room Temp.	33.6	33.6
0.001 M HCl	50 °C	64.2	64.2
0.001 M HCl	80 °C	67.8	67.8

Table 6.3: Percentage total silver ion uptake by merino wool after 10 minutes using a 250 mg/kg Ag⁺ solution.

Merino wool pre-treated with:	Temperature	Uptake Ag ⁺ (mg/kg)	% Ag ⁺ Uptake
0.1 M HCl	Room Temp.	249.1	99.6
0.1 M HCl	50 °C	244.8	97.9
0.1 M HCl	80 °C	244.0	97.6
0.001 M HCl	Room Temp.	59.2	23.7
0.001 M HCl	50 °C	82.2	32.9
0.001 M HCl	80 °C	102.0	40.8

Table 6.4: Percentage total silver ion uptake by merino wool after 10 minutes using a 500 mg/kg Ag^+ solution.

Merino wool pre-treated with:	Temperature	Uptake Ag^+ (mg/kg)	% Ag^+ Uptake
0.1 M HCl	Room Temp.	400.8	80.2
0.1 M HCl	50 °C	460.4	92.1
0.1 M HCl	80 °C	444.5	88.9
0.001 M HCl	Room Temp.	64.5	12.9
0.001 M HCl	50 °C	90.5	18.1
0.001 M HCl	80 °C	121.2	24.2

The removal of silver ions from solution by 0.1 M HCl and 0.001 M HCl pre-treated merino wool in the first few minutes is likely due to the immediate precipitation of silver chloride. Chloride ions present under the surface of merino wool likely provide a greater attraction towards silver ions and as silver diffuses into the fibre to precipitate as silver chloride nanoparticles. The proposed mechanism of such will be discussed further in section 6.6. The level of chlorine doping by 0.1 M HCl is 100 times greater than that of the doping by 0.001 M HCl. Additionally, the pH of 0.1 M HCl pre-treated merino wool fibres is approximately 3.2, compared to a pH of 5.0 for 0.001 M HCl pre-treated merino wool.

The more acidic pH of 0.1 M HCl pre-treated merino wool provides more preferable reaction conditions for the precipitation of silver chloride. Additionally, the amount of chloride present within the doped fibre is sufficient enough to react with all silver ions, leading to a complete removal of silver from solution. On the other hand, as discussed above the availability of chloride ions within merino wool doped by 0.001 M HCl pre-treated merino wool is much a lesser amount. Therefore, the attraction of silver by chloride ions within the fibre will be less. Unlike 0.1 M HCl pre-treated merino wool, the quantity of chloride present is not great enough to precipitate the entire quantity of silver ions from solution. Additional to this, the fibre's pH of 5.0 is less beneficial for the formation of silver chloride. It is for these reasons that the uptake of silver by 0.001 M HCl pre-treated merino wool, due to the precipitation of silver chloride, is notably less than that of 0.1 M HCl pre-treated merino wool in the first 10 minutes of soaking within silver solution.

In the case of 0.001 M HCl pre-treated merino wool, following the initial precipitation of silver chloride, it is observed that further silver ions are absorbed by the fibres for the remainder of the 72 hour soaking period (Fig. 6.27 to 6.29). For example, after 10 minutes soaking at room temperature, composites prepared using a 500 mg/kg Ag^+ take up approximately 13 % silver from solution. This value is increased to approximately 37 % after 72 hours soaking. When preparation is undertaken at 80 °C however the percentage uptake increases from 24 to 100 % by increasing the soaking time from 10 minutes to 72 hours. With this additional absorption, the resultant composites progressively become more peach, yellow or yellow/brown in their colour, as both soaking times and preparation temperature are increased (Fig. 6.14 to 6.16). This indicates that the additional silver ions taken up by merino wool likely penetrate further within the fibre and subsequently are reduced by merino wool, forming yellow-coloured silver nanoparticles.

With extended soaking of 0.1 M HCl pre-treated merino wool in a silver solution the high proportion of silver removed from solution remains (Fig. 6.27 to 6.29), yet the colour is observed to change, becoming more grey or brown (Fig. 6.3 to 6.5). This change in colour is noted to be more significant as the preparation temperature increases from room temperature, to 50 °C, to 80 °C. As discussed above, with the extended soaking periods at elevated temperatures it is likely that there is a reduction of silver ions to silver metal by proteins present within merino wool. Although, as no further silver ions are absorbed by the fibre over this period the reduced silver ions must be that of those present within the silver chloride matrix. It is also possible that at 80 °C the formation of silver chloride is not as favoured as at room temperature. This is suggested when, using a 500 mg/kg Ag^+ solution for preparation, the uptake of silver ions from solution is reduced to 89 % in comparison to the typical complete removal of silver ions (>97 %). Alternatively, it may be that the reduction of Ag^+ to Ag^0 is the preferable competing reaction.

6.3 Scale Up

As with the merino wool - silver nanoparticle composites (refer to section 5.4), when considering the commercial application of preparation procedures, merino wool fabric was initially applied as the base material for ease of scaling up. Two sizes of merino wool fabric samples were used: 2×2 cm and 3×8 cm. However, again the colours of the resulting merino wool fabric-silver chloride nanoparticle products were found to be uneven, both on the smaller and larger samples (Fig. 6.30). As the merino wool fabric is in a woven form, during the initial doping of merino wool by Cl^- , are likely not able to evenly diffuse into the fibres. Subsequently the diffusion of Ag^+ ions would also be hindered in such a manner. In addition, residual oils or wax from the mechanical process of weaving may also interfere with the diffusion process of Cl^- or Ag^+ ions. The unequal diffusion argument is an equivalent explanation for the uneven colouring observed for merino wool - silver nanoparticle composites. However, the precipitation of silver chloride occurs on first contact of Ag^+ with Cl^- , unlike the reduction of Ag^+ to Ag^0 which occurs over time, after diffusion of silver ions into the merino wool fibre by N-containing amino acids. Therefore, for this reason, the colours of merino wool - silver chloride nanoparticle composites are patchier in appearance (Fig. 6.30) to their silver nanoparticle composite analogues (Fig. 5.26, section 5.4).

Figure 6.30: Merino wool fabric coloured by silver chloride nanoparticles, 0.001 M HCl pre-treated (upper), 0.1 M HCl pre-treated (lower): a) 100 mg/kg Ag^+ ; b) 250 mg/kg Ag^+ ; c) 500 mg/kg Ag^+ ; d) 500 mg/kg Ag^+ .

Due to the clean colours obtainable through the colouring of wool in its top form, this method was favoured to that of the undesired result observed through the colouring of pre-woven fabric. Thus, the preparation of larger quantities of wool dyed by silver chloride nanoparticles was undertaken on wool in its top form only, with subsequent spinning and weaving after the colouring process was complete. As is observed in sections 6.1.1.1.1 and 6.1.1.2.1, higher concentrations of silver are required in order to obtain a vibrant colour. This is due to higher proportions of silver chloride precipitating within the fibre and thus, higher proportions of silver are formed within the silver chloride matrix. The higher concentration of silver nanoparticles subsequently gives rise to a more highly coloured material.

The sample size was initially increased from 0.05 g to 2 g merino wool so as to confirm the process was successful on a somewhat enlarged scale. The process was later scaled up to 100 to 500 g quantities and will be discussed later. Figure 6.31 provides examples of the 2 g merino wool - silver chloride nanoparticle composites that consist of 1.3, 2.2, 3.8 and 4.9 wt %. The method of sample preparation included soaking 2 g merino wool in 200 cm³ of a 500 mg/kg Ag⁺ solution for 15 minutes. The colour was effectively changed from peach/pink to purple by simultaneously increasing the availability of Cl⁻ within the fibre and decreasing the fibre's pH, prior to treatment with the silver solution. This is a direct scale up from the small scale tests previously discussed, of which the method is outlined in section 2.2.3.

Figure 6.31: Merino wool - silver chloride nanoparticle composites consisting of: a) 1.3 wt % Ag⁺; b) 2.2 wt % Ag⁺; c) 3.8 wt % Ag⁺; d) 4.9 wt % Ag⁺.

In order to obtain a clean clear colour, a high concentration of silver solution is required with short soak periods. A complete uptake of silver ions from solution is observed for the dark purple sample (Fig. 6.31d). This composite uses 0.1 M HCl pre-treated merino wool as the base material. This provides an environmentally friendly process whereby the waste water solution contains no heavy metals but consists of a very dilute solution of nitric acid (pH ~5.9). However, from an economical point of view, when compared to an intensely coloured yellow merino wool - silver nanoparticle composite, five times the amount of silver is required to gain an intense purple colour for merino wool - silver chloride nanoparticle composites. It should also be noted that unlike the scaled up method of preparation for merino wool - silver nanoparticle composites, a complete uptake of silver ions is not observed for all colours of merino wool - silver nanoparticle composites. As the availability of Cl^- ions decreases and pH of the fibre increases, the uptake of silver from solution decreases.

For example, when a 0.001 M HCl pre-treatment is applied to merino wool before silver treatment, only an approximate 26 % uptake of silver from solution is obtained and the resulting colour is pink (Fig. 6.31b). Therefore, 74 % remains in solution following preparation; approximately 370 mg/kg Ag^+ . This is not ideal for commercial application, as the large content of silver from the wastewater would need removal. Alternatively, the silver solution could be increased to the required concentration with additional silver ions and the solution recycled for future colouring processes. The preparation of silver chloride composites, coloured peach/pink to pale purple, would thus be more labour intensive and not as environmentally friendly when compared to the merino wool - silver nanoparticle composite analogues. Further research is required so as to obtain a complete uptake from the silver solution, whilst also maintaining a clean crisp colour for such colours.

As with silver nanoparticle composites, crossbred wool yarns in their top form were correspondingly dyed using silver chloride nanoparticles, with the intention of the preparation of a carpet sample. In this case, 100 to 500 g of merino wool fibres (0.1 M HCl pre-treated) were soaked in 10,000 to 50,000 cm^3 silver nitrate for 15 minutes. The coloured top was provided to AgResearch, Christchurch, New Zealand, whom

spun the wool from its top form (Fig. 6.32a). As with merino wool - silver nanoparticle composites, despite not having a measurable electrical conductivity, merino wool coloured with silver chloride nanoparticles showed antistatic properties during the spinning process. As silver chloride itself is a non-conducting ionic solid, the antistatic properties likely arise due to the presence of silver nanoparticles present within silver chloride. A large carpet sample, 750×750 cm in size, was subsequently woven from the spun yarns by Wools of NZ Ltd, Ilkley, United Kingdom (Fig. 6.32b). This carpet sample coloured with silver chloride nanoparticles, together with its silver nanoparticle dyed counterpart, has been showcased by Wools of NZ Ltd as part of their international marketing operation.

Figure 6.32: Crossbred wool coloured by silver chloride nanoparticles: a) dyed top and spun forms; b) woven into a carpet sample.

6.4 Alternative Silver Halide Nanoparticle Composites

6.4.1 Doping of Merino Wool with Fluoride, Bromide and Iodide Ions

From the successful results obtained for the preparation of merino wool - silver chloride nanoparticle composites, the preparation of alternative silver halide nanoparticle composites was deemed appropriate. Using a preparation method analogous to that of the silver chloride composites, merino wool fibres were initially doped with fluoride, bromide or iodide ions (typically 0.1 M NaX, where $X = F^-$, Br^- or I^-), with the pH of the soaking solution being adjusted to one of 3, 7 or 11 (refer to section 2.2.1). The dried fibres were subsequently treated with silver nitrate (100, 250 or 500 mg/kg Ag^+) for 10 minutes. The visual results of the prepared silver halide composites are offered in Figures 6.33, 6.36 and 6.40. The CIE L^* , a^* , b^* values for the samples are provided in Appendix XIII.

6.4.2 Physical Characterisation and Morphology

6.4.2.1 Silver Composites of Merino Wool Doped with Fluoride Ions

The resulting composites of merino wool, pre-treated with fluoride ions and then exposed to silver ions, range in colour from very pale yellow to yellow/brown (Fig. 6.33). The intensity in colour increases as the concentration of silver solution increases and the pH becomes more alkaline. The observed colours are very dissimilar in their physical appearance when compared to the silver chloride analogues (Fig. 6.25), yet are comparable to the merino wool - silver nanoparticle composites (refer to section 5). The measured CIE values for each of these composites are provided in Table 6.5, illustrating the similarity of a^* and b^* colour values of a merino wool - silver nanoparticle and that of the fluoride doped analogue. Silver fluoride is highly soluble in water, having a solubility of approximately 6×10^7 times greater than AgI ($K_{sp}(AgI) = 3.0 \times 10^{-6}$ g / 100 g H_2O). Therefore it follows that using the preparation methods employed, AgF is highly unlikely to form. As opposed to silver fluoride, silver nanoparticles, or an alternative form of silver, will preferentially form.

Figure 6.33: Merino wool doped with 0.1 M NaF and subsequently treated with AgNO_3 : a) 100 mg/kg Ag^+ ; b) 250 mg/kg Ag^+ ; c) 500 mg/kg Ag^+ .

Table 6.5: CIE values of a merino wool - silver composite and fluoride and chloride doped analogues.

Merino wool doped with:	Ag^+ Concentration (mg/kg)	pH	L^*	a^*	b^*	475 nm brightness
F^-	500	3	69.32	1.21	12.00	29.96
Cl^-	500	3	36.96	12.95	5.67	7.72
No dopant	500	8	78.45	-0.34	9.81	45.77

SEM images, at increasing magnifications, of a silver composite of merino wool, pre-treated with fluoride ions and prepared under alkaline conditions, are offered in Figure 6.34. The fluoride pre-treated composite appears equivalent in appearance to that of a merino wool - silver nanoparticle composite, whereby untreated merino wool was used as the base material (Fig. 5.5). At low magnifications the fluoride pre-treated composite fibre appears synonymous to the untreated analogue. Even at 10,000 times magnification the nanoparticles remain concealed on the surface of the fibre. Due to lack of instrument availability, TEM studies were unfortunately unable to be undertaken so as to determine similarities of the two composites, by comparison of cross sections of the fibres.

Figure 6.34: SEM images (SEI) at increasing magnifications of a merino wool - silver fluoride composite, prepared using 500 mg/kg Ag^+ .

Figure 6.35 offers the results from EDS elemental mapping of a silver composite of merino wool doped with fluoride ions. Silver, mapped in green, is noted to be evenly distributed across the fibre. However, the presence of fluorine within the composite is not detected by EDS and thus has not been mapped. The observed morphological similarity between both the silver composite of merino wool doped with fluoride ions (Fig. 6.35) and the merino wool - silver nanoparticle composite (Fig. 5.5), as discussed above, in addition to the lack of fluorine present, further contributes to the considered argument. That is to say, silver composites of merino wool, pre-treated with fluoride ions, consist of merino wool and silver nanoparticle and not merino wool and silver fluoride nanoparticles. The composition of silver composites prepared using merino wool doped with fluoride ions will be discussed further in section 6.5 on the confirmation of silver species.

Figure 6.35: A SEM image of a merino wool - silver fluoride nanoparticle composite (prepared by soaking: 10 m, 0.1 M NaF (adjusted pH = 3); 15 m, AgNO_3), together with the individual EDS maps of S and Ag, and their respective overlay.

6.4.2.2 Silver Composites of Merino Wool Doped with Bromide Ions

Under acidic conditions ($\text{pH} = 3$), the resulting silver composites of merino wool, doped with bromide ions, are a comparable purple colour to that of the silver chloride analogues (Fig. 6.36). When being removed from silver solution, during the final stages of preparation, the composites are white. The observed purple colour develops over a period of 24 hours when exposed to natural light, as does silver chloride composites. Measured CIE values for both a merino wool - silver bromide and a merino wool - silver chloride composite, prepared concurrently, are offered in Table 6.6. As can be seen, all of L^* , a^* , b^* and 475 nm brightness values are similar to one another and thus have a similar colour as observed by the eye. However, the silver chloride analogue is noted to have slightly greater red hues, as observed by an a^* value of 12.95, in comparison to that of 11.60 for silver bromide composites. The silver bromide composite is furthermore noted to be slightly lighter in colour, having measured L^* and 475 nm brightness values higher than that of silver chloride. Additionally, as was also observed for the silver chloride analogues, when the pH of the pre-treated fibre becomes more alkaline the ability for silver bromide similarly decreases. A change in colour is therefore noted from purple at $\text{pH} = 3$, to peach at $\text{pH} = 7$ and yellow at $\text{pH} = 11$. Therefore, again under highly alkaline conditions it is most likely that silver nanoparticles, or an alternative form of silver are produced, preferential to that of silver chloride.

Figure 6.36: Merino wool doped with 0.1 M NaBr and subsequently treated with AgNO₃: a) 100 mg/kg Ag⁺; b) 250 mg/kg Ag⁺; c) 500 mg/kg Ag⁺.

Table 6.6: CIE values of merino wool - silver bromide and merino wool - silver chloride composites.

Merino wool doped with:	Ag ⁺ Concentration (mg/kg)	pH	L*	a*	b*	475 nm brightness
Br ⁻	500	3	39.13	11.60	5.18	9.00
Cl ⁻	500	3	36.96	12.95	5.67	7.72

Imaging undertaken by SEM of a merino wool - silver bromide composite in backscatter mode (Fig. 6.37) additionally shows a material with similar morphological characteristics to that of its silver chloride counterpart (Fig.6.7). Again, nanoparticles are present across the fibre in what appear to be isolated aggregates. The population of silver bromide nanoparticles similarly appear in much greater quantities where cuticle plates overlap, as noted as bright white areas in the SEM micrographs. Comparatively speaking, the aggregates of silver bromide nanoparticles do not appear to occur with the same apparent regularity as that of silver chloride across the remainder of cuticle plate. EDS elemental mapping, shown in Figure 6.38, confirms that these bright white areas are silver bromide. This is made apparent as the white areas in the secondary electron SEM image, correspond to the more intense green and blue areas, indicating silver and bromine respectively.

Figure 6.37: SEM images (backscatter) at increasing magnifications of a merino wool - silver bromide composite, prepared using 500 mg/kg Ag⁺.

Figure 6.38: A SEM image of a merino wool - silver bromide nanoparticle composite (prepared by soaking: 10 m, 0.1 M NaBr (adjusted pH = 3); 15 m, AgNO₃), together with the individual EDS maps of S, Ag and Br, and their respective overlay.

TEM analyses of merino wool - silver bromide nanoparticle composites again show that the formed nanoparticles are chiefly present under the surface of the fibre (Fig. 6.39). As with silver chloride nanoparticle composites prepared using 0.1 M HCl, the size of nanoparticles present within silver bromide composites varies. The nanoparticles range in size from approximately 10 to 60 nm. This is a narrower distribution to that of the silver chloride composites which additionally showed larger particles of up to 100 nm. Twinning planes are again observed, suggesting that non-spherical particles, despite their spherical first appearance at lower magnifications (Fig. 6.39a vs. 6.39b). The merino wool - silver bromide composite cross section, offered in Figure 6.39a, has been cut on an angle and as such shows an area of the fibre in which cuticle plates overlap. The overlapping of cuticle plates is indicated by an arrow. Nanoparticles are noted to have also formed in this area. This is likely due to the ease of penetration of silver ions

into the fibre followed by the nano-precipitation of silver bromide, on contact with bromide ions.

Figure 6.39: TEM micrographs of a cross section of a merino wool - silver bromide nanoparticle composite at increasing magnifications.

6.4.2.3 Silver Composites of Merino Wool Doped with Iodide Ions

Merino wool - silver iodide nanoparticle composites are bright yellow in colour when prepared in acidic conditions (fibre pH = 3). For a composite prepared using a 500 mg/kg Ag^+ solution this colour was characterised as having high whiteness (L^*) and brightness (475 nm), with values of 77.30 and 33.27 respectively (refer to Appendix XIII). The yellowness of the sample is confirmed by a high b^* value: 27.58. Unlike the silver chloride and silver bromide analogues, the colour of merino wool - silver iodide nanoparticle composites does not develop over time in natural light. Instead, the yellow colour appears within a few moments of merino wool, doped with iodide ions, coming into contact with the silver nitrate solution. This indicates that the cause of the colour of silver iodide composites is different to that of silver chloride and silver bromide. As was also observed with silver composites of merino wool, doped with either chloride or bromide, when the pH of the base fibre is raised from 3 to 7 to 11, the colour of the resultant composite is noted to change to a yellow/brown colour. The transition in colour from bright yellow to yellow/brown is gradual over the pH change. Thus, given the related results for the other halides it again suggests that silver nanoparticles are formed, via a redox reaction with proteins present in merino wool, rather than a change in size or shape of silver iodide nanoparticle.

Figure 6.40: Merino wool doped with 0.1 M NaI and subsequently treated with AgNO_3 : a) 100 mg/kg Ag^+ ; b) 250 mg/kg Ag^+ ; c) 500 mg/kg Ag^+ .

SEM micrographs of a merino wool - silver iodide nanoparticle composite taken at increasing magnifications in backscatter mode (Fig. 6.41), show dissimilar results to that of the silver bromide (Fig. 6.37) and silver chloride analogues (Fig. 6.7). Unlike composites prepared with merino wool doped with chloride or bromide, silver iodide nanoparticles are noted to be more evenly distributed across the entire fibre. Negligible agglomerations of nanoparticles are observed. The even distribution of nanoparticles also continues where cuticle plates meet; an area predominantly known for aggregation to occur in silver chloride and silver bromide composites. EDS elemental mapping of a silver composite of iodide doped merino wool shows a strong relationship between silver and iodide, validating that the nanoparticles are silver iodide. The greater intensity of silver and iodide in the forefront of the elemental maps is likely due to its favourable position to the detector and not greater proportions of silver iodide nanoparticles. The right hand side of the image is shadowed and thus elemental levels diminish in intensity.

Figure 6.41: SEM images (backscatter) at increasing magnifications of a merino wool - silver iodide composite, prepared using 500 mg/kg Ag^+ .

Figure 6.42: A SEM image of a merino wool - silver iodide nanoparticle composite (prepared by soaking: 10 m, 0.1 M NaBr (adjusted pH = 3); 15 m, AgNO_3), together with the individual EDS maps of S, Ag and I, and their respective overlay.

In the SEM image taken at 10,000 times magnification, silver iodide nanoparticles are suggested to be monodisperse spherical particles (Fig. 6.41). TEM imaging confirms the apparent spherical nature of silver iodide nanoparticles (Fig. 6.43b). The sizes of particles are not as monodisperse as that implied by SEM. However, the size variation is much narrower than that observed for silver chloride or silver bromide composites, with nanoparticles ranging in size from approximately 10 to 30 nm. Despite soaking times in silver solution being identical, silver iodide nanoparticles are noted to penetrate into the core of the fibre to a much higher degree to that of composites with alternative halides. Whereas silver chloride and silver bromide composites saw nanoparticles located up to 0.3 μm beneath the merino wool fibres surface, merino wool - silver iodide composites sees the presence of nanoparticles up to 2 μm beneath. The TEM image taken at lower magnifications (Fig. 6.43a) interestingly shows that, additional to

nanoparticle formation within cortical cells within the fibre, there is a preferential formation of nanoparticles in the area in which cortical cells meet. This will be discussed in further detail in section 6.6, on the mechanisms of formation of silver halide nanoparticles.

Figure 6.43: TEM micrographs of a cross section of a merino wool - silver iodide nanoparticle composite at increasing magnifications.

6.5 Confirmation of Silver Species

Silver species present within merino wool - silver halide nanoparticle composites were initially suggested by SEM imaging in backscatter mode. Elemental analysis by EDS consequently insinuated that silver was present as a halide compound. Following this, synchrotron radiation XRD and XANES, and XPS were used in an endeavour to distinguish the phases of all silver species present.

6.5.1 Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS)

SEM images, taken in backscatter mode, of merino wool - silver halide nanoparticle composites prepared using halide pre-treated merino wool and subsequent soaking in 500 mg/kg Ag⁺ for 15 minutes are offered in Figure 6.44. The intensity of the signal of a backscattered SEM image is strongly related to the atomic number of the specimen, with elements of greater atomic number appearing much lighter. Therefore, silver present within the composite will appear whiter in the image in comparison to the elements C, N, O, S.

The entire surface of a merino wool fibre pre-treated with fluoride ions and then with silver, is noted to be much lighter in colour in comparison to that of the carbon tape background (Fig. 6.44a). This indicates the presence of an element with a much greater atomic mass, i.e. silver. This outcome is very similar to the resulting backscatter SEM images of merino wool - silver nanoparticle composites (Fig. 5.17, section 5.21). Conversely, the resulting backscatter images of composites of merino wool pre-treated with chloride or bromide ions and then silver are very dissimilar to the fluoride pre-treated analogue (Fig 6.44b & 6.44c). Silver nanoparticle species appear as bright white dots across the fibre surface. However, the spread of silver species is not regular and aggregates appear; more so in the case of merino wool pre-treated with bromide ions in comparison to that of chloride. On the other hand, the nanoparticulate silver species present within a merino wool composite, pre-treated with iodide ions and then silver, are observed to have a uniform distribution across the fibre (Fig. 6.44d).

Figure 6.44: SEM (backscatter) of a merino wool - silver composite: a) merino wool doped with F^- ions; and merino wool - silver halide composites: b) merino wool doped with Cl^- ions; c) merino wool doped with Br^- ions; d) merino wool doped with I^- ions.

Spectra for the EDS elemental analysis of merino wool composites, pre-treated with iodide ions and then silver, are offered in Figures 6.45 to 6.48. For all samples, peaks relating to carbon, nitrogen, oxygen and sulphur, present within proteins that form the bulk of wool, are noted. The peak relating to $Ag L\alpha$, present at 2.98 keV, is additionally observed for all halide pre-treatments of merino wool. The occurrence of this peak confirms the presence of silver, as was initially suggested by SEM imaging in backscatter mode. Peaks for chlorine ($Cl K\alpha$: 2.62 keV), bromine ($Br L\alpha$: 1.48 keV) and iodine ($I L\alpha$: 3.94 keV) also appear for the respective composites of merino wool doped with chloride, bromide and iodide ions and then treated with silver. This suggests that silver is likely bound in a compound with each of the respective halides within the composites. A peak relating to fluorine in the fluoride doped composite is

absent, indicating that silver fluoride is not formed and that fluoride ions must wash out, or are not taken up by merino wool.

Figure 6.45: EDS elemental analysis spectrum of a merino wool - silver composite, using a NaF pre-treatment.

Figure 6.46: EDS elemental analysis spectrum of a merino wool - silver chloride composite.

Figure 6.47: EDS elemental analysis spectrum of a merino wool - silver bromide composite.

Figure 6.48: EDS elemental analysis spectrum of a merino wool - silver iodide composite.

6.5.2 Synchrotron Radiation X-Ray Diffraction (XRD)

Figure 6.49 provides synchrotron XRD patterns for the prepared merino wool - silver (F⁻ pre-treated merino wool) and merino wool - silver halide nanoparticle composites: silver chloride, silver bromide and silver iodide. Silver chloride and silver bromide both crystallize in the fcc structural lattice type; therefore AgCl 200 and AgBr 200 peaks are observed at 20.7 and 19.9 degrees 2-theta respectively, confirming the presence of these crystalline species. AgI, on the other hand has a wurtzite structural lattice type, and as such the most intense peak present is the AgI 002 peak centered at 14.5 degrees 2-theta. Of particular interest is that crystalline silver is also present within the merino wool - silver chloride and -silver bromide nanoparticle composites, as indicated by a peak present at 24.4 degrees 2-theta, relating to the Ag 111 planes (Fig. 6.50A). The peak for silver is not observed for the composite pre-treated with fluoride ions however. This implies that the silver, as indicated by EDS analysis to be present within the composite, is in a non-crystalline form or that the nanoparticles are too small or present to too low a concentrations to diffract x-rays.

Figure 6.49: Synchrotron Radiation XRD patterns for merino wool - silver halide nanoparticle composites: a) merino wool-Ag (pre-treated with F⁻); b) merino wool-AgCl; c) merino wool-AgBr; d) merino wool-AgI.

Figure 6.50: Expanded Synchrotron Radiation XRD patterns for merino wool - silver halide nanoparticle composites: a) merino wool - Ag (pre-treated with F⁻); b) merino wool - AgCl; c) merino wool - AgBr; d) merino wool - AgI.

Due to the Ag 111 peak lying very close to the AgI 110 peak, situated at 25.2 degrees 2-theta, it is difficult to distinguish clearly whether crystalline silver exists in the silver iodide nanoparticle composite (Fig. 6.50A). However, when expanding the segment of the XRD pattern overlay to the area in which the Ag 200 peak is located, it appears evident that crystalline silver is not present (Fig. 6.50B). A detailed explanation for the presence of silver within silver chloride or silver bromide composites, and the absence of crystalline silver within silver iodide samples, will be discussed in further detail in section 6.8, on the colour of merino wool - silver halide nanoparticle composites.

6.5.3 Synchrotron Radiation X-Ray Absorption Near Edge Structure (XANES)

XRD provides data for the crystalline phases of silver within the merino wool - silver halide composites. XANES on the other hand, enables characterisation of both crystalline and amorphous phases of silver. For this reason, synchrotron radiation XANES studies were undertaken on a series of merino wool - silver chloride nanoparticle composites to determine the crystalline and amorphous phases of silver present and their composition. Silver chloride composites, consisting of increasing weight percentages of silver (1.3, 2.2, 3.8, 5.0 wt %) were prepared. This was done by simultaneously altering the pH prior to treatment with silver nitrate (as outlined in section 2.2.1). The colour of these composites ranged from dark purple, through peach to pale pink (Fig. 6.51).

Figure 6.51: Merino wool - silver chloride nanoparticle composite samples (2 g) analysed by synchrotron radiation XANES, consisting of: a) 5.0 wt % Ag^+ ; b) 3.8 wt % Ag^+ ; c) 2.2 wt % Ag^+ ; d) 1.3 wt % Ag^+ .

The XANES results suggest that three phases of silver are present within merino wool - silver chloride nanoparticle composites: silver chloride, silver metal and silver oxide. It is likely that other species of silver exist, due to interactions of silver with proteins within merino wool, however available standards to measure interactions of silver with such species are not available. Therefore, the given results can only be taken as an indication of the potential proportions of silver species within the composites. For each

composite, the measured data have been deconvoluted into the three silver entities, following the equation below (where E is energy):

$$\text{data (E)} \rightarrow a \cdot \text{Ag (E)} + b \cdot \text{Ag}_2\text{O (E)} + c \cdot \text{AgCl (E)} + mx + d$$

In the spectra, the untreated data are plotted, with the proportions of silver species indicated by the strength of their plotted normalised absorbance. The sum of the most suitable combination of silver species is offered by a curve of the intensity as a function of energy (I(E)). The spectra pertaining to merino wool - silver nanoparticle composites loaded with 5.0, 3.8, 2.2 and 1.3 wt % Ag^+ are provided in Figures 6.52 to 6.55. The composition summaries for the respective composites are provided in Table 6.7.

Table 6.7 shows that the change in colour from dark purple (Fig. 6.51a) to pale pink (Fig. 6.51d) sees a decrease in the amount of silver chloride and a simultaneous increase in silver and silver oxide. It is suggested that silver chloride and silver are the two most dominating species in samples colour is purple. In samples peach/pink in colour however, the proportion of silver oxide is noted to increase dramatically. For example, when the composite sample is dark purple (Fig. 6.51a), the proportion of silver chloride is approximately 98 %. A small amount of silver (~2 %) is observed, with an insignificant proportion of silver oxide additionally being present. In the spectrum related to this sample (Fig. 6.52), the experimental data follows the curve for silver chloride almost identically due to the very large proportion of silver chloride. As the contributions of silver and silver oxide are very small, straight lines are observed for the two species.

When compared to the dark purple sample, the amount of silver chloride in that coloured mid purple (Fig. 51b) decreases to approximately 90 %. The amounts of silver and silver oxide simultaneously increase to 6 and 4 % respectively. The spectrum in Figure 6.53 shows that the curve for the normalised absorbance pertaining to silver chloride decreases and the curves for silver and silver oxide simultaneously increase. As the composite colour changes from purple to dark peach (Fig. 51c), the proportion of silver chloride decreases notably, to approximately 62 % (Fig. 6.54). The amount of

silver increases only slightly to that of the mid purple sample, from 6 to 9 %. Yet the proportion of silver oxide increases considerably, to approximately 29 %. In the pale pink sample (Fig. 51d), silver oxide is in fact proposed as the dominant species, at approximately 45 % (Fig. 55). The amount of silver chloride is noted to decrease to 43 %, with the amount of silver increasing to 12 %. It is noted in the spectra relating to these composites (Fig. 6.52 to 6.55), that as the colour changes from dark purple to pale pink the intensity of the normalised absorbance for silver chloride decreases as that of silver oxide simultaneously increases, until the proportions of the two species are comparable. This essentially shows that as the pH of pre-treated sample preparation becomes more alkaline, the ability of silver chloride to form decreases and the likelihood of silver oxide formation increases.

Figure 6.52: Synchrotron XANES spectrum relating to dark purple coloured merino wool - silver chloride nanoparticle composite (Fig. 51a; 5.0 wt % Ag^+).

Figure 6.53: Synchrotron XANES spectrum relating to mid purple coloured merino wool - silver chloride nanoparticle composite (Fig. 51b; 3.8 wt % Ag^+).

Figure 6.54: Synchrotron XANES spectrum relating to dark peach coloured merino wool - silver chloride nanoparticle composite (Fig. 51c; 2.2 wt % Ag^+).

Figure 6.55: Synchrotron XANES spectrum relating to light pink coloured merino wool - silver chloride nanoparticle composite (Fig. 51d; 1.3 wt % Ag^+).

Table 6.7: Composition results for merino wool - silver chloride nanoparticle composites as obtained from XANES data.

Sample	Spectrum	% AgCl		% Ag		% Ag ₂ O		Red χ^2
			+/-		+/-		+/-	
Fig. 51 a - Dark purple	Fig. 6.52	97.98	0.005	1.89	0.005	0.14	0.007	1.91E-05
Fig. 51b - Mid purple	Fig. 6.53	90.77	0.004	5.84	0.004	3.95	0.006	1.08E-05
Fig. 51c - Dark peach	Fig. 6.54	61.89	0.005	9.16	0.005	29.77	0.007	1.64E-05
Fig. 51d - Pale pink	Fig. 6.55	43.67	0.007	12.11	0.007	45.17	0.010	3.38E-05

6.5.4 X-Ray Photoelectron Spectroscopy (XPS)

Sections 6.1.3 and 6.4.2 above, discussed the visual effect in which the pH of the halide doped merino wool fibre has on the resulting silver composite. It was suggested that when chloride, bromide or iodide pre-treated merino wool was used as the base material under alkaline conditions for composite preparation, silver nanoparticles or an alternative oxidised species (most likely silver oxide as implied by XANES analyses above) preferentially form, over and above the formation of silver halide nanoparticles. This assumption was made on the basis that the ability for silver to precipitate with a halide anion decreases as the pH increases. Additionally, the colours of the resulting composites were comparable to that of merino wool - silver nanoparticle composites studied in depth in section 5. Due to the high solubility of silver fluoride in aqueous solutions, fluoride pre-treated merino wool, on the other hand, is thought to form silver nanoparticles at all pHs. The intensity of the colour increases as the pH is increased from 3 to 11, suggesting that silver nanoparticles form with greater ease as the pH becomes more alkaline.

Under acidic conditions, the EDS elemental analysis, discussed above, indicate the presence of silver and not fluoride within silver composites of merino wool doped with fluoride ions. The presence of silver and not silver fluoride, within composites prepared using fluoride doped merino wool as the base material, has additionally been confirmed by XPS analysis. Using XPS spectroscopy it has also been confirmed that under alkaline conditions, chloride, bromide or iodide pre-treated merino wool similarly form silver composites rather than their silver halide counterparts. The silver halide composites have been observed to form when the halide doped fibre is prepared under acidic conditions, prior to treatment with silver nitrate.

Appendix XVII, XVIII, XIX and XXI provide XPS spectra for silver halide composites of merino wool, prepared using fluoride, chloride, bromide or iodide doped merino wool as the base material. Tables 6.8 to 6.10 provide a summary of the positions of peaks present within the respective S 2p spectra, the Ag 3d spectra, and the corresponding halide spectra that result from the studied composites. According to the literature, bands corresponding silver halides in the Ag 3d spectrum occur between

367.7 eV and 368.1 eV. From previous studies, positions of 367.8, 368.1, 367.7 and 368.0 eV have been stated for the respective silver fluoride, chloride, bromide and iodide compounds^{6,7}. It is noted in Table 6.8, that only when composite preparation for chloride, bromide and iodide doped merino wool is carried out under acidic conditions (pre-treated fibre pH = 3), are peaks in the vicinity observed. As expected, a peak related to silver fluoride is not present for either acidic or alkaline preparation conditions. The experimental positions of the peaks related to AgCl, AgBr and AgI in the Ag 3d spectra occur at 368.1, 367.8 and 368.2 eV respectively. These values are all in correspondence with the literature.

Table 6.8: Positions of peaks present in the XPS Ag 3d spectra of halide pre-treated merino wool composites post treatment with silver nitrate.

Halide Pre-treatment	pH	Position of Peak (eV)	
		Relating to: Ag-X/(Ag ⁰)	Ag ⁰ /Ag-S-
0.1 M NaF	3	n/a	368.7
0.1 M NaF	11	n/a	368.7
0.1 M NaCl	3	367.8	n/a
0.1 M NaCl	11	n/a	368.6
0.1 M NaBr	3	368.1	n/a
0.1 M NaBr	11	n/a	368.6
0.1 M NaI	3	368.5	n/a
0.1 M NaI	11	n/a	368.7

On the other hand, when halide doped composites of silver are prepared under alkaline conditions (ph = 11) the band related to silver bound to a halide species is not observed. Instead a peak at higher binding energies is noted, appearing at 368.6-368.7 eV. The position of this peak is in accordance with that observed in merino wool - silver nanoparticle composites. Within such composites the peak, centred at 368.6 eV, relates to silver metal and/or silver species interacting with sulfur entities present within amino acids in which merino wool consists (refer to section 6.5). The peak at similar binding energies is also noted to occur in composites of merino wool doped with fluoride ions prepared under acidic conditions. As mentioned above, given the aqueous reaction conditions, silver fluoride nanoparticles will not form. Silver nanoparticles, formed by the reduction of silver ions to silver metal by merino wool, are instead present.

Table 6.9 provides information on the presence and absence of peaks, relating to Ag-X bonds, within F 1s, Cl 2p, Br 3d_{5/2} and I 3d_{5/2}. According to the literature, the positions of peaks for silver fluoride, silver chloride, silver bromide and silver iodide compounds occur at 682.8, 198.4, 68.3 and 619.4 eV respectively ^{6,7}. Again, the silver composites prepared using chloride, bromide or iodide doped merino wool, and under acidic conditions, show the presence of the corresponding silver halide. The obtained experimental peaks outlined in Table 6.9 are noted to be in accordance to the literature values.

Table 6.9: Positions of peaks present in the respective XPS F 1s, Cl 2p, Br 3d_{5/2} and I 3d_{5/2} XPS spectra of halide pre-treated merino wool composites post treatment with silver nitrate.

Halide Pre-treatment	pH	Position of Peak (eV) Relating to:			
		F-Ag	Cl-Ag	Br-Ag	I-Ag
0.1 M NaF	3	n/a	-	-	-
0.1 M NaF	11	n/a	-	-	-
0.1 M NaCl	3	-	198.3	-	-
0.1 M NaCl	11	-	n/a	-	-
0.1 M NaBr	3	-	-	68.6	-
0.1 M NaBr	11	-	-	n/a	-
0.1 M NaI	3	-	-	-	620.1
0.1 M NaI	11	-	-	-	n/a

In the merino wool - silver nanoparticle composites discussed in section 5.5, the XPS studies undertaken indicated that silver nanoparticles interact directly with sulfur, present in the proteins cystine, cysteine and cysteic acid which make up wool. The interaction between the two moieties is observed as a –S-Ag bond, occurring at approximately 162 eV within the S 2p spectrum. A similar interaction between silver and sulfur, of silver composites of halide doped merino wool prepared under basic conditions is observed in the S 2p spectrum. Only under acidic conditions for silver composites of chloride, bromide and iodide doped merino wool is this peak absent. The Ag 3d, S 2p and halide XPS results discussed substantiate that, with the exception of fluoride, merino wool - silver halide nanoparticle composites are successfully prepared under acidic conditions. Conversely, when preparation is undertaken under basic conditions, merino wool - silver nanoparticle composites are formed. XPS studies, in particular those owing to merino wool - silver chloride nanoparticle composites, will be

discussed in further detail in section 6.7, on the proposed binding and stabilisation of nanoparticles within the composites.

Table 6.10: Positions of peaks present in the S 2p spectra of halide pre-treated merino wool composites post treatment with silver nitrate.

Halide Pre-treatment	pH	Position of Peak (eV) Relating to: -S-Ag
0.1 M NaF	3	162.2
0.1 M NaF	11	162.2
0.1 M NaCl	3	n/a
0.1 M NaCl	11	162.3
0.1 M NaBr	3	n/a
0.1 M NaBr	11	162.3
0.1 M NaI	3	n/a
0.1 M NaI	11	162.2

6.6 Silver Halide Nanoparticles: Proposed Mechanism of Formation of Silver Halide Nanoparticles

The formation of silver halide nanoparticles within wool fibres was studied using EDS and TEM analysis. Silver chloride will be used as the example, to which silver bromide and iodide are believed to also follow. EDS elemental analysis of merino wool fibres doped with chloride ions show that chloride is present throughout the entire fibre. Figures 6.56 and 6.57 provide elemental maps of cross sections of chloride pre-treated merino wool and visually show that this statement is true for both 10 minute and 24 hour soaking periods in 0.1 M NaCl (pH adjusted to pH = 3 in the final 3 minutes) respectively. Chloride is expressed in each of the elemental maps and overlays by green. It is noted that chloride is present consistently and evenly throughout both the exterior and interior of the fibre. Understandably, a relationship between chloride and sulfur is not observed due to the like charges of both species. Instead it is most likely that chlorine associates with positively charged functional groups within amino acids in merino wool. This is suggested by XPS results as discussed in section 3.3.2 on the characterisation of merino wool doped with chloride ions.

Figure 6.56: A SEM image of a cross section of a merino wool fibre treated with 0.1 M NaCl (10 m, fibre pH = 3) together with the individual EDS maps of S and Cl and the respective overlay.

Figure 6.57: A SEM image of a cross section of a merino wool fibre treated with 0.1 M NaCl (24 h, fibre pH = 3) together with the individual EDS maps of S and Cl and the respective overlay.

After the preparation of merino wool - silver chloride nanoparticle composites, through the soaking of chloride pre-treated merino wool in silver nitrate solution, it is observed through EDS mapping that chloride no longer remains in the centre of the fibre (Fig. 6.58 & 6.59). Instead, it is present in high quantities in isolated domains on what appears to be the surface of the fibre. SEM and TEM micrographs provided in sections 6.1.1.2 & 6.1.1.3 however indicate that nanoparticles are present under the fibres surface, by up to 300 nm. The change in locality of chloride within the fibre suggests that a chemical bond between merino wool and chlorine is not formed through the doping process. Chloride ions are therefore highly mobile within the fibre prior to silver chloride nanoprecipitation. A relationship between silver-containing species and sulfur is not observed.

Figure 6.58: A SEM image of a cross section of a merino wool - silver chloride nanoparticle composite (prepared by soaking: 10 m, 0.1 M NaCl (fibre pH = 3); 15 m, AgNO₃), together with the individual EDS maps of S, Ag and Cl and the respective overlay.

Figure 6.59: A SEM image of a cross section of a merino wool - silver chloride nanoparticle composite (prepared by soaking: 24 h, 0.1 M NaCl (fibre pH = 3); 15 m, AgNO₃) together with the individual EDS maps of S, Ag and Cl and the respective overlay.

It should be noted that the resulting silver composites from both the 10 minute and 24 hour chloride soaking periods discussed above, were the same visual colour. This suggests that a 10 minute soaking period in 0.1 M NaCl solution is applicable for the chloride pre-treatment process. Within this time period, it is believed that merino wool has reached its saturation point for chloride, or that the amount of chloride ions present within the fibre is great enough to react with the available silver ions present in the silver nitrate solution in which the pre-treated fibres are immersed. Therefore, longer soaking times in chloride solutions is not required being any longer than 10 minutes.

It is believed that when silver ions from solution diffuse into the fibre, chloride ions are attracted and travel from the centre of the fibre to the outer limits. On contact, silver and chloride ions will precipitate. The growth of silver chloride nanoparticles is likely due to coagulation among the oligomer type particles initially precipitated that are within close local proximity to each other, or due to Ostwald ripening, the growth of larger particles by dissolution of the smaller ones. It is likely that it is the physical interior composition of the merino wool fibre, i.e. cortical cells etc, which limits and controls the size of the nanoparticle formed. However, the external factors can also alter the nanoparticle size. For example, by keeping the concentration of silver constant, the particle size can be controlled by controlling both the availability of chloride ions (concentration of chloride-containing dopant) and the pH of the pre-treated merino wool fibres. By decreasing the availability of chloride ions or making the pH more alkaline, the ability of silver chloride to form consequently decreases. This leads to the fewer nanoparticles forming. It is thought that due to fewer particles forming, fewer will be in the immediate proximity of one another and thus aggregation of particles will be less. This consequently results in the formation of smaller particles and the consequent effect on the colour.

When preparation of merino wool - silver chloride nanoparticle composites are prepared at elevated temperature with long soaking periods two competing reactions occur; that of the silver chloride precipitation and also the reduction of silver ions to silver nanoparticles within the wool. For example, when chloride pre-treated merino wool is soaked in a silver nitrate solution for 24 hours at 50 °C, EDS studies of the resulting composite show that again silver chloride is present at the surface of the composite. However, silver is also noted throughout the centre of the fibre and a relationship between silver and sulfur is noted (Fig. 6.60). Higher levels of sulfur are present on the top right portion of the fibre that sees a correspondingly high proportion of silver also appearing. This is unlike the 15 minute soaking period in which silver was restricted to the outer limits of the fibre only and no relationship of silver with sulfur was noted (Fig. 6.58). With the extended soaking time at the elevated temperature, silver ions within the fibre are more mobile, being able to diffuse into the centre of the fibre. Once within the fibre, proteins will reduce silver ions to silver, with subsequent nanoparticle formation. The colour of the composite prepared using the outlined methodology is

observed to be purple/grey/brown in colour (refer to section 6.1.1.1). The reason for this is therefore due to the combination of purple and yellow colours due to the formation of silver nanoparticles in addition to silver chloride nanoparticles.

Figure 6.60: A SEM image of a cross section of a merino wool - silver chloride nanoparticle composite (prepared by soaking: 24 h, 0.1 M NaCl (adjusted pH = 3); 24 h, AgNO₃ at 50 °C) together with the individual EDS maps of S, Ag and Cl and the respective overlay.

Phase analysis of obtained synchrotron radiation XRD data confirms that extending the soaking period at 50 °C sees an increase in the proportion of silver in the composite (Table 6.11). When 0.1 M HCl pre-treated merino wool is used for preparation, the percentage of silver present within the composite increases from 5.1 to 13.7 %. On the other hand, In comparison to 0.1 M HCl pre-treated merino wool, the availability of chloride ions is much less when 0.001 M HCl is implemented to pre-treat merino wool. Therefore a lesser amount of silver ions precipitate silver chloride on first contact. With the longer soaking periods greater amounts of silver ions are able to enter the centre of the fibre and subsequently become reduced by merino wool. Thus, when 0.001 M HCl pre-treated merino wool is used for composite preparation, the percentage of silver increases dramatically from 18.0 to 64.8 % when the soaking time is increased to 24 hours and the reaction is undertaken at 50 °C.

Table 6.11: Phase analysis of merino wool - silver chloride nanoparticle composites by synchrotron radiation XRD data.

Concentration of HCl Pre-treatment	Preparation Conditions	AgCl (%)	Ag (%)	+/-
0.1M	500ppm, RT, 15 m	94.9	5.1	0.022
0.1M	500ppm, 50 °C, 24 h	86.3	13.7	0.047
0.001M	500ppm, RT, 15 m	82.0	18.0	0.123
0.001M	500ppm, 50 °C, 24 h	35.2	64.8	0.256

6.7 Silver Halide Nanoparticles: Proposed Binding of Nanoparticles to Merino Wool

Given the proposed mechanism of formation of silver chloride nanoparticles within merino wool provided above, composites were studied via XPS in order to gain an understanding of the mode of binding between nanoparticle and fibre. The composite studied was prepared following the typical methodology using 0.1 M NaCl pre-treated merino wool (adjusted pH = 3), with a 10 minute soak period in a 500 mg/kg Ag⁺ solution. As was initially suggested by EDS studies, as outlined above, the XPS spectrum relating to S 2p confirms that the silver-sulfur relationship observed in merino wool - silver nanoparticle composites does not occur for merino wool - silver chloride nanoparticle composites (Fig. 6.61). This is indicated by an absence of a peak at approximately 162 eV, which is indicative of sulfur binding to a heavy metal, such as silver.

When comparing the S 2p spectra of chloride doped merino wool (Fig. 61b) to its silver chloride analogue (Fig. 61a), it is observed that the apparent proportions of the peaks owing to sulfhydryl, disulfide and oxidised sulfur remain comparable (Table 12). However, there is a notable broadening of these peaks. Both sulfhydryl- and disulfide-related peaks increase in their FWHM, from 1.3 to 2.1, whereas the peak related to oxidised sulfur increases from 2.3 to 4.0. The parallel increase in FWHM of all peaks within the S 2p spectrum of merino wool - silver chloride nanoparticle composites is indicative of a more varied surrounding environment for each functional group. This

varied environment is due to the addition of silver chloride nanoparticles being formed within the fibre. However, as the positions of the sulfur peaks remain stable, as do the proportions of these peaks, it may be concluded that sulfur does not play a role in the stabilisation of silver chloride nanoparticles within merino wool fibres.

Figure 6.61: XPS spectra of S 2p for a) merino wool - silver chloride nanoparticle composite and b) 0.1 M HCl pre-treated merino wool.

Table 12: Proportions of peaks present in the S 2p spectra.

Sample	Position of peak (eV)	Peak Relating to	% Peak Area
Cl ⁻ doped merino wool	163.8	-S-H	52 %
	165.0	-S-S-	34 %
	168.3	-S(ox)	14 %
Merino wool-AgCl composite	164.3	-S-H	54 %
	166.0	-S-S-	31 %
	168.7	-S(ox)	15 %
		-SO-Ag	

The N 1s spectrum of the merino wool - silver chloride nanoparticle composite, when compared to chloride pre-treated merino wool alone, sees a minimal broadening in the fitted peaks. The FWHM is observed to increase to 1.8, from 1.6. The comparable FWHM of the base material and the composite suggest that chloride ions may interact with nitrogen containing amino acids in both. As mentioned in section 3.3.2, the position of nitrogen interacting with chloride is typically located at 401.3 eV⁸ and thus would be incorporated within the band centred at 400.2 eV. The slight broadening, following the formation silver chloride nanoparticles within the composite, would therefore again be due to an increase in the disorder in the immediate environment of nitrogen containing functional groups. A shift in the position of the peak assigned to amine, amide and imine groups at approximately 400.2 eV, and a shift in the position of the peak for oxidised nitrogen species at approximately 402 eV are not observed. However, a distinct increase in the proportion of oxidised nitrogen is observed, from 14 to 30 %. This suggests that there may be an interaction between oxidised nitrogen and silver ions present on the surface of silver chloride nanoparticles. Nevertheless, as there is no shift in this peak, it is likely not a chemical bond but, instead a stabilising force only.

Figure 6.62: XPS spectra of N 1s for a) merino wool - silver chloride nanoparticle composite and b) 0.1 M HCl pre-treated merino wool.

A broad and weak peak, centred at 200.2 eV, is observed in the Cl 2p XPS spectrum owing to chloride pre-treated merino wool (Fig. 6.63b). The position of this peak is in accordance with that of nitrogen interacting with chloride ions, as was suggested by N 1s XPS results above. However, the large FWHM of 4.6 indicates the band incorporates the many varied environments in which chloride is present to, within merino wool fibres. In comparison to chloride pre-treated merino wool, the Cl 2p signal relating to the merino wool - silver chloride nanoparticle is much stronger. EDS studies, discussed above, of merino wool doped with chloride ions show that chloride is present throughout the entire fibre (Fig.6.56). Chloride, within merino wool - silver chloride nanoparticle composites on the other hand, is present just below the fibre surface, where silver chloride nanoparticles are formed (Fig. 6.58). The depth of penetration of photons by XPS is typically 1.5 to 5 nm. Thus higher concentrations of chloride closer to the fibre surface will lead to a stronger signal. It is for this reason that the intensity of the peak within the Cl 2p spectrum of the silver chloride composite is observed to be much stronger than the chlorine doped base material.

Two distinct peaks are observed in the Cl 2p spectrum relating to the merino wool - silver chloride nanoparticle composite (Fig. 6.63a). The peak centred at 200.0 eV again incorporates a range of chlorine environments, including $-N-Cl-$. However, a new peak at lower binding energies additionally appears, due to the formation of silver chloride nanoparticles within merino wool fibres. This peak is positioned at 198.3 eV and is in accordance with studies of silver bound to chloride stated in the literature ⁶. Accordingly, the peak is observed to have the stronger intensity of the two, contributing to 60 % of the total chlorine within the composite. Silver chloride itself will make up the core of the nanoparticles, with ions on the surface only interacting with amino acids within merino wool.

Figure 6.63: XPS spectra of Cl 2p for a) merino wool - silver chloride nanoparticle composite and b) 0.1 M HCl pre-treated merino wool.

The C 1s XPS spectrum of the merino wool - silver chloride nanoparticle composite in comparison to merino wool doped with chloride ions shows a distinct broadening in the peak relating to carbon bound to nitrogen or oxygen, and also in that peak relating to carboxyl and amide groups (Fig. 6.64). The position of the peak owing to -C-N and -C-O remains at 286.2 eV, the same position as the base material, yet the observed FWHM widens from 1.5 to 2.3. This indicates significant changes in the surrounding environment, through the introduction of silver chloride nanoparticles. It also suggests the binding of either carbon or nitrogen, through oxygen, to silver; or the potential binding of nitrogen to chloride.

The peak relating to carboxyl and amide groups broadens considerably in the silver chloride nanoparticle composite, with the FWHM increasing from 1.7 in the chloride doped merino wool base material to 3.3. Additionally a shift in this peak to lower binding energies is observed to occur, moving from 288.1 to 287.4 eV. The broadening again is due to the disorder introduced by the formation of silver chloride nanoparticles within merino wool. The shift in this peak however is likely due to carboxyl groups within merino wool interacting with silver ions on the surface of silver chloride nanoparticle composites.

Figure 6.64: XPS spectra of C 1s for a) merino wool - silver chloride nanoparticle composite and b) 0.1 M HCl pre-treated merino wool.

As was first discussed in section 6.5 and subsequently will be discussed in further detail relating to merino wool - silver halide composites, in section 6.10 to follow, silver nanoparticles are formed within the silver chloride lattice on exposure to UV light. According to the literature the positions of peaks for Ag^0 ($3d_{5/2}$) and Ag-Cl ($3d_{5/2}$)

within the Ag 3d spectrum occur at binding energies of 368.2 and 368.1 eV respectively^{9,6}. Therefore, the peak present at 368.1 eV in the measured Ag 3d spectrum for a merino wool - silver chloride nanoparticle composite likely encompasses both Ag⁰ and AgCl (Fig. 6.65). In comparison to merino wool - silver nanoparticle composites, the position of this peak is at lower binding energies; c.f. 368.6 eV in silver nanoparticle composites versus 368.1 eV in silver chloride nanoparticle composite. This indicates that the silver nanoparticles formed within merino wool - silver chloride nanoparticle composites, prepared using the method outlined above, do not interact with sulfur-containing amino acids within merino wool. The lack of an Ag-S- interaction was additionally noted in the S 2p spectrum, discussed above. The presence of silver bound to oxygen is also noted in the Ag 3d spectrum, with a peak, located at 369.4 eV, relating to silver interacting with oxygen. The interaction with oxygen is likely through carboxyl- or oxidised nitrogen-containing amino acids, as has been suggested by C 1s and N 1s spectra above.

Figure 6.65: XPS spectra of Ag 3d for a merino wool - silver chloride nanoparticle composite.

From the XPS results detailed above, it can be concluded that silver chloride nanoparticles may be stabilised within the merino wool composites by interactions of silver ions at the surface of the nanoparticles with oxygen groups present within proteins. In particular, the N 1s spectrum implies an interaction between oxidised nitrogen species and silver. A bond to carboxyl containing amino acids is suggested in both C 1s and Ag 3d spectra. In addition to silver interactions, chloride ions within silver chloride nanoparticles are also implied to interact with nitrogen containing amino acids, thus further stabilising the nanoparticles. This interaction is suggested by N 1s, Cl 2p and C 1s spectra.

6.8 Colour of Merino Wool - Silver Halide Nanoparticle Composites

6.8.1 Development of Colour

The purple or peach colour of merino wool - silver chloride nanoparticle composites is observed to develop over time following the treatment of chloride doped merino wool with a silver-containing solution. The colour develops only when exposed to light. The same is true for merino wool - silver bromide nanoparticle composites. However, as mentioned in section 6.4.2.3 above, merino wool - silver iodide nanoparticle composites colour immediately and a development over time is not observed. The colour of such composites will be discussed further in section 6.8.2. As an example of this phenomenon, Figure 6.66 gives a visual development of the purple colour of a silver chloride composite. Over a 48 hour time period, one half of the sample was exposed to natural light (Fig. 6.66a), whereas the other half was kept in the dark (Fig. 6.66b). The composite was prepared using 0.1 M HCl pre-treated merino wool. The half of the sample that is not exposed to light is noted to remain the original white of merino wool. However, the half exposed to light, colours to purple, reaching an apparent constant intensity in the final 14 hours of the 48 hour time period.

Figure 6.66: A comparison of the colour development of a merino wool (0.1 M HCl pre-treated) - silver chloride nanoparticle composite in natural light over a 48 h time period, to that kept in the dark.

Additionally, the white to purple or peach colour development of merino wool - silver chloride nanoparticle composites was followed using the Hunter Colour Quest instrument. This instrument has a Daylight 65 fluorescent lamp installed that has a light quality that resembles outdoor light. Undertaking the experiment on the Hunter Colour Quest instrument allowed CIE L^* , a^* , b^* values (Fig. 6.67 & 6.68) to be obtained, whilst also allowing for the simultaneous collection of UV-vis absorption over the 48 hour time period (Figs. 6.69 & 6.71). Immediately after soaking in a silver solution, merino wool, pre-treated with 0.1 M HCl, is white in colour (Fig. 6.67). This is indicated by high L^* and 457 nm brightness values and a^* and b^* values very near zero. As time proceeds L^* and 457 nm brightness values drop. The a^* value becomes more positive indicating an increase in red hues, and the b^* value becomes more negative, indicating an increase in blue hues. After approximately 5 hours of exposure to light emitted from the Daylight 65 lamp, L^* , a^* and 457 nm brightness values stabilise and remain stable over the following 41 hours. The b^* value on the other hand, after the aforementioned initial decrease, increases somewhat. All values remain stable for the hours 24 - 48. Therefore, one may conclude that the complete development of purple colour by merino wool - silver chloride nanoparticle composites takes approximately 24 hours at room temperature. Similarly, the development of the peach colour of merino wool - silver nanoparticle composites is observed to have reached completion after 24 hours (Fig. 6.68).

Figure 6.67: CIE Colourquest values following the development of the purple colour of a merino wool - silver nanoparticle composite.

Figure 6.68: CIE Colourquest values following the development of the peach colour of a merino wool - silver nanoparticle composite.

The development of the purple colour of the composite, prepared using 0.1 M HCl pre-treated merino, is also indicated in the UV-vis absorption spectrum, whereby the peak centred at *c.* 520 - 535 nm increases in intensity over the 48 hour time period (Fig. 6.69). As time proceeds, absorption in the yellow-green region of the visible spectrum increases. Consequently, the amount of purple light reflected, green's complementary colour, simultaneously increases (Fig. 6.70). Thus the composite becomes more highly coloured to the eye. The observed peak is broad, indicating a diverse distribution in particle size. This confirms the TEM results discussed in section 6.1.1.3. As with the plotted CIE L*, a*, b* values (Fig. 6.67), the UV-vis absorption spectrum implies that a constant colour is obtained after 24 hours. The intensity of the peak, owing to the purple colour of the composite, reaches a maximum after 5 hours. However, a yellow shift in the spectrum is noted from *c.* 520 to 535 nm after 24 hours, which subsequently remains stable for the remainder of the 48 hour time period. The yellow shift increases the reflected red hues of purple light that is reflected. Thus, the resulting composite is red-violet in colour, as observed (Fig. 6.66).

Figure 6.69: UV-vis spectra following the development of the purple colour of a merino wool - silver nanoparticle composite.

Figure 6.70: A colour wheel. Complementary colours are those directly opposite from each other.

The peak owing to the peach colour of merino wool - silver chloride nanoparticle composites, using 0.001 M HCl pre-treated merino wool as the base material, appears at *c.* 460 nm in the UV-vis absorption spectrum (Fig. 6.71). In a parallel to that of the purple coloured composite, the intensity of the absorption peak, by a developing peach-coloured composite, increases as time proceeds. The observed peak lies within the blue-green region of the visible spectrum, therefore reflecting the peach colour (or red/orange on the colour wheel: Fig. 6.70) of the composite that is observed. Absorption in this region reaches a maximum after 24 hours which, as with the purple-coloured example, remains stable for the remainder of the 48 hour time period, indicating a constant colour has been obtained. Again, the observed peak within the spectrum is suggested to be broad, yet less so than the peak relating to the purple-coloured composite. The broadness of a peak indicates a diverse particle size distribution. TEM results, discussed in section 6.1.2.3, indicate that the particle size distribution of peach-coloured composites to be smaller than that of purple-coloured composites, consistent with the narrower peak. However, in saying this, as the Hunter Colour Quest instrument cuts off at 400 nm, it is difficult to ascertain the actual broadness of the peak at wavelengths below this value. The statements above are therefore a combination of fact and extrapolation from the available results.

Figure 6.71: UV-vis spectra following the development of the peach colour of a merino wool - silver nanoparticle composite.

An *in-situ* reaction was also undertaken on the synchrotron radiation XRD beamline, in order to determine the nature of crystalline silver species present during the purple colour development. Merino wool fibres, pre-treated with 0.1 M HCl, were placed in a 500 mg/kg Ag^+ solution and agitated for 15 minutes. The fibres were then rinsed with distilled water and blotted dry. All processes were undertaken in the dark. The white merino wool fibres were then mounted in the sample holder as shown in Figure 6.72a, and placed in the beam of synchrotron radiation. Over a period of 30 minutes within the beam, the merino wool, unmasked by kapton tape, became purple in colour (Fig. 6.72b). The XRD pattern for the AgCl 200 and Ag 111 peaks for time periods $t = 0, 5, 15, 30$ minutes are offered in Figures 6.73 and 6.74 respectively.

Figure 6.72: a) Merino wool - silver chloride nanoparticle composite at $t = 0$; b) Merino wool - silver chloride nanoparticle composite after being exposed to synchrotron radiation ($t = 30$).

The pattern relating to the AgCl 200 peak at $t = 0$ confirms that silver chloride is present within the fibre when the fibre is white (Fig. 6.73). As the time proceeds from 0 to 30 minutes, the intensity of this peak is observed to decrease slightly. At $t = 0$, in the pattern relating to Ag 111, no peak is observed (Fig. 6.74). However, with the small decrease of the AgCl 200 peak over time, the formation of a peak relating to Ag 111 is observed, which intensifies over the 30 minute period the fibres are in the beam. This suggests that it is indeed the silver nanoparticles which are formed within the silver chloride lattice that accounts for the purple colour of merino wool - silver chloride nanoparticle composites. The results from both the monitoring of colour development of time when exposed to Daylight 65 light via the Hunter Colour Quest and the *in situ* synchrotron reaction confirm that photons of light are required for the development of the colour of silver chloride nanoparticles. This adheres to the theoretical explanation of why silver chloride solid becomes purple in colour when exposed to sunlight (refer to section 1.3.2.2.2) and will be discussed in further detail below.

Figure 6.73: Synchrotron radiation XRD pattern showing the AgCl 200 peak as the purple colour develops for a merino wool - silver chloride nanoparticle composite.

Figure 6.74: Synchrotron radiation XRD pattern showing the Ag 111 peak as the purple colour develops for a merino wool - silver chloride nanoparticle composite.

6.8.2 Proposed Explanation for Observed Colour of Merino Wool - Silver Halide Nanoparticle Composites

TEM analysis undertaken on merino wool fibres coloured by silver or silver chloride nanoparticles determines that for all colours obtained, the nanoparticles are spherical in shape (Fig. 6.75). A distinct decrease in the average crystallite size is observed for the colours from purple to peach to yellow. Were all colours due to silver nanoparticles alone, one would assume that the change in size affects the collective oscillation of conduction band electrons within the particle, simultaneously shifting the position of the plasmon band and thus the reflected colour observed by the eye. However, the silver and silver chloride systems are very different.

Figure 6.75: TEM images of cross sections of merino wool coloured with silver-based nanoparticles embedded in resin: a) silver chloride: purple, b) silver chloride: peach, c) silver: yellow.

The silver chloride system is a very interesting one. Much like in the photographic process, when a silver halide species is exposed to UV light, a photon is absorbed by the halide ion and an electron is generated. This electron is highly mobile, moving through the silver chloride lattice, becoming trapped within a defect or impurity centre. Mobile interstitial silver ions in the crystal become attracted to the traps and are consequently reduced to atomic silver. Equations 1 and 2 below show a schematic representation of silver halides ($X = \text{Cl}$ or Br) when exposed to light or radiation of an appropriate wavelength.

The silver ion can then combine with the electron to produce a silver atom:

Subsequent photo-electrons and interstitial silver ions migrate alternately to the same trap to enhance the cluster of silver atoms, subsequently forming nanoparticles of silver within the silver halide lattice¹⁰. The presence of crystalline silver within silver halides was confirmed by synchrotron radiation XRD, as indicated above (Fig. 6.74).

It is therefore thought that the colour of merino wool - silver chloride nanoparticle composites arises from surface plasmon resonances of the formed silver nanoparticles within a surrounding medium of a different refractive index. Because silver chloride has a higher refractive index in comparison to wool (2.1¹¹ and 1.5¹² respectively) the effect is to shift the absorption band characteristically found at *c.* 430 nm in the merino wool - silver composite to longer wavelengths; merino wool coloured peach typically absorbing at *c.* 460 nm and merino wool coloured purple at *c.* 530 nm (Fig. 6.76). The extent to which the absorption band shifts, appears dependent upon the thickness of the surrounding silver chloride, i.e. the size of the AgCl particle. As the refractive index of silver bromide is 2.2¹³, very similar to that of silver chloride, it follows that merino wool - silver bromide nanoparticle composites are akin in colour to that of the silver chloride analogues. Evidence of this is provided by the comparable curves of both merino wool - silver chloride and -silver bromide in the UV-vis absorption spectra shown in Figure 6.78 below.

Figure 6.76: UV-vis spectra of a) merino wool coloured yellow with silver nanoparticles; b) merino wool coloured peach with silver chloride nanoparticles; c) merino wool coloured purple with silver chloride nanoparticles.

The theory in which the colour observed in silver halide composites is due to silver nanoparticles within a surrounding medium of higher refractive index is further confirmed when merino wool - silver or silver chloride samples are treated with sodium thiosulphate. A profound change in colour from peach or purple to yellow occurs (Fig. 6.77). Sodium thiosulphate dissolves silver chloride, removing it from the composite. Nanoparticulate silver remains in the merino wool, a medium of much lower refractive index, thus appearing comparable to merino wool - silver nanoparticle composites.

Figure 6.77: Merino wool coloured by silver; a) and silver chloride nanoparticles; b) and c) treated with sodium thiosulfate to dissolve and remove silver chloride.

Despite silver iodide also having a refractive index of 2.2^{11} , merino wool - silver iodide nanoparticle composites have a very different colour when compared to their silver chloride or silver bromide analogues. As has been outlined, merino wool-silver chloride and -silver bromide nanoparticle composites are purple in their appearance whereas silver iodide nanoparticle composites are pale yellow in colour. Consequently, the maxima within the UV-vis spectrum of merino wool-silver chloride and silver bromide composites occurs at *c.* 530 nm, while the maxima of those coloured by silver iodide occur at *c.* 415 nm (Fig. 6.78).

Figure 6.78: UV-vis absorption spectra for merino wool-AgX nanoparticle composites.

In addition, unlike the silver chloride and silver bromide analogues, the colour of the merino wool - silver iodide composite does not develop when exposed to UV light. Instead, the colour occurs almost instantly on the contact of merino wool, doped with iodide ions, with silver nitrate solution. This indicates that the observed yellow colour is due to the silver iodide nanoparticles themselves rather than the colour being due to photochemically formed silver nanoparticles within the silver iodide matrix.

6.9 Colourfastness Testing

6.9.1 Colourfastness to Washing

In order to determine the robustness of the colour of merino wool - silver chloride nanoparticle composites, colour fastness tests to washing and rubbing were undertaken. Colourfastness tests on merino wool - silver chloride nanoparticle composites to shampooing were undertaken at AgResearch, Christchurch using the Australian/NZ Standard 2111.19.2 test (section 2.3.9.1.1). The results from this test, when purple-coloured silver chloride nanoparticle composites (prepared using 0.1 M HCl pre-treated merino wool), loaded with 4.9 wt % silver are analysed are provided in Table 6.13. As is indicated, the pass level for the change in shade of colour of the tested sample is 4, whereas the pass level for the staining of wool of cotton by the sample is 3. The maximum obtainable value is 5. Merino wool coloured by silver chloride nanoparticles reaches and/or surpasses the pass levels for each of the tests, scoring 4 to 5, 5 and 4 to 5 for each of the respective tests. These results indicate that the colour of such samples is stable to washing with a shampoo.

Table 6.13: Results from colourfastness testing on merino wool - silver chloride nanoparticle composites to shampooing.

Sample Form	Test		Score	Pass Level
Top	AS/NZS 2111.19.2	Change of shade	4-5	4
Top	AS/NZS 2111.19.2	Staining on wool	5	3
Top	AS/NZS 2111.19.2	Staining on cotton	4-5	3
Carpet	AS/NZS 2111.19.2	Change of shade	4-5	4
Carpet	AS/NZS 2111.19.2	Staining on wool	5	3
Carpet	AS/NZS 2111.19.2	Staining on cotton	4-5	3

6.9.2 Colourfastness to Rubbing

Colourfastness tests of merino wool - silver chloride nanoparticle composites to rubbing were also undertaken at AgResearch, Christchurch. The Australian/NZ Standard 2111.19.1 test was used (section 2.3.9.1.2), which monitors the transfer of colour from the coloured material to a cotton fabric that rubs the surface of the sample. The test is studied in two conditions, with the cotton rubbing fabric being either dry or wet. Table 6.14 provides the results for merino wool - silver chloride nanoparticle samples tested for colourfastness to rubbing. Figure 6.86 shows the pieces of the rubbed cotton fabrics, after colourfastness to rubbing tests have been undertaken. According to Australian and New Zealand Standards, textiles must score a minimum value of 3 to 4 for dry rubbing and a minimum of 3 for wet rubbing to pass this test. A score of 1 signifies maximum staining of the rubbing fabric and 5, no staining of the rubbing fabric. Merino wool coloured by silver chloride nanoparticles reaches or exceeds the required pass level in wet and dry rubbing conditions in both top and carpet forms.

Table 6.14: Results from colourfastness testing on merino wool - silver chloride nanoparticle composites to rubbing in both wet and dry conditions.

Sample Form	Test	Score	Pass Level
Top	AS/NZS 2111.19.1 Wet	3-4	3
Top	AS/NZS 2111.19.1 Dry	3-4	3-4
Carpet	AS/NZS 2111.19.1 Wet	3-4	3
Carpet	AS/NZS 2111.19.1 Dry	3-4	3-4

Figure 6.79: Cotton fabric implemented for colourfastness to rubbing tests (AS/NZS 2111.19.1), undertaken in: a) wet conditions and b) dry conditions.

6.9.3 Colourfastness to Chlorinated Swimming Pool Water

The Australian Standard 2001.4.5 test for the colourfastness of merino wool - silver chloride nanoparticle composites to chlorinated swimming pool water were, like the shampooing and rubbing tests above, again undertaken at AgResearch, Christchurch (section 2.3.9.1.3). Merino wool coloured by silver chloride nanoparticles score identically for both top and carpet samples for the change of shade and staining of either wool or cotton by the tested composite, with measured values of 4, 4 to 5 and 5 respectively. A score of 1 implies a severe change in colour or staining and 5, that of no change in colour or staining. A pass for this test is a score of 3. Therefore as silver chloride composites surpass this value (Table 6.15) it can be concluded that such samples may be worn with confidence in such chlorine-containing environments.

Table 6.15: Results from colourfastness testing on merino wool - silver chloride nanoparticle composites to chlorinated swimming pool water.

Sample Form	Test		Score	Pass Level
Top	AS 2001.4.5	Change of shade	4	3
Top	AS 2001.4.5	Staining on wool	4-5	3
Top	AS 2001.4.5	Staining on cotton	5	3
Carpet	AS 2001.4.5	Change of shade	4	3
Carpet	AS 2001.4.5	Staining on wool	4-5	3
Carpet	AS 2001.4.5	Staining on cotton	5	3

6.10 Stability of Colour to Light

6.10.1 Merino Wool - Silver Chloride Nanoparticle Composites

6.10.1.1 Merino Wool - Silver Chloride Nanoparticle Composites Prepared Using 0.1 M HCl and 0.001 M HCl Pre-treated Merino Wool

Merino wool - silver chloride nanoparticle composites are observed to have colour stability issues when exposed to light for long periods of time. Figure 6.87 expresses the colour change of silver chloride composites, prepared using either 0.1 M or 0.001 M HCl pre-treated merino wool as the base material, over a thirteen week exposure period to natural light. A distinct greying/browning of the composites is observed to occur over this period.

Figure 6.80: Expressing the visual colour change of merino wool - silver chloride nanoparticle composites over a period of 13 weeks in natural light. Composites were prepared using: a) 0.1 M HCl and b) 0.001 M HCl pre-treated merino wool as the respective base materials.

The colour change of merino wool - silver chloride nanoparticle composites, over the thirteen week time period, by obtaining CIE L^* , a^* , b^* values. The results for the respective purple- and pink-coloured silver chloride composites are graphed in

Figures 6.88 and 6.89 below. The changes in the obtained CIE values for each sample are provided in Table 6.16. This change was calculated by the difference in the respective CIE value at time = 90 days, compared to time = 0 days. Therefore, the greater the Δ value, the greater the deviation from the original colour for that colour coordinate. From these results we see that both purple and pink merino wool - silver chloride nanoparticle composites have large deviations in all L^* , a^* and b^* values, confirming the significant change in colour as observed by the eye. Of note, is that for both composites the largest increase is noted for the b^* value, indicating that the greatest increase in colour is in that of the yellow hues.

Figure 6.81: The change in colour over time of a purple merino wool-AgCl composite (prepared using 0.1 M HCl doped merino wool, adjusted pH = 3), as measured by CIE L^* , a^* , b^* values.

Figure 6.82: The change in colour over time of a pink merino wool-AgCl composite (prepared using 0.001 M HCl doped merino wool, adjusted pH = 3), as measured by CIE L*, a*, b* values.

Table 6.16: The measured change in CIE L*, a*, b* values of merino wool - silver chloride nanoparticle composites (prepared using 0.1 M or 0.001 M HCl doped merino wool).

Sample treated with:	Original Colour	ΔL^*	Δa^*	Δb^*	Δ 457 nm Brightness
0.1 M HCl	Purple	2.81	-4.21	5.25	-0.31
0.001 M HCl	Pink	-3.06	-3.62	3.70	-3.55

The colour instability of merino wool - silver chloride nanoparticle composites was further confirmed when lightfastness tests, using the ISO test method 105-BO2:1994, were additionally undertaken on composites prepared using 0.1 M HCl pre-treated merino wool, in both top and carpet form. These tests were performed at AgResearch, Christchurch, as is outlined in section 2.3.9.1.4. Tested samples are scored on a scale from 1 to 8, whereby a score of 1 indicates poor colourfastness and 8 indicates excellent colourfastness with exposure to light. To pass this test a score of 5 or greater must be obtained by the studied material. Merino wool coloured with silver chloride nanoparticles however do not pass, achieving a score of 2 to 3 for both top and carpet forms (Table 6.17). An image showing the change in colour of the composite, in its top form, after lightfastness testing is provided in Figure 6.90. Therefore, despite showing very positive results for the composites colour stability to shampooing, rubbing and to

the exposure of chlorinated swimming pool water as outlined above, research is required in order to halt the change of the colour of merino wool - silver nanoparticle composites when exposed to light. As such, preliminary studies into the attempted minimisation of the change in colour are outlined in section 6.10.3.

Table 6.17: Results from lightfastness tests on merino wool - silver chloride nanoparticle composites.

Sample Form	Test	Score	Pass Level
Top	ISO 105-BO2:1994	2-3	5
Carpet	ISO 105-BO2:1994	2-3	5

Figure 6.83: The resulting colour change of a merino wool - silver chloride nanoparticle composite following lightfastness testing (ISO 105-BO2:1994).

6.10.1.2 Case Study: Merino Wool - Silver Chloride Nanoparticle Composite Prepared Using 0.1 M HCl Pre-treated Merino Wool

In an attempt to further study the change in colour of purple-coloured merino wool - silver chloride nanoparticle composites with exposure to natural light, a test parallel to that undertaken on merino wool - silver nanoparticle composites was carried out. In this test a merino wool - silver chloride nanoparticle composite, prepared using 0.1 M HCl pre-treated merino wool, was placed in an envelope with half the sample exposed to natural light and half of the sample kept in the dark of the envelope interior (Fig. 6.91a). After a period of thirteen weeks a distinct change in colour between fibres placed in the dark, in comparison to those in the light, was observed. The area of the composite exposed to natural light becomes more purple/grey/brown, whereas the change in colour of the portion kept in the dark was not immediately apparent (Fig. 6.91b). The portions of the composites exposed to both environments were studied by Hunterlab ColourQuest, XPS and synchrotron radiation XRD. The results from these studies will be considered in the discussion following.

Figure 6.84: Stability of merino wool - silver chloride nanoparticle composites to light and dark: a) experimental setup and b) resulting colour of composite exposed to light (upper portion) and no light (lower portion).

6.10.1.2.1 Characterisation of Colour

The obtained CIE L^* , a^* , b^* values of the merino wool - silver chloride nanoparticle composites exposed to natural light, or kept in the dark, in comparison to a reference sample are provided in Table 6.18. The portion of the sample kept in the dark is noted to have similar measured CIE values to that of the reference. Only a very minimal reddening and yellowing of the sample occurs. This is indicated by the respective increases of both a^* and b^* values from 11.16 to 13.68 and 0.16 to 0.99. A minimal darkening is also noted by a decrease in L^* and 457 nm Brightness values from 36.04 to 35.68 and 9.78 to 8.53 respectively. On the other hand, when the merino wool - silver chloride nanoparticle composite is exposed to natural light the composite notably becomes greyer in colour. A significant increase in the b^* value, from 0.16 to 5.41 is noted, indicating an increase in the yellow hues of the composite. Additionally, a small decrease, from 11.16 to 8.95, in the a^* value is observed. This indicates that the red hues of the sample decrease slightly, with the amount of green hues simultaneously increasing. The measured L^* and 457 nm Brightness values increase minimally suggesting a slight lightening of the sample. It is therefore the combination of the said increase in yellow hue and decrease in red hue that results in the sample visually appearing more grey/brown.

Table 6.18: CIE L^* , a^* , b^* values of a merino wool - silver nanoparticle composite kept in the dark or exposed to natural light.

Sample	L^*	a^*	b^*	457 nm Brightness
Reference	36.04	11.16	0.16	9.78
Dark	35.68	13.68	0.99	8.53
Light	38.85	8.95	5.41	8.47

6.10.1.2.2 Synchrotron Radiation X-Ray Diffraction (XRD)

Phase analysis information, obtained from synchrotron radiation XRD data, for the discussed merino wool - silver chloride nanoparticle composites kept in the dark or exposed to light is provided in Table 6.19. A reference material of a recently prepared silver chloride composites prepared using the identical methodology, is offered as a comparison. These data show that with exposure to light the proportion of silver metal increases significantly, from 3.8 to 19.6 %, in comparison to the reference. Consequently the proportion of silver chloride decreases from 96.2 to 80.4 %. It is likely that given the extended periods of exposure to natural light the UV-induced reduction of silver ions within the silver chloride lattice continues. Therefore the greater proportions of silver nanoparticles, coloured yellow, within silver chloride will discolour the composite. This theory is substantiated by the given increase of yellow hues within the composite indicated by an increase in the CIE b* value, discussed above.

Table 6.19: Phase analysis of merino wool - silver chloride nanoparticle composites as obtained by synchrotron radiation XRD data.

Concentration of HCl Pre-treatment	Sample Conditions	AgCl (%)	Ag (%)	+/-
0.1 M	Reference	96.2	3.8	0.015
0.1M	Composite kept in the dark for 13 weeks	94.9	5.1	0.022
0.1M	13 weeks exposure to natural light	80.4	19.6	0.058

Although being by a much lesser amount, the sample kept in the dark for the 13 week period is also observed to increase in its silver proportion; from 3.8 to 5.1 %. As the sample was kept in the dark the UV-induced reduction of silver ions to silver metal is not a viable rationale for the said increase. Instead, it is more likely that amino acids surrounding silver chloride nanoparticles reduce silver ions to silver with a mechanism similar to that outlined in section 5.5. As was discussed, the reduction of silver ions by amino acids at room temperature is minimal and a long time period is required in order to see results, by a yellowing of the sample. Therefore, the increase of silver within the merino wool - silver chloride nanoparticle composite with exposure to natural light for 13 weeks is most likely due to a combination of both the UV and amino-induced

reduction of silver ions within the silver chloride lattice. Given the above results, the UV-induced reduction is the predominant reduction mechanism. However, it is suggested that approximately 1 % of the ~16 % increase of silver within the silver chloride composite may be associated to silver ions reduced by amino acids.

6.10.1.2.3 X-ray Photoelectron Spectroscopy

XPS studies were additionally undertaken on merino wool - silver chloride nanoparticle composites, either kept in the dark or exposed to natural light, in order to determine further the cause for the observed colour change from purple to grey with exposure to light. From these studies, in conjunction with synchrotron radiation XRD results, theories for the colour change have been proposed. Additional studies are required however in order to gain a greater understanding of the processes that take place when silver chloride nanoparticle composites are exposed to natural light. The obtained XPS spectra for Ag 3d, N 1s and S 2p are provided in Figures 6.92, 6.93 and 6.94 respectively. For ease of comparison, Tables 20, 21 and 22 provide summaries of the peaks present in the given spectrum. Interestingly, the XPS results from studies of merino wool - silver chloride nanoparticle composites are comparable to those undertaken on merino wool - silver nanoparticle composites (refer to section 5.5). That is to say, the positions and proportions of peaks within Ag 3d (Fig. 6.92) and N 1s spectra (Fig. 6.93), for both silver chloride composites exposed to natural light and that kept in the dark for the thirteen week period, remain stable. Additionally, despite the positions of peaks remain comparable the proportions of peaks with the S 2p spectra (Fig. 6.94) are very dissimilar.

The constant positions and relative peak proportions within the Ag 3d and N 1s spectra indicates that nitrogen is likely not responsible for the distinct darkening in colour observed for the composites when exposed to natural light. However, the same cannot be said for the different silver species in the Ag 3d spectrum. The positions of Ag^+ and Ag^0 occur in the same relative binding energies and thus the reduction of silver ions within the silver chloride matrix to silver nanoparticles, as indicated by synchrotron radiation XRD and discussed in section 6.10.1.2.2 above, will not be apparent using XPS as a characterisation method.

The S 2p spectra of the merino wool - silver chloride nanoparticle composites are very dissimilar and thus, in addition to the increase in silver nanoparticles within the silver chloride matrix, are also likely to contribute to the colour change of composites kept in the dark, compared to that exposed to natural light (Fig. 6.94). To elaborate further, the analysed portion of the composite that was kept in the dark has the expected peaks of a merino wool - silver chloride nanoparticle composite (Fig 6.94a). The bands associated with -S-H, -S-S- and -S-O₃H- / -S-O-Ag are present. However, the proportion of the band owing to oxidised sulfur is noted to increase significantly when compared to the same composite studied soon after preparation. The ratio of -S-H and -S-S- : -S-O₃H- / -S-O-Ag is noted to change from 1 : 0.2 for the merino wool - silver chloride nanoparticle composite recently prepared, to 1 : 1.9 for the sample kept in the dark for thirteen weeks. This is in agreement with the argument that amino acids may also be contributing to the increase in silver species noted by synchrotron radiation XRD. However in this case, it appears that the sulfur-containing amino acids, cystine and cysteine, and not the nitrogen containing species, that may contribute to the reduction of silver due to the significant increase in the proportion of oxidised sulfur.

In comparison, when the composite is exposed to natural light for the thirteen week time period, the proportion of oxidised silver increases even more substantially (Fig. 6.92b). The peak relating to oxidised silver is so large that the umbrella peak relating to sulfhydryl and disulfide bonds is dwarfed to the degree where individual peaks for the respective bonds cannot be confidently allocated. For this reason a single peak owing to an average of sulfhydryl and disulfide bonds has been fitted. The -S-H and -S-S- : -S-O₃H- / -S-O-Ag ratio is noted to increase from 1 : 1.9 for the composite kept in the dark, to 1 : 9.6 for the composite exposed to light. Additionally, a new broad band appears at higher binding energies; that of 170.2 eV. A similar dramatic increase in the oxidised species of sulfur was noted for merino wool - silver nanoparticle composites (Fig. 5.61b, section 5.7.2), and was suggested to be due to the photooxidation of wool by UV radiation present in natural light. This photodegradation process may be catalysed by the silver species within the wool. Assuming the photodegraded wool affects the refractive index of that of the original wool matrix, the dielectric constant of the surrounding environment of the silver chloride nanoparticles would consequently be altered. Therefore the surface plasmon resonance effects and thus the reflected colour would consequently be affected, changing in colour from purple to the purple/grey observed. This effect would be in combination with the increase in silver nanoparticles within the silver chloride matrix as indicated by synchrotron radiation XRD. Additionally, the yellow colour of photodegraded wool may also act in affecting the original purple colour of merino wool - silver chloride nanoparticle composites.

Figure 6.85: XPS Ag 3d spectra of merino wool - silver nanoparticle composite kept in: a) dark; b) natural light.

Table 20: Positions of peaks present in the Ag 3d spectrum.

Merino wool - silver chloride nanoparticle composite exposed to:	Position of peak (eV)	Peak Relating to	% Peak Area
Dark	368.0	Ag ⁰	59
Light	368.2	Ag-Cl	63
Dark	369.4	Ag-O-	41
Light	369.6	Ag-O-	37

Figure 6.86: XPS N 1s spectra of merino wool - silver nanoparticle composite kept in: a) dark; b) natural light.

Table 21: Positions of peaks present in the N 1s spectrum.

Merino wool - silver chloride nanoparticle composite exposed to:	Position of peak (eV)	Peak Relating to	% Peak Area
Dark	400.3	Amino groups	85
Light	400.4	Amino groups	83
Dark	402.3	-N(ox) -NO-Ag	15
Light	402.1	-N(ox) -NO-Ag	17

6- MERINO WOOL - SILVER HALIDE NANOPARTICLE COMPOSITES: NANOPARTICLES FORMED IN THE PRESENCE OF MERINO WOOL

Figure 6.87: XPS S 2p spectra of merino wool - silver nanoparticle composite kept in: a) dark; b) natural light.

Table 22: Positions of peaks present in the S 2p spectrum.

Merino wool - silver chloride nanoparticle composite exposed to:	Position of peak (eV)	Peak Relating to	% Peak Area
Dark	163.7, 165.0	-S-H -S-S-	34
Light	164.7	-S-H -S-S-	7
Dark	168.9	-SO ₃ H -SO-Ag	66
Light	168.5	-SO ₃ H -SO-Ag	72
Light	170.2	-S(ox)-?	21

6.10.2 Merino Wool - Silver Bromide and Merino Wool - Silver Iodide Nanoparticle Composites

Following a comparative experiment to that of merino wool - silver chloride nanoparticle composites, merino wool - silver bromide and merino wool - silver iodide nanoparticle composites were similarly exposed to natural light for a thirteen week time period. The colour of the respective silver bromide and silver iodide composites over the thirteen week period were monitored via the Hunterlab ColourQuest instrument, whereby CIE L^* , a^* , b^* values obtained at intervals. Shifts in the colour over time are provided graphically in Figures 6.95 and 6.96 below. The change in the obtained CIE L^* , a^* , b^* values for each sample, at time = 90 days in comparison to time = 0 days, are provided in Table 6.23. The related values for a merino wool - silver chloride nanoparticle composite have also been provided as a reference.

From these results, it is noted that much like merino wool - silver chloride nanoparticle composites, their silver bromide analogue is also unstable in its colour when exposed to light for extended periods of time (Fig. 6.95, Table 6.23). Again, significant changes in both a^* and b^* values are observed. It is also observed that there is a significant change in L^* and 457 nm Brightness values indicating an increased lightening of the sample over time. On the other hand, the colour stability of merino wool - silver iodide nanoparticle composites far surpasses that of the silver chloride and silver bromide analogues. Figure 6.96 shows insignificant changes to L^* , a^* , b^* and 457 nm brightness values over the thirteen week time period. For each measured colour coordinate it is noted that a flat line is effectively given. When calculating the change in obtained CIE L^* , a^* , b^* values for silver iodide composites, at time = 90 days in comparison to time = 0 days, minimal values are obtained. These changes are likely to be due to the difficulties in reproducing measurement conditions due to the fibrous nature of the composite material. That is to say, fibres may not always be at the same angle or height to the detector and thus this will introduce slight inconsistencies with each measurement taken.

Figure 6.88: The change in colour over time of a merino wool - AgBr composite (prepared using 0.1 M NaBr doped merino wool, adjusted pH = 3), as measured by CIE L*, a*, b* values.

Figure 6.89: The change in colour over time of a merino wool - AgI composite (prepared using 0.1 M NaI doped merino wool, adjusted pH = 3), as measured by CIE L*, a*, b* values.

Table 6.23: The measured change in CIE L*, a*, b* values of merino wool - silver halide nanoparticle composites (prepared using 0.1 M NaX doped merino wool, where X = Cl, Br or I, adjusted pH = 3).

Sample treated with:	ΔL^*	Δa^*	Δb^*	$\Delta 457 \text{ nm}$ Brightness
0.1 M HCl (Reference)	- 2.81	4.21	5.25	0.31
0.1 M NaBr	- 9.40	4.44	4.22	5.72
0.1 M NaI	0.40	0.34	1.01	0.42

Tables 6.24 to 6.29 provide information on XPS spectra relating to merino wool - silver iodide nanoparticle composites exposed to natural light for thirteen weeks, compared to that of the same composite kept in the dark for the same time period. The spectra associated to the data provided in Tables may be referred to in Appendix XXII. What is noted from this data is that no significant shifts in the positions of any of peaks within each of the respective O 1s, N 1s, I 3d, C 1s, Ag 3d and S 2p XPS spectra are observed. Instead the peak positions of composites kept in the dark compared to those exposed to natural light remain almost identical, within $\pm 0.2 \text{ eV}$ of each other. In addition, the percentage areas of the compared peaks, and their corresponding full width at half maximum (FWHM), remain comparable. Therefore, it may be concluded that no changes occur to the chemical species present within merino wool - silver iodide nanoparticle composites over a thirteen week period when exposed to natural light. The stability of chemical species as indicated by XPS results, in addition to the stability and consistency of colour over time, indicate that merino wool coloured by silver iodide nanoparticles therefore have great potential for the future application in fashion or interior furnishings.

Table 6.24: Positions of peaks present in the O 1s XPS spectra of a merino wool - silver iodide nanoparticle composite after 13 weeks being kept in the dark or exposure to natural light.

Merino wool - silver iodide nanoparticle composite exposed to:	Peak Relating to:	Position of Peak (eV)	% Area	FWHM
Dark	Average of O environments	531.7	81.8	1.6
Light	Average of O environments	531.7	77.9	1.5
Dark	-CO-O-	533.3	18.2	1.6
Light	-CO-O-	533.2	22.1	1.5

Table 6.25: Positions of peaks present in the N 1s XPS spectra of a merino wool - silver iodide nanoparticle composite soon after 13 weeks being kept in the dark or exposure to natural light.

Merino wool - silver iodide nanoparticle composite exposed to:	Peak Relating to:	Position of Peak (eV)	% Area	FWHM
Dark	Amino groups, -N ⁺ - -I ⁻	400.2	89.3	1.4
Light	Amino groups, -N ⁺ - -I ⁻	400.2	89.5	1.5
Dark	-N(ox), -N-O ⁻ - - Ag ⁺	401.4	10.7	1.4
Light	-N(ox), -N-O ⁻ - - Ag ⁺	401.5	10.5	1.5

Table 6.26: Positions of peaks present in the I 3d XPS spectra of a merino wool - silver iodide nanoparticle composite soon after 13 weeks being kept in the dark or exposure to natural light.

Merino wool - silver iodide nanoparticle composite exposed to:	Peak Relating to:	Position of Peak (eV)	% Area	FWHM
Dark	Ag-I (3d _{5/2})	619.9	n/a	3.4
Light	Ag-I (3d _{5/2})	620.1	n/a	5.0

Table 6.27: Positions of peaks present in the O 1s XPS spectra of a merino wool - silver iodide nanoparticle composite soon after 13 weeks being kept in the dark or exposure to natural light.

Merino wool - silver iodide nanoparticle composite exposed to:	Peak Relating to:	Position of Peak (eV)	% Area	FWHM
Dark	-C-C, -C-H, -C-S	285.0	69.7	1.2
Light	-C-C, -C-H, -C-S	285.0	70.6	1.2
Dark	-C-N, -C-O, -C-O ⁻ - - Ag ⁺ , -C-N-O ⁻ - - Ag ⁺ , -C-N ⁺ - -I ⁻	286.2	20.6	1.5
Light	-C-N, -C-O, -C-O ⁻ - - Ag ⁺ , -C-N-O ⁻ - - Ag ⁺ , -C-N ⁺ - -I ⁻	286.2	18.9	1.4
Dark	-C-OO ⁻ - -Ag ⁺ , -NH-CO	288.3	9.7	1.7
Light	-C-OO ⁻ - -Ag ⁺ , -NH-CO	288.3	10.5	1.9

Table 6.28: Positions of peaks present in the Ag 3d XPS spectra of a merino wool - silver iodide nanoparticle composite soon after 13 weeks being kept in the dark or exposure to natural light.

Merino wool - silver iodide nanoparticle composite exposed to:	Peak Relating to:	Position of Peak (eV)	% Area	FWHM
Dark	$\text{Ag}^0 (3d_{5/2}), \text{Ag}^+ - \text{I}^-$	368.6	n/a	1.8
Light	$\text{Ag}^0 (3d_{5/2}), \text{Ag}^+ - \text{I}^-$	368.3	n/a	1.6

Table 6.29: Positions of peaks present in the S 2p XPS spectra of a merino wool - silver iodide nanoparticle composite soon after 13 weeks being kept in the dark or exposure to natural light.

Merino wool - silver iodide nanoparticle composite exposed to:	Peak Relating to:	Position of Peak (eV)	% Area	FWHM
Dark	-S-H	163.9	25.8	1.2
Light	-S-H	163.9	23.1	1.2
Dark	-S-S-	165.1	16.7	1.2
Light	-S-S-	165.2	15.5	1.2
Dark	-SO ₃ H	168.4	57.5	2.1
Light	-SO ₃ H	168.4	61.4	2.1

The change in colour of merino wool - silver chloride nanoparticle composites, over time when exposed to light poses a problem for the real world application of such textiles for clothing or interior furnishings, including carpets. In such applications, it would not be a desirable trait to the consumer, for the merino wool - silver chloride textile to discolour. Given the discolouration will be greater in areas more highly exposed to natural light, the colour degradation across the garment or carpet may be uneven and therefore potentially deemed less desirable still. Therefore, it is believed to be important to minimise or halt the colour degradation of merino wool - silver chloride nanoparticle composites.

As was indicated by synchrotron radiation XRD phase analysis, discussed above in section 6.5.2, a suggested reason for the change in colour is due to the further reduction of silver and thus the increase in yellow hues combining with purple, thus dirties its colour. Therefore, tests whereby specific UV filters and electron scavengers are applied to merino wool coloured with silver chloride nanoparticles provides an opportunity for future research. The purpose of using such treatments is to absorb UV

radiation before it reaches the composite, thereby preventing the Ag^+ to Ag^0 reduction induced by UV light.

6.11 Antimicrobial Testing

Antimicrobial testing for merino wool - silver halide nanoparticle composites was carried out against the bacteria *Staphylococcus aureus*, in an equivalent testing to that undertaken on merino wool - silver nanoparticle composites. The methodology for these studies is outlined in section 2.3.12. Figure 6.106 illustrates the antimicrobial ability of merino wool - silver chloride nanoparticle composites prepared using merino wool pre-treated with decreasing concentrations of hydrochloric acid: 0.1, 0.01, 0.001, 0.0001 M HCl. Zones of inhibited bacterial growth are visible around all composite fibres, therefore indicating positive tests for their antimicrobial properties. Measured zones of inhibition, together with loadings of silver, are provided in Table 6.33. When the silver chloride composite is prepared using 0.1 M HCl, the loading of silver is 4.9 wt % and the zone of inhibition is measured to be 2.31 mm. As the concentration of hydrochloric acid decreases from 0.1 to 0.0001 M, the loading of silver within the composite is noted to decrease from 4.9 to 1.3 wt %. Therefore, as the loading of silver decreases, it follows that the zones of inhibition simultaneously decrease from 2.31 to 1.15 mm. This equates to inhibition zones of 65 to 115 times the fibre diameters.

Figure 6.90: HCl pre-treated merino wool subsequently treated with AgNO_3 : 7) 0.1 M HCl; 8) 0.01 M HCl; 9) 0.001 M HCl; 10) 0.0001 M HCl.

Table 6.30: Zones of bacterial inhibition for merino wool - silver chloride nanoparticle composites tested against *Staphylococcus Aureus*.

Sample Number	Merino wool pre-treated with:	Weight percentage of silver	Zone of Inhibition (mm)
7	0.1 M HCl	4.9	2.3
8	0.01 M HCl	3.8	2.0
9	0.001 M HCl	2.2	1.6
10	0.0001 M HCl	1.3	1.3

When comparing the zones of inhibition of merino wool - silver chloride nanoparticle composites prepared using the *in situ* method, discussed above, to that of when nanoparticles are prepared in the presence of merino wool using an external reducing agent (Fig. 4.41, section 4.9), it is noted that the latter has larger bacterial inhibition zones, i.e. 2.3 vs. 3.0 mm. The reason for the lesser antimicrobial ability of silver chloride composites prepared by the *in situ* method, is likely due to nanoparticles being present under the fibres surface, in comparison to being predominantly above the fibres surface using the alternative method. Therefore, the ability of silver ions to migrate from the composite will be less for the *in situ* prepared composites due to the greater distance.

The antimicrobial ability of silver composites prepared using merino wool fibres doped with fluoride, chloride, bromide or iodide ions, with subsequent fibre pH-adjustment to 11, 7 or 3, are assessed in Figures 6.107 to 6.110. Composites were prepared using a 0.1 M sodium halide solution for fibre pre-treatment and a 500 mg/kg Ag^+ solution, with a fifteen minute soaking period. Tables 6.34 to 6.37 provide information on the weight percentage of silver present within the composites and the measured zones of inhibition. As has been discussed previously in section 6.5, on the characterisation of silver species, it was implied that when merino wool is doped with fluoride ions the resulting silver composite consists of silver nanoparticles and not silver fluoride. This is due to the high solubility of silver fluoride in aqueous solutions. Therefore, given the aforementioned preparation conditions, it will not precipitate. The resulting composites, prepared using fluoride doped merino wool, consist of approximately 1-1.5 wt % silver for all pHs. Given the apparent similarity of silver loadings for the composites prepared at varying pHs, the zones of inhibition are also comparable, measuring approximately 0.90 to 0.93 mm (Fig. 6.107, Table 6.34).

Figure 6.91: F^- pre-treated merino wool with pH adjustment, subsequently treated with AgNO_3 : 11) pH = 11; 12) pH = 7; 13) pH = 3.

Table 6.31: Zones of bacterial inhibition for silver composites of merino wool pre-treated with F⁻ when tested against *Staphylococcus Aureus*.

Sample Number	Merino wool pre-treated with:	pH adjustment	Weight percentage of silver	Zone of Inhibition (mm)
11	0.1 M NaF	11	1.5	0.93
12	0.1 M NaF	7	1.1	0.91
13	0.1 M NaF	3	1.2	0.90

The antimicrobial results of merino wool - silver chloride (Fig. 6.108, Table 6.35) and merino wool - silver bromide (Fig. 6.109, Table 6.36) nanoparticle composites prepared at the three different pHs are comparable, both in terms of silver loadings and inhibition zones of bacterial growth. It is noted that as the preparation pH increases from acidic to neutral to basic the zones of inhibition decrease from approximately 2 to 0.9 - 1.0 mm. What is particularly interesting is that despite lesser proportions of silver being present within the composites when prepared at pH = 7 the measured zone of inhibition is greater than that of composites prepared at pH = 11. For example, chlorine doped merino wool, pH adjusted to 7, contains 1.3 wt % silver and has an inhibition zone of 1.4 mm, compared to when it is prepared at pH = 11, whereby the wt % is 1.8, yet the zone of inhibition is but 1.1 mm. At pH = 11 the resulting composite is in fact merino wool - silver, not merino wool - silver chloride or silver bromide (refer to section 6.5). At pH = 7 however, silver chloride is still formed but however, in a much reduced amount. As was discussed in section 1.3.3 it is generally understood that it is silver ions, and not silver itself, that acts as the anti-microbial agent. Given that at pH = 7 ionic silver will be present in silver chloride, or silver bromide, rather than metallic silver, it will therefore act as a more effective antimicrobial agent, despite being present in a lesser quantity.

Figure 6.92: Cl^- pre-treated merino wool with pH adjustment, subsequently treated with AgNO_3 :
14) pH = 11; 15) pH = 7; 16) pH = 3.

Table 6.32: Zones of bacterial inhibition for silver composites of merino wool pre-treated with Cl^- when tested against *Staphylococcus Aureus*.

Sample Number	Merino wool pre-treated with:	pH adjustment	Weight percentage of silver	Zone of Inhibition (mm)
14	0.1 M NaCl	11	1.8	1.1
15	0.1 M NaCl	7	1.3	1.4
16	0.1 M NaCl	3	4.9	2.1

Figure 6.93: Br⁻ pre-treated merino wool with pH adjustment, subsequently treated with AgNO₃:
20) pH = 11; 21) pH = 7; 22) pH = 3.

Table 6.33: Zones of bacterial inhibition for silver composites of merino wool pre-treated with Br⁻ when tested against *Staphylococcus Aureus*.

Sample Number	Merino wool pre-treated with:	pH adjustment	Weight percentage of silver	Zone of Inhibition (mm)
20	0.1 M NaBr	11	1.6	0.91
21	0.1 M NaBr	7	1.1	0.94
22	0.1 M NaBr	3	4.7	1.98

When merino wool is doped with iodide ions, the antimicrobial properties of the resulting silver iodide nanoparticle composites (Fig. 6.110) are observed to be much less to that of the silver chloride or silver bromide analogues (Fig. 6.108 & 6.109). The loading of silver in silver iodide composites, using the equivalent preparation method, is a lesser amount, 3.1 vs 4.7 wt %, however the measured zone of inhibition is not proportionately smaller. When prepared at pH = 3 and 7, inhibition zones are in fact measured to be comparable to that of those composites prepared at pH = 11, i.e. merino wool - silver nanoparticle composites (Table 6.37). This is an interesting result, implying that silver iodide nanoparticles are strongly stabilised by proteins within merino wool, therefore reducing the release and migration of silver ions that hinder

microbial growth. The high insolubility of silver iodide may also play a factor in the inability of silver ions to migrate.

Figure 6.94: I^- pre-treated merino wool with pH adjustment, subsequently treated with $AgNO_3$: 17) pH = 11; 18) pH = 7; 19) pH = 3.

Table 6.34: Zones of bacterial inhibition for silver composites of merino wool pre-treated with I^- when tested against *Staphylococcus Aureus*.

Sample Number	Merino wool pre-treated with:	pH adjustment	Weight percentage of silver	Zone of Inhibition (mm)
17	0.1 M NaI	11	1.7	0.86
18	0.1 M NaI	7	1.3	0.92
19	0.1 M NaI	3	3.1	0.96

6.12 Summary

Merino wool - silver halide nanoparticle composites have been prepared by doping merino wool fibres with halide ions prior to treatment with a silver nitrate solution. On entering the fibre, silver ions become into contact with halide ions and the precipitation of silver halide nanoparticles occurs just below the fibre surface. The halides which provided the successful precipitation with silver ions were chloride, bromide and iodide. Silver chloride nanoparticle composites were the predominant focus of this chapter with bromide and iodide being used as comparative examples. Merino was also doped with fluoride ions. However, the solubility of silver fluoride is approximately 6×10^7 times greater than AgI and thus given the aqueous conditions the composites are prepared in, silver fluoride will not precipitate.

When merino is coloured with silver chloride nanoparticles the resulting composites range in colour from dark purple, through purple greys to pink and peach. The colour of merino wool - silver chloride nanoparticle composites is white, immediately after treatment. The development of colour occurs over a 24 hour period, when exposed to natural light. The shade of the colour can be tuned by systematically altering the pH of the chloride pre-treatment. This may be achieved by either controlling the concentration of hydrochloric acid, or adjusting the pH of a chloride-containing solution using a non chloride containing acid.

The colour of merino wool - silver chloride nanoparticle composites is due to the surface plasmon resonances of silver nanoparticles within silver chloride nanoparticles. Both silver chloride and silver bromide are photoactive materials. When exposed to UV radiation a photochemical reduction of silver ions to silver metal occurs. Consequently, silver nanoparticles within the silver chloride/bromide lattice are formed with the composites darkening from white to a purple colour over an approximate twenty four hour period. The reflected colour is different from the yellow colour observed in merino wool - silver nanoparticle composites as the refractive index of silver chloride or silver bromide differs to that of TSC or wool. The refractive indexes of silver chloride and silver bromide are comparable, 2.1 and 2.2 respectively, thus the observed colour of

merino wool - silver bromide nanoparticle composites are analogous to that of the silver chloride counterparts.

The size of the silver chloride or bromide particle, i.e. the thickness of the medium surrounding the formed silver nanoparticles, additionally affects the observed colour. This was confirmed by SEM and TEM analysis of composites. Those purple in colour have a larger nanoparticle diameter, measured up to 100 nm, whereas composites pink in colour have an average diameter ranging from 10 to 25 nm. The colour of silver iodide nanoparticle composites on the other hand, develops immediately rather than on exposure to light. Therefore the colour of these composites appears to be due to their interaction of light themselves rather than that of formation silver nanoparticles within silver iodide.

The presence of the silver halide species within merino wool - silver chloride, - silver bromide or - silver iodide composites was firstly established by EDS, and subsequently by synchrotron radiation XRD and XPS. Compositional elemental analysis by synchrotron radiation XANES was also undertaken on silver chloride nanoparticle composites. The results from XRD experiments additionally indicated the presence of silver within silver chloride and silver bromide composites. For a silver chloride composite, the amount of silver increased as the sample became purple in colour, confirming that it is the colour is due to silver nanoparticles within the silver halide nanoparticles. The presence of silver nanoparticles within merino wool - silver iodide nanoparticle composites was not observed, thereby substantiating the argument in that the colour of such composites is due to their interaction of light themselves.

XPS results showed the requirement of an acidic pH of the pre-treated fibre for the successful preparation of silver halide composites. When an alkaline pH was implemented the resultant composite instead consisted of silver nanoparticles rather than the required silver halide counterpart. The results from XANES experiments showed that as the pH of pre-treated sample preparation increases from pH = 3, the ability of silver chloride to form decreases and the likelihood of silver oxide formation increases. This is coupled with a change in colour from dark purple to pale pink. AA indicates that the uptake of silver from solution decreases as the pH of the pre-treated

fibre increases. In addition, TEM studies confirm that fewer nanoparticles form and those formed have a smaller particle size.

XPS studies were also undertaken on composites to determine the mode of stabilisation of silver halide nanoparticles within the merino wool fibres. These studies imply that silver chloride nanoparticles are stabilised by an interaction of silver ions with carboxyl groups or oxidised nitrogen species within merino wool. Additionally, it is suggested that there is an interaction of chloride with nitrogen. This combinatorial stabilisation of nanoparticles within wool lead to the stability of colour - i.e. minimal loss of nanoparticles - to shampooing, rubbing and to chlorinated pool water solutions. Simulated washability testing using a washing powder containing sodium thiosulfate however sees the leaching of silver chloride resulting in a composite yellow in colour due to the remaining silver nanoparticles. Thus washing with such a detergent is not recommended.

As with merino wool - silver nanoparticle composites, the silver chloride and silver bromide analogues show instability in colour when exposed to UV radiation. The purple colour of silver chloride composites becomes greyer over time. Synchrotron radiation XRD studies indicate that this change in colour is due to an increased formation of silver nanoparticles within the fibres due to the photochemical reduction process. In addition, XPS suggests that merino wool itself may become photooxidised, changing its dielectric constant and thus altering the surface plasmon resonance effects and reflected colour. However, additional studies are required to further characterise and understand the processes that occur during exposure of composites to natural light which cause the observed colour change. Silver iodide nanoparticles on the other hand show great potential as colourants for wool, exhibiting stable colours and elemental species over a long time period. The attempted minimisation of colour degradation of silver chloride composites was attempted by applying both UV filters and electron scavengers. UV filters proved unsuccessful. Electron scavengers showed some promise, however, further studies are required. There is the potential for harnessing the photosensitivity of merino wool – silver nanoparticle composites to monitor the amount of UV radiation absorbed, or to act reversibly. Yet further research in this field is also required.

Finally, silver halide nanoparticle composites tested positive for their antimicrobial activity against the Gram positive bacterium *Staphylococcus aureus*. Zones of microbial inhibition of merino wool - silver nanoparticle composites were noted between 65 and 115 times the fibre diameter, for samples loaded with 1.3 to 4.9 wt % silver. The antimicrobial properties of silver bromide nanoparticle composites are similar to that of silver chloride. In comparison, the silver iodide nanoparticle counterparts show reduced antimicrobial properties. This may be due to the high level of insolubility of silver iodide in comparison to silver chloride or bromide, or that the silver iodide nanoparticles are strongly stabilised by proteins within merino wool, therefore reducing the release and migration of silver ions that hinder microbial growth. Antistatic properties for silver chloride nanoparticle composites were also noted whilst coloured fibres were spun from fibre to yarn, greatly simplifying the spinning process.

6.13 References

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7 CONCLUSIONS

Merino wool, and to a lesser extent crossbred wool, have been successfully coloured with silver or silver halide nanoparticles using three novel and proprietary approaches. A range of desirably coloured textiles have been obtained. For the preparation of wool - silver nanoparticle composites two different procedures were utilised. The first method included the preparation of silver nanoparticles in the presence of the wool fibres, using an external reducing agent/stabilising agent (trisodium citrate (TSC)), with the *in situ* binding of nanoparticles to the surface of the fibre. Using this methodology the merino wool - silver nanoparticle composites range in colour from yellow through to gold, red/brown and finally black/brown. The composite colour is controlled by increasing the concentration and volume of the reducing agent used. For example, when low amounts of TSC are implemented (10 μ L, 1 w/w % TSC) the composite is yellow. By increasing the TSC amount used to 50 μ L, 10 w/w % TSC the resulting composite is black/brown.

Merino - silver nanoparticle composites were also prepared using the reducing nature of proteins present within wool for nanoparticle formation. With nanoparticle formation, *in situ* binding of nanoparticles within the fibre occurs. This is a highly innovative and novel approach that provides a substantial improvement to the current environmentally problematic dyeing processes. Silver is completely removed from solution during composite preparation, with the resulting product consisting of only merino wool and silver. The waste solution contains no heavy metals but instead consists of a very dilute solution of nitric acid (pH ~5.9). The composites range in colour from very pale yellow, through gold to tan and brown. The colour is dependent upon the concentration of silver solution, the soaking time of fibres in solution and the temperature used for preparation.

The successful preparation of wool - silver halide nanoparticle composites included the *in situ* precipitation of nanoparticles within the wool fibre. This was accomplished by doping the wool, with one of the halides, Cl^- , Br^- or I^- , prior to treatment with a silver containing solution. The colour of merino wool - silver chloride or - silver bromide nanoparticle composites can be tuned from pink to peach to purple. The colour

develops over a period of approximately twenty four hours with exposure to UV light, post sample preparation. The pH of the doped fibre or the availability of chloride ions within the doped fibre, prior to treatment with a silver containing solution determines the composite colour. The intensity of the colour may be increased or decreased by altering the concentration of the silver solution used. Merino wool - silver iodide nanoparticle composites are pale yellow in colour, with the colour alternatively occurring almost immediately with contact of iodide doped merino wool fibres with silver solution. As the pH of the pre-treated fibres becomes less acidic the ability to form silver halides decreases and thus the preparation of merino wool - silver halide nanoparticle composites is not as environmentally friendly as the preparation methods for merino wool - silver nanoparticle composites, as outlined above.

The colour of the wool - silver or - silver halide nanoparticle composites is due to surface plasmon resonances. The reflected colour observed by the eye is dependent upon the size of the nanoparticle, in addition to the refractive index of the stabilising agent surrounding the particle. As the particle size of silver nanoparticles increases there is a shift in the plasmon band in the UV-vis spectrum to higher wavelengths and thus a shift in colour from yellow to brown to black is observed. Both silver chloride and silver bromide are photoactive materials, a property typically harnessed within the photographic industry. When exposed to UV radiation, these materials darken from white to a purple colour, due to the photochemical reduction of silver ions to silver metal, with silver nanoparticles consequently forming within the silver chloride/bromide lattice. As the refractive index of silver chloride and silver bromide are comparable, yet differ to that of the reducing/stabilising agent implemented, TSC, or merino, the reflected colour is altered.

SEM and TEM analysis of merino wool - silver chloride or - silver bromide composites suggests the size of the particle additionally affects the observed colour. Those composites pink in colour have an average diameter ranging from 10 to 25 nm. However when the thickness of silver chloride surrounding the formed silver nanoparticles increases, i.e. when the nanoparticle diameters are increased to up to 100 nm, the composites are purple in colour. The colour of silver iodide nanoparticle composites on the other hand, is noted to develop immediately rather than on exposure

to light. The colour of these composites therefore appears to be due to the interaction of light with the silver iodide nanoparticles themselves rather than that of formation silver nanoparticles within silver iodide.

The presence of the silver and silver halide species present within merino wool composites was firstly confirmed by EDS, and subsequently by synchrotron radiation XRD. The results from XRD experiments on silver chloride and silver bromide composites additionally indicated the presence of silver. For a silver chloride composite, the amount of silver increased as the sample became purple in colour, confirming that it is the colour is due to silver nanoparticles within the silver halide nanoparticles. The presence of silver nanoparticles within merino wool - silver iodide nanoparticle composites was not observed, thereby substantiating the argument in that the colour of such composites is due to their interaction of light themselves. Compositional elemental analysis of the silver species present in merino wool - silver chloride nanoparticle composites was additionally undertaken by synchrotron radiation XANES. The results from these experiments showed that as the pH of pre-treated sample increases from pH = 3, the ability of silver chloride to form decreases and the likelihood of silver oxide formation increases. A change in colour from dark purple to pale pink is simultaneously noted as the pH increases, as the dominant species changes from silver chloride to silver oxide.

SEM and TEM studies of merino wool - silver nanoparticle composites show that when an external reducing agent is used for merino wool - silver nanoparticle composite preparation the nanoparticles are predominantly bound to the surface of the fibres only. XPS studies suggest that these nanoparticles bind to merino through TSC, which acts as a reducing and stabilising agent for nanoparticle formation and thereby simultaneously acting as a linker. It is indicated that TSC binds through carboxylate groups to either sulfur or nitrogen containing groups of proteins present on the wool fibres surface.

On the other hand, when merino wool - silver nanoparticle composites are prepared using the reducing nature of wool, nanoparticles are present throughout the centre of the fibre and typically not at the surface. The predominant bond that stabilises the nanoparticles formed within the fibres is indicated by XPS studies to be a direct linkage

between silver and sulfur. It is suggested that in the presence of silver the disulfide bond in cystine amino acids breaks and an Ag-S- bond is formed. However it is not the sulfur containing species which act as the reducing agent to effectively reduce Ag^+ to Ag^0 for the formation of silver nanoparticles. Instead it is implied that nitrogen containing functional groups, in the close vicinity to silver associated to sulfur act in this function. This is implied by a large increase in the proportion of oxidised nitrogen species in the XPS N 1s spectrum, when comparing the merino wool substrate to the silver nanoparticle composite.

The Ag-S- bond is a strong and stable bond and thus silver nanoparticles are strongly bound within the merino wool fibres, as implied by the insignificant leaching of silver when composites undergo simulated washability tests. This very positive result reduces current reservations regarding the potential environmental impact of textiles that contain silver. The colour stability of silver nanoparticle composites also exceeds the pass levels for tests relating to shampooing and rubbing, and for colour stability against chlorinated swimming pool water. However, the colour of merino wool - silver nanoparticle composites are not stable when exposed to UV light for long periods of time. Nor are they stable to air only. Merino wool - silver nanoparticle composites are noted to lighten in colour when exposed to sunlight and darken (become grey/brown) in colour when exposed to air only. For the darkening of samples in air XRD results indicate that silver is no longer in its crystalline form. XPS show a dramatic increase in the oxidised forms of silver. Amorphous silver oxide and silver sulfide, both of which are black in colour, likely form and thus would provide the darkened colour of the composite. The lightening of merino wool - silver nanoparticle composites with extended exposure periods to UV light may be due to change in the dielectric constant of merino due to photooxidation, or the formation of an oxide layer on the surface of the silver nanoparticles. Each of which would alter the surface plasmon resonance effects of the nanoparticles and thus the reflected colour observed by the eye. Further studies are required however, in order to gain a greater understanding of the colour degradation process so that it may be minimised.

Silver halide nanoparticles, and in particular silver chloride, within merino - silver halide nanoparticle composites are suggested by XPS studies to be stabilised by an

interaction of silver ions with carboxyl groups or oxidised nitrogen species within merino wool. Additionally, there interactions between the chloride ions of silver chloride and nitrogen moieties within merino wool are suggested. The combined stabilisation of silver halide nanoparticles within wool lead to the stability of colour to shampooing, rubbing and to chlorinated pool water solutions, whereby the composites exceeded the value required to pass the tests. Simulated washability testing using a washing powder containing sodium thiosulfate however resulted in a dramatic colour change of the composites. Silver chloride was leached resulting in a composite yellow in colour due to the silver nanoparticles which remained. Washing with such a sodium thiosulfate containing detergent is therefore not recommended.

As with merino wool - silver nanoparticle composites, silver chloride and silver bromide analogues show instability in colour when exposed to UV light, with a greying of colour over time. Synchrotron radiation XRD indicates that this change in colour is due to an increased formation of silver nanoparticles within the fibres due to the photochemical reduction process. Additionally, XPS suggests an increased oxidation of sulfur species, as was similarly observed for the silver nanoparticle analogues. Therefore the proposed photooxidation of merino and its altered dielectric constant and surface plasmon resonance effects may also contribute to the discolouration of silver chloride composites. Tests for the attempted minimisation of colour degradation of silver chloride composites were undertaken by applying both UV filters and electron scavengers. UV filters showed little promise whereas electron scavengers showed a slight minimisation. Further studies into both the colour degradation process and the minimisation of this are required.

The discolouration of merino wool - silver nanoparticle or - silver chloride nanoparticle composites is an undesirable trait for the potential application in the apparel or interior furnishing industries. Further research is therefore required in order to stop this from occurring. There is the potential for merino wool - silver nanoparticle composites to be dyed over top of the silver dye so that discolouration of the textile becomes inconspicuous. In terms of merino wool - silver chloride nanoparticle composites, the photosensitivity could be harnessed so as to monitor the amount of UV radiation absorbed, or for the colour change to act reversibly. However, considerable research

into this field is required. On the other hand, merino wool - silver iodide nanoparticle composites exhibiting stable colours and elemental species over a long time period and thus show great potential as colourants for wool.

Merino wool - silver nanoparticle or - silver chloride nanoparticle composites both tested positive for their antistatic and antimicrobial properties. With high loadings of silver, merino wool - silver nanoparticle composites, prepared using an external reducing agent, showed a measurable electrical conductivity of up to $4.4 \times 10^{-5} \text{ S cm}^{-1}$. Silver nanoparticle composites, prepared using the reducing nature of wool, and silver chloride nanoparticle composites do not have a measurable conductivity, yet both exhibit antistatic properties, greatly simplifying the spinning process. The greatest antimicrobial properties of the composites against *Staphylococcus Aureus* were noted for merino wool coloured with silver nanoparticle, prepared using an external reducing agent. This was then followed by silver halide composites and finally silver nanoparticle composites prepared using the reducing nature of wool. This is due to the loading and availability of silver nanoparticles to microbes, i.e. being attached to the surface of the wool fibres, in comparison to being present just below the fibres surface and throughout the fibres core for the respective three composites. Additionally, the strong bond between silver and sulfur existing in the composites, prepared without an external reducing agent, will limit the transport of silver ions. These composites were also tested in terms of their activity against the Gram negative bacterium *E. coli*, showing antibacterial properties for composite fibres spun into yarn form.

In summary, a range of desirable colours are obtained through the colouring of wool by silver or silver halide nanoparticles. Over short testing periods the colours are stable to washing, rubbing and to exposure to chlorinated swimming pool water. The insignificant leaching of silver during simulated washability tests implies nanoparticles are strongly bound to the fibres, eliminating environmental concerns for the disruption of ecosystems by leached silver. The prepared silver and silver halide nanoparticle composites exhibit antistatic and antimicrobial properties, providing a high value multifunctional material. Numerous applications within fashion and interior furnishing industries are therefore apparent. For example: high end fashion garments in which the colour and intrinsic value of silver are promoted; or high quality sportswear, where the

colour, value and antimicrobial properties, in order to combat body odour, is promoted; or high quality interior furnishings, including carpets and seat coverings for motor vehicle or aircrafts, where the colour, value, antimicrobial and antistatic properties are promoted. However, the evident setback for applications in these fields is the colour instability to light of silver, silver chloride and silver bromide nanoparticles, and thus further studies are required to eliminate this problem. Alternative options exist for the exploitation of the photosensitivity of silver halide nanoparticles within the merino wool composites, or the possibility of using silver or silver halide nanoparticles in combination with other strong dyes for the production of coloured woollen fabrics.

8 APPENDICES

APPENDIX I

Carding	A process carried out by a card (or carding machine). It involves opening clumps of wool, disentangling and mixing the fibres and the removal of vegetable matter as preparation for subsequent steps in yarn manufacture.
Combing	The straightening and parallelising of fibres and the removal short fibres and impurities.
Count	The mass per unit length of a slubbing, yarn, sliver or top – measured in tex or kilotex.
Crossbred wool	Coarse (or strong) wool, commonly used in carpets and generally coarser than around 32 microns. Often obtained from Romney sheep and breeds derived from this breed.
Drafting (or drawing)	Reduce the linear density of a sliver, top or roving, e.g. by the action of two pairs of rollers rotating at different speeds (roller drafting).
Folding (twisting or plying)	Combining two or more singles yarns using twist, to form a folded or plied yarn.
Gill box	A drafting machine using in worsted and semi-worsted processing, in which the motion of the fibres is in part controlled by pins fixed on moving bars (fallers).
Gilling (or pin drafting)	A system of drafting in which the direction of the fibres relative to one another in a sliver is controlled by pins. This action improves the fibre alignment and parallelisation in the sliver.
Hank (or skein)	A quantity of yarn in coiled form.
Loose stock	Wool without structure, e.g. scoured wool.
Lubricating	Applying a processing oil (in a water emulsion) to wool prior to carding.
Peralta rollers (or web purifier)	A pair of high pressure, smooth steel rollers on a woollen card. They crush vegetable matter in tiny fragments, making their removal much easier.
Ring spinning	A spinning system in which twist is inserted in a yarn by using a

	revolving traveller (that moves around a ring). The yarn is wound onto a spinning tube because the rotational speed of the tube is greater than that of the traveller.
Roving	A fine, well-aligned strand of fibres, the form in which wool is fed to a worsted ring spinning frame.
Semi-worsted system	A high-speed yarn manufacturing route, involving carding, gilling and ring spinning.
Setting	The process of conferring stability on a fibrous structure, e.g. yarn, by physical (steam/heat) or chemical means.
Sliver	A relatively thick strand of fibres in continuous form without twist.
Slub	An abnormally thick place in a yarn.
Slubbing	The strands of fibre from a woollen card that have been consolidated by the rubbing action of the condenser.
Tex	The unit of linear density (1 tex = 1 gram per kilometre).
Top	Combed sliver, the output from topmaking, characterised by a high level of fibre parallelisation and homogeneity, and an absence of short fibres.
Topmaking	The first stage of the worsted yarn manufacturing route, involving carding, gilling and combing.
Twist	The number of turns in a yarn, per metre.
Vegetable matter	Seeds, twigs, leaves, burrs etc. that contaminate some wools.
Woollen system	The route for producing yarn, involving a condenser card and spinning.
Worsted system	The route for producing yarn, involving carding, gilling, combing and ring spinning.
Yarn	A continuous strand of twisted threads of wool used in weaving or knitting.
Yarn scouring	Washing of finished yarn to remove processing lubricants and dirt acquired during processing.

APPENDIX II

Hunter ColourQuest CIE values for merino wool - silver nanoparticle composites prepared using raw merino wool and altering reaction temperature, concentration and soak time in Ag⁺ solution.

Room Temperature:

Sample	Time (hours)	L*	a*	b*	475 nm brightness
100 mg/kg	0	75.24	-0.74	3.70	49.71
	0.2	78.58	-0.32	3.72	48.56
	0.5	77.63	-0.40	4.17	49.44
	1	79.86	-0.39	4.15	48.7
	5	76.76	-0.47	4.4	46.33
	16	77.22	-0.58	4.63	46.11
	24	76.68	-0.84	4.75	47.05
	48	76.25	-1.04	4.66	46.44
	72	77.65	-1.00	5.53	48

Sample	Time (hours)	L*	a*	b*	475 nm brightness
250 mg/kg	0	75.24	-0.74	3.70	49.71
	0.2	77.72	-0.04	3.94	49.3
	0.5	78.30	-0.22	4.32	48.57
	1	77.49	-0.68	4.97	48.7
	5	78.26	-0.44	5.42	48.98
	16	79.01	-0.67	6.24	47.88
	24	78.06	-0.87	6.92	48.66
	48	77.89	-1.23	6.99	46.33
	72	78.79	-0.98	8.74	47.03

Sample	Time (hours)	L*	a*	b*	475 nm brightness
500 mg/kg	0	75.24	-0.74	3.70	49.71
	0.2	73.42	-0.13	5.36	48.53
	0.5	75.6	-0.39	5.41	48.71
	1	79.59	-0.43	5.89	47.88
	5	78.46	-0.48	8.11	46.18
	16	78.45	-0.34	9.81	45.77
	24	79.77	-0.28	10.86	45.31
	48	78.61	-0.30	12.05	45.72
	72	79.13	-0.30	13.12	43.89

50 °C:

Sample	Time (hours)	L*	a*	b*	475 nm brightness
100 mg/kg	0	75.24	-0.74	3.70	49.71
	0.2	71.59	-0.35	4.01	49.34
	0.5	76.14	-0.96	4.94	48.87
	1	76.28	-1.21	5.58	42.3
	5	75.59	-1.03	8.25	42.65
	16	76.11	-1.24	10.11	41.02
	24	76.39	-1.51	12.56	40.48
	48	73.95	-1.57	15.86	34.77
	72	76.83	-0.41	21.46	34.44

Sample	Time (hours)	L*	a*	b*	475 nm brightness
250 mg/kg	0	75.24	-0.74	3.70	49.71
	0.2	78.22	-0.71	4.40	49.65
	0.5	78.05	-0.52	4.60	45.03
	1	77.09	-0.8	7.33	45.61
	5	77.18	-1.22	10.77	43.06
	16	74.32	-0.24	16.87	36.54
	24	72.12	0.18	21.5	28.84
	48	69.42	2.28	25.4	22.81
	72	68.65	3.03	27.54	19.6

Sample	Time (hours)	L*	a*	b*	475 nm brightness
500 mg/kg	0	75.24	-0.74	3.70	49.71
	0.2	78.73	-0.78	6.56	48.09
	0.5	72.40	-0.86	7.41	42.53
	1	76.68	-0.58	10.4	39.17
	5	78.62	-0.56	16.65	40.51
	16	70.34	1.22	20.18	31.66
	24	68.32	3.34	24.9	22.71
	48	64.91	7.06	30.75	16.75
	72	56.84	7.32	26.99	12.43

80 °C:

Sample	Time (hours)	L*	a*	b*	475 nm brightness
100 mg/kg	0	75.24	-0.74	3.70	49.71
	0.2	78.38	-0.95	7.67	47.38
	0.5	77.41	-1.48	9.69	44.29
	1	77.48	-1.97	12.88	44.81
	5	75.90	0.18	23.14	32.12
	16	70.45	1.10	24.16	25.9
	24	67.90	2.48	25.72	21.86
	48	64.28	5.01	28.26	17.42
	72	53.33	6.38	26.43	10.49

Sample	Time (hours)	L*	a*	b*	475 nm brightness
250 mg/kg	0	75.24	-0.74	3.70	49.71
	0.2	76.63	-1.37	9.67	44.86
	0.5	75.67	-1.66	13.01	39.2
	1	77.95	-0.76	18.46	38.24
	5	74.98	2.97	25.85	29.2
	16	69.77	3.01	26.24	20.28
	24	68.82	4.34	28.92	21
	48	55.98	10.05	31.90	10.25
	72	40.71	9.73	25.70	4.84

Sample	Time (hours)	L*	a*	b*	475 nm brightness
500 mg/kg	0	75.24	-0.74	3.70	49.71
	0.2	75.77	-0.97	14.11	38.51
	0.5	72.05	-0.73	17.86	31.1
	1	71.41	1.20	18.97	30.49
	5	63.39	3.87	26.14	16.13
	16	56.22	6.79	29.5	11.11
	24	51.18	8.83	28.91	8.54
	48	43.67	8.98	25.34	5.97
	72	38.68	11.52	26.57	3.99

APPENDIX III

Hunter ColourQuest CIE values for merino wool - silver nanoparticle composites prepared using KOH pre-treated merino wool and altering reaction temperature, concentration and soak time in Ag⁺ solution.

Room Temperature:

Sample	Time (hours)	L*	a*	b*	475 nm brightness
100 mg/kg	0	75.24	-0.79	3.70	47.81
	0.2	76.47	-1.51	4.21	47.22
	0.5	77.02	-0.66	4.19	48.39
	1	76.23	-0.56	4.89	48.56
	5	76.46	-0.74	5.06	47.48
	16	77.05	-0.38	5.84	47.85
	24	75.98	0.32	6.38	48.01
	48	74.25	0.95	7.04	47.94
	72	74.00	1.26	7.63	47.55

Sample	Time (hours)	L*	a*	b*	475 nm brightness
250 mg/kg	0	75.24	-0.79	3.70	47.81
	0.2	76.27	-0.28	5.16	48.38
	0.5	75.03	-1.04	5.44	47.68
	1	75.11	-0.22	5.87	48.55
	5	75.64	-0.14	6.52	48.53
	16	76.16	0.25	7.76	47.14
	24	74.92	0.78	8.77	47.00
	48	74.26	1.16	9.99	46.87
	72	74.79	1.95	11.87	46.23

Sample	Time (hours)	L*	a*	b*	475 nm brightness
500 mg/kg	0	75.24	-0.79	3.70	47.81
	0.2	76.42	-0.16	5.98	48.23
	0.5	75.21	-0.19	6.37	46.54
	1	76.03	-0.25	6.94	46.75
	5	75.21	0.22	9.11	46.48
	16	74.90	0.84	10.63	45.99
	24	74.32	1.28	11.75	45.28
	48	74.06	1.30	13.02	45.67
	72	74.13	2.54	14.26	44.87

50 °C:

Sample	Time (hours)	L*	a*	b*	475 nm brightness
100 mg/kg	0	75.24	-0.79	3.70	47.81
	0.2	76.38	-1.21	6.77	47.88
	0.5	76.14	-0.48	9.04	46.00
	1	75.48	-0.37	11.43	45.22
	5	75.80	0.10	21.96	40.01
	16	74.25	1.07	23.16	30.25
	24	68.88	2.33	25.27	22.63
	48	63.99	5.11	27.62	18.42
	72	58.27	5.98	27.68	12.49

Sample	Time (hours)	L*	a*	b*	475 nm brightness
250 mg/kg	0	75.24	-0.79	3.70	47.81
	0.2	76.06	-1.27	8.99	45.91
	0.5	75.32	-1.04	10.01	44.66
	1	75.19	-0.11	16.64	39.10
	5	74.85	1.89	20.30	30.13
	16	70.21	3.33	25.14	21.49
	24	66.53	6.34	28.84	14.06
	48	54.86	9.13	29.00	11.65
	72	46.06	10.02	25.64	6.39

Sample	Time (hours)	L*	a*	b*	475 nm brightness
500 mg/kg	0	75.24	-0.79	3.70	47.81
	0.2	74.07	-0.91	10.36	40.64
	0.5	71.94	-0.26	15.47	37.68
	1	70.85	0.89	18.90	34.82
	5	65.44	3.10	24.91	20.25
	16	58.06	5.98	27.22	16.54
	24	53.27	8.80	28.91	12.97
	48	45.57	9.26	30.01	9.05
	72	40.14	11.52	27.57	5.63

80 °C:

Sample	Time (hours)	L*	a*	b*	475 nm brightness
100 mg/kg	0	75.24	-0.79	3.70	47.81
	0.2	77.83	-1.22	9.87	37.51
	0.5	76.14	-1.00	13.09	30.05
	1	75.23	-0.52	18.98	28.49
	5	73.86	0.87	25.16	26.13
	16	69.45	1.46	26.73	15.45
	24	60.88	4.48	27.81	10.84
	48	58.11	6.21	26.99	10.97
	72	51.04	7.38	27.01	10.49

Sample	Time (hours)	L*	a*	b*	475 nm brightness
250 mg/kg	0	75.24	-0.79	3.70	47.81
	0.2	74.59	0.11	25.16	30.13
	0.5	72.94	2.04	25.45	28.41
	1	70.67	3.16	26.34	20.11
	5	68.55	4.27	29.06	18.44
	16	58.13	10.85	32.00	15.34
	24	50.97	11.43	31.91	11.63
	48	48.22	12.01	28.53	10.25
	72	41.63	12.73	28.00	11.01

Sample	Time (hours)	L*	a*	b*	475 nm brightness
500 mg/kg	0	75.24	-0.79	3.70	47.81
	0.2	74.41	0.39	18.97	29.49
	0.5	69.39	3.88	26.14	26.32
	1	61.24	4.30	27.04	16.13
	5	59.36	5.24	28.91	14.67
	16	56.22	10.79	29.66	11.11
	24	51.18	16.63	28.22	5.99
	48	43.67	18.61	25.06	4.87
	72	36.52	18.52	21.32	3.45

APPENDIX IV

The uptake of silver ions from solution by raw merino wool. The concentration of the silver solution and time and temperature of soaking are altered.

100 mg/kg Ag⁺:

Room Temperature

Time (hours)	Residual Ag⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.03	63.9	36.2	36.2
0.2	51.1	49.0	49.0
0.5	48.8	51.3	51.3
1	44.1	56.0	56.0
2	37.8	62.3	62.3
3	32.5	65.6	65.6
5	30.6	68.5	68.5
16	27.1	72.0	72.0
24	21.8	73.2	73.2
48	19.8	77.6	77.6
72	18.9	79.2	79.2

50 °C

Time (hours)	Residual Ag⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.03	70.5	29.5	29.5
0.2	49.2	50.8	50.8
0.5	37.2	62.8	62.8
1	32.0	68.0	68.0
2	27.1	72.9	72.9
3	20.8	79.2	79.2
5	18.1	81.9	81.9
16	12.7	85.3	85.3
24	8.5	87.5	87.5
48	3.3	91.7	91.7
72	1.6	92.4	92.4

80 °C

Time (hours)	Residual Ag⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.03	5.8	54.2	54.2
0.2	5.0	68.0	68.0
0.5	2.7	77.3	77.3
1	1.7	81.3	81.3
2	0.3	92.8	92.8
3	1.6	98.4	98.4
5	0.31	99.7	99.7
16	0.06	99.9	99.9
24	0.03	100.0	100.0
48	0.08	99.9	99.9
72	0.02	100.0	100.0

250 mg/kg Ag⁺:**Room Temperature**

Time (hours)	Residual Ag⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.03	190.2	59.8	23.9
0.2	187.8	62.2	24.9
0.5	174.4	75.6	30.3
1	172.4	77.6	31.1
2	166.0	84.0	33.6
3	154.4	95.6	38.3
5	145.4	104.6	41.9
16	137.4	112.6	45.1
24	138.6	111.4	44.6
48	120.2	129.8	51.9
72	115.2	134.8	53.9

50 °C

Time (hours)	Residual Ag⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.03	175.2	74.8	29.9
0.2	154.8	95.2	38.1
0.5	141.4	108.6	43.5
1	132.6	117.4	47.0
2	118.6	131.4	52.6
3	109.6	140.4	56.2
5	98.8	151.2	60.5
16	91.2	158.8	63.5
24	84.6	165.4	66.2
48	74.6	175.4	70.2
72	66.1	183.9	73.6

80 °C

Time (hours)	Residual Ag⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.03	94.8	155.2	62.1
0.2	84.7	165.3	66.1
0.5	49.1	200.9	80.3
1	48.5	201.5	80.6
2	39.3	210.7	84.3
3	29.4	220.6	88.2
5	23.2	226.8	90.7
16	14.8	235.3	94.1
24	7.8	242.2	96.9
48	0.1	250.0	100.0
72	0.2	249.9	99.9

500 mg/kg Ag⁺:**Room Temperature**

Time (hours)	Residual Ag⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.03	452.4	47.6	9.5
0.2	447.1	52.9	10.6
0.5	437.8	62.2	12.4
1	421.8	78.2	15.6
2	411.3	88.7	17.7
3	398.8	101.2	20.2
5	391.8	108.2	21.6
16	369.3	130.7	26.1
24	370.3	129.7	25.9
48	355.8	144.2	28.8
72	347.3	152.7	30.5

50 °C

Time (hours)	Residual Ag⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.03	431.0	69.0	13.8
0.2	390.0	110.0	22.0
0.5	361.5	138.5	27.7
1	229.5	270.5	54.1
2	225.5	274.5	54.9
3	205.5	294.5	58.9
5	195.5	304.5	60.9
16	149.7	350.3	70.1
24	132.1	367.9	73.6
48	119.5	380.5	76.1
72	111.2	388.8	77.8

80 °C

Time (hours)	Residual Ag⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.03	276.0	197.5	39.5
0.2	240.4	233.1	46.6
0.5	193.4	250.1	50.0
1	238.3	261.7	52.3
2	203.8	296.2	59.2
3	187.4	312.6	62.5
5	145.6	337.9	67.6
16	99.2	384.3	76.9
24	74.1	412.4	82.5
48	6.9	440.6	88.1
72	1.6	451.9	90.4

APPENDIX V

The uptake of silver ions from solution by KOH pre-treated merino wool. The concentration of the silver solution and time and temperature of soaking are altered.

100 mg/kg Ag⁺:

Room Temperature

Time (hours)	Residual Ag ⁺	Amount Uptaken	% Uptake
0	0	0	0
0.03	46.7	38.1	53.3
0.2	41.9	58.1	58.1
0.5	37.6	62.4	62.4
1	36.9	63.1	63.1
2	30.6	69.4	69.4
3	25.3	74.7	74.7
5	23.4	76.6	76.6
16	22.9	77.1	77.1
24	19.6	80.4	80.4
48	12.6	87.4	87.4
72	11.7	88.3	88.3

50 °C

Time (hours)	Residual Ag ⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.03	61.9	38.1	38.1
0.2	40.6	59.4	59.4
0.5	28.6	71.4	71.4
1	23.4	76.6	76.6
2	18.5	81.5	81.5
3	12.2	87.8	87.8
5	11.5	88.5	88.5
16	10.4	89.6	89.6
24	7.9	92.1	92.1
48	6.4	93.6	93.6
72	5.4	94.6	94.6

80 °C

Time (hours)	Residual Ag⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.03	5.8	94.2	94.2
0.2	5.0	95.0	95.0
0.5	2.7	97.3	97.3
1	1.7	98.3	98.3
2	0.3	99.8	99.8
3	0.2	99.9	99.9
5	0.3	99.8	99.8
16	0.2	99.8	99.8
24	0.2	99.9	99.9
48	0.1	99.9	99.9
72	0.0	100.0	100.0

250 mg/kg Ag⁺:**Room Temperature**

Time (hours)	Residual Ag⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.03	178.6	71.4	28.6
0.2	176.2	73.8	29.5
0.5	162.8	87.2	34.9
1	160.8	89.2	35.7
2	154.4	95.6	38.2
3	142.8	107.2	42.9
5	141.8	108.2	43.3
16	125.8	124.2	49.7
24	124.0	126.0	50.4
48	112.6	137.4	55.0
72	103.6	146.4	58.6

50 °C

Time (hours)	Residual Ag⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.03	162.6	87.4	35.0
0.2	142.2	107.8	43.1
0.5	128.8	121.2	48.5
1	120.0	130.0	52.0
2	106.0	144.0	57.6
3	97.0	153.0	61.2
5	86.2	163.8	65.5
16	80.6	169.4	67.8
24	69.0	181.0	72.4
48	67.0	183.0	73.2
72	63.5	186.5	74.6

80 °C

Time (hours)	Residual Ag⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.03	84.6	165.4	66.2
0.2	64.5	185.5	74.2
0.5	38.9	211.1	84.4
1	38.3	211.7	84.7
2	29.1	220.9	88.4
3	19.2	230.9	92.3
5	17.0	233.0	93.2
16	0.8	249.3	99.7
24	1.9	248.2	99.3
48	0.1	250.0	100.0
72	0.2	249.9	99.9

500 mg/kg Ag⁺:**Room Temperature**

Time (hours)	Residual Ag⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.03	421.1	78.9	15.8
0.2	415.8	84.2	16.8
0.5	406.5	93.5	18.7
1	390.5	109.5	21.9
2	380.0	120.0	24.0
3	367.5	132.5	26.5
5	360.5	139.5	27.9
16	348.0	152.0	30.4
24	339.0	161.0	32.2
48	324.5	175.5	35.1
72	306.0	194.0	38.8

50 °C

Time (hours)	Residual Ag⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.03	407.5	92.5	18.5
0.2	366.5	133.5	26.7
0.5	338.0	162.0	32.4
1	196.0	304.0	60.8
2	192.0	308.0	61.6
3	182.0	318.0	63.6
5	152.0	348.0	69.6
16	106.2	393.8	78.8
24	98.6	401.4	80.3
48	96.0	404.0	80.8
72	87.7	412.3	82.5

80 °C

Time (hours)	Residual Ag⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.03	276.0	224.0	44.8
0.2	240.4	259.6	51.9
0.5	193.4	306.6	61.3
1	181.8	318.2	63.6
2	160.3	339.7	67.9
3	157.9	342.1	68.4
5	145.6	354.4	70.9
16	99.2	400.8	80.2
24	74.1	425.9	85.2
48	6.9	493.1	98.6
72	1.6	498.4	99.7

APPENDIX VI

The uptake of silver ions from solution by raw merino wool. Towards upscale: reducing the concentration of silver nitrate solutions in order to achieve a 100 % uptake of Ag^+ from solution. The concentration of the silver solution and time and temperature of soaking are altered.

50 mg/kg Ag^+ :

50 °C

Time (hours)	Residual Ag^+	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.2	2.9	47.1	94.2
0.5	0.3	49.7	99.4
1	0.1	49.9	99.7
5	0.2	49.8	99.6
16	0.1	49.9	99.8
24	0.0	50.0	99.9
48	0.0	50.0	100.0
72	0.0	50.0	100.0

80 °C

Time (hours)	Residual Ag^+	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.2	3.3	46.7	93.4
0.5	1.5	48.5	96.9
1	0.4	49.6	99.2
5	0.4	49.6	99.2
16	0.0	50.0	99.9
24	0.0	50.0	99.9
48	0.1	49.9	99.8
72	0.0	50.0	100.0

100 mg/kg Ag⁺:**50 °C**

Time (hours)	Residual Ag⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.2	8.0	92.0	92.0
0.5	6.8	93.2	93.2
1	5.4	94.7	94.7
5	3.3	96.7	96.7
16	1.6	98.4	98.4
24	1.0	99.0	99.0
48	0.3	99.7	99.7
72	0.1	99.9	99.9

80 °C

Time (hours)	Residual Ag⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.2	4.3	95.7	95.7
0.5	2.6	97.4	97.4
1	1.6	98.4	98.4
5	0.3	99.7	99.7
16	0.1	99.9	99.9
24	0.0	100.0	100.0
48	0.1	99.9	99.9
72	0.0	100.0	100.0

150 mg/kg Ag⁺:**50 °C**

Time (hours)	Residual Ag⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.2	18.1	131.9	87.9
0.5	13.0	137.0	91.3
1	8.4	141.6	94.4
5	6.5	143.5	95.7
16	5.2	144.9	96.6
24	3.4	146.6	97.8
48	2.9	147.1	98.1
72	0.2	149.8	99.9

80 °C

Time (hours)	Residual Ag⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.2	16.2	133.8	89.2
0.5	14.5	135.5	90.3
1	6.8	143.2	95.5
5	2.4	147.6	98.4
16	0.1	149.9	99.9
24	0.1	149.9	99.9
48	0.1	149.9	99.9
72	0.3	149.7	99.8

APPENDIX VII

The uptake of silver ions from solution by KOH pre-treated merino wool.
Towards upscale: reducing the concentration of silver nitrate solutions in order to achieve a 100 % uptake of Ag^+ from solution. The concentration of the silver solution and time and temperature of soaking are altered.

50 mg/kg Ag^+ :

50 °C

Time (hours)	Residual Ag^+	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.2	0.5	49.6	99.1
0.5	0.4	49.6	99.2
1	0.1	49.9	99.7
5	0.1	49.9	99.7
16	0.1	49.9	99.8
24	0.2	49.8	99.6
48	0.2	49.8	99.6
72	0.2	49.9	99.7

80 °C

Time (hours)	Residual Ag^+	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.2	0.6	49.5	98.9
0.5	0.5	49.5	99.0
1	0.5	49.6	99.1
5	0.1	49.9	99.8
16	0.1	49.9	99.8
24	0.2	49.8	99.6
48	0.2	49.8	99.6
72	0.2	49.8	99.7

100 mg/kg Ag⁺:

50 °C

Time (hours)	Residual Ag⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.2	6.2	93.9	93.9
0.5	3.2	96.8	96.8
1	1.4	98.6	98.6
5	0.6	99.4	99.4
16	0.2	99.8	99.8
24	0.0	100.0	100.0
48	0.1	99.9	99.9
72	0.0	100.0	100.0

80 °C

Time (hours)	Residual Ag⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.2	3.6	96.4	96.4
0.5	0.6	99.4	99.4
1	0.5	99.6	99.6
5	0.1	99.9	99.9
16	0.6	99.5	99.8
24	0.2	99.8	99.8
48	0.1	99.9	99.9
72	0.1	99.9	99.9

150 mg/kg Ag⁺:

50 °C

Time (hours)	Residual Ag⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.2	13.2	136.8	90.1
0.5	10.1	139.9	91.1
1	5.9	144.1	95.6
5	0.5	149.5	98.2
16	0.1	149.9	99.0
24	0.1	149.9	99.9
48	0.1	149.9	100.0
72	0.3	149.7	100.0

80 °C

Time (hours)	Residual Ag⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.2	14.9	135.1	91.2
0.5	13.3	136.7	93.3
1	10.2	139.8	96.1
5	2.6	147.4	99.7
16	2.2	147.8	99.9
24	0.1	149.9	99.9
48	0.0	150.0	99.9
72	0.0	150.0	99.8

APPENDIX VIII

Antimicrobial testing of merino wool - silver nanoparticle composite fibres against *Staphylococcus Aureus* and *E.Coli* bacteria.

Figure 8.1: Antimicrobial testing against *Staphylococcus Aureus* by merino wool composites loaded with:

a-c) 0.5 wt % Ag^+ ; d-f) 1.0 wt % Ag^+ ; g-i) 1.5 wt % Ag^+ . a), d), g): prior to washing; b), e), h): post 3×24 h washing periods; c), f), i): after 13 weeks exposure to natural light.

E. Coli

Figure 8.2: Antimicrobial testing against *E. Coli* by merino wool composites loaded with: a-c) 0.5 wt % Ag⁺; d-f) 1.0 wt % Ag⁺; g-i) 1.5 wt % Ag⁺. a), d), g): prior to washing; b), e), h): post 3 × 24 h washing periods; c), f), i): after 13 weeks exposure to natural light.

Table 8.1: Zones of microbial inhibition by merino wool - silver nanoparticle composites, in their fibre form, against *Staphylococcus aureus* or *E. coli*.

Code	Loading of Ag (wt %)	Sample	Bacteria	Zone of Inhibition (mm)
Fig. 8.1a	0.5	Prior to washing	<i>S. aureus</i>	0.000
Fig. 8.1b	0.5	Post 3 × 24 h washing periods	<i>S. aureus</i>	0.000
Fig. 8.1c	0.5	After 13 weeks exposure to natural light	<i>S. aureus</i>	0.000
Fig. 8.2a	0.5	Prior to washing	<i>E. coli</i>	0.000
Fig. 8.2b	0.5	Post 3 × 24 h washing periods	<i>E. coli</i>	0.000
Fig. 8.2c	0.5	After 13 weeks exposure to natural light	<i>E. coli</i>	0.000
Fig. 8.1d	1.0	Prior to washing	<i>S. aureus</i>	0.005
Fig. 8.1e	1.0	Post 3 × 24 h washing periods	<i>S. aureus</i>	0.005
Fig. 8.1f	1.0	After 13 weeks exposure to natural light	<i>S. aureus</i>	0.000
Fig. 8.2d	1.0	Prior to washing	<i>E. coli</i>	0.005
Fig. 8.2e	1.0	Post 3 × 24 h washing periods	<i>E. coli</i>	0.005
Fig. 8.2f	1.0	After 13 weeks exposure to natural light	<i>E. coli</i>	0.000
Fig. 8.1g	1.5	Prior to washing	<i>S. aureus</i>	0.010
Fig. 8.1h	1.5	Post 3 × 24 h washing periods	<i>S. aureus</i>	0.010
Fig. 8.1i	1.5	After 13 weeks exposure to natural light	<i>S. aureus</i>	0.000
Fig. 8.2g	1.5	Prior to washing	<i>E. coli</i>	0.010
Fig. 8.2h	1.5	Post 3 × 24 h washing periods	<i>E. coli</i>	0.010
Fig. 8.2i	1.5	After 13 weeks exposure to natural light	<i>E. coli</i>	0.000

APPENDIX IX

Hunter ColourQuest CIE values for merino wool - silver chloride nanoparticle composites prepared using 0.1 M HCl pre-treated merino wool, 500 mg/kg Ag⁺ solution and altering reaction temperature and soak time in Ag⁺ solution.

500 mg/kg:

Temperature	Time (hours)	L*	a*	b*	475 nm brightness
Room Temperature	0	75.05	-0.77	4.74	61.51
	0.25	35.79	13.33	5.91	6.23
	0.5	40.15	9.89	4.42	9.66
	1	42.72	9.87	4.71	9.16
	5	45.94	8.64	4.14	13.31
	24	47.93	7.63	4.09	14.80
	48	48.58	6.57	4.19	15.22

Temperature	Time (hours)	L*	a*	b*	475 nm brightness
50 °C	0	75.05	-0.77	4.74	61.51
	0.25	43.08	7.49	3.15	11.83
	0.5	44.86	7.62	3.27	12.95
	1	45.00	7.07	3.55	12.34
	5	45.58	6.81	1.95	13.95
	24	48.78	6.11	1.48	16.52
	48	44.97	5.71	2.32	13.40

Temperature	Time (hours)	L*	a*	b*	475 nm brightness
80 °C	0	75.05	-0.77	4.74	61.51
	0.25	47.00	5.49	3.13	14.54
	0.5	41.33	5.71	2.75	10.98
	1	42.20	6.05	3.67	11.88
	5	44.70	5.64	4.36	12.51
	16	49.62	6.80	13.01	12.66
	24	48.97	6.91	13.84	13.02

APPENDIX X

Hunter ColourQuest CIE values for merino wool - silver chloride nanoparticle composites prepared using 0.1 M HCl pre-treated merino wool, 500 mg/kg Ag⁺ solution and altering reaction temperature and soak time in Ag⁺ solution.

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100 mg/kg:

Temperature	Time (hours)	L*	a*	b*	475 nm brightness
Room Temperature	0.03	62.96	5.19	3.43	29.01
Room Temperature	0.17	62.02	5.34	4.22	28.79
Room Temperature	0.5	60.01	5.52	4.19	28.35
50 °C	0.03	63.95	4.82	4.03	29.83
50 °C	0.17	64.71	4.29	4.53	30.67
50 °C	0.5	65.84	3.78	5.93	33.18
80 °C	0.03	67.32	4.05	4.98	33.30
80 °C	0.17	68.15	3.71	7.05	34.11
80 °C	0.5	69.13	2.67	7.36	34.02

500 mg/kg:

Temperature	Time (hours)	L*	a*	b*	475 nm brightness
Room Temperature	0.03	43.07	9.18	4.45	11.36
Room Temperature	0.17	42.14	9.58	4.51	10.67
Room Temperature	0.5	40.54	9.66	4.52	9.87
50 °C	0.03	46.61	7.67	3.51	14.04
50 °C	0.17	46.74	7.58	3.50	14.09
50 °C	0.5	46.58	7.26	3.41	14.06
80 °C	0.03	48.21	6.95	3.79	15.11
80 °C	0.17	49.55	6.24	4.21	15.19
80 °C	0.5	50.00	6.39	5.50	15.71

APPENDIX XI

Hunter ColourQuest CIE values for merino wool - silver chloride nanoparticle composites prepared using 0.001 M HCl pre-treated merino wool, 500 mg/kg Ag⁺ solution and altering reaction temperature and soak time in Ag⁺ solution.

Temperature	Time (hours)	L*	a*	b*	475 nm brightness
Room Temperature	0	75.05	-0.77	4.74	61.51
	0.25	54.43	16.21	19.88	13.00
	0.5	53.67	14.62	18.89	12.88
	1	50.93	11.95	12.44	12.09
	5	49.86	9.98	12.19	12.96
	24	48.01	10.01	12.37	12.16
	48	47.39	9.62	12.00	11.49

Temperature	Time (hours)	L*	a*	b*	475 nm brightness
50 °C	0	75.05	-0.77	4.74	61.51
	0.25	56.69	15.56	19.79	14.67
	0.5	55.67	11.80	21.18	13.52
	1	57.51	14.09	23.50	13.87
	5	53.88	10.52	20.17	13.24
	24	54.37	6.48	20.08	13.31
	48	53.81	7.24	20.23	13.74

Temperature	Time (hours)	L*	a*	b*	475 nm brightness
80 °C	0	75.05	-0.77	4.74	61.51
	0.25	53.66	6.04	10.25	16.67
	0.5	50.74	6.10	16.43	12.16
	1	51.51	8.10	18.71	11.87
	5	48.18	9.46	25.68	7.92
	24	36.60	7.74	20.55	4.40
	48	37.35	9.50	23.75	4.07

APPENDIX XII

Hunter ColourQuest CIE values for merino wool - silver chloride nanoparticle composites prepared using 0.001 M HCl pre-treated merino wool, 500 mg/kg Ag⁺ solution and altering reaction temperature and soak time in Ag⁺ solution.

100 mg/kg:

Temperature	Time (hours)	L*	a*	b*	475 nm brightness
Room Temperature	0.03	68.71	5.88	7.50	33.23
Room Temperature	0.17	70.84	4.56	6.23	36.07
Room Temperature	0.5	72.47	3.92	5.80	39.53
50 °C	0.03	67.80	3.66	6.73	32.70
50 °C	0.17	70.85	4.11	8.46	38.65
50 °C	0.5	76.03	4.42	9.67	41.64
80 °C	0.03	76.97	2.41	10.44	42.56
80 °C	0.17	70.12	2.09	10.55	38.29
80 °C	0.5	67.58	1.87	9.45	31.84

500 mg/kg:

Temperature	Time (hours)	L*	a*	b*	475 nm brightness
Room Temperature	0.03	53.21	15.12	18.98	12.53
Room Temperature	0.17	53.55	15.16	19.87	12.19
Room Temperature	0.5	53.41	15.23	20.35	11.84
50 °C	0.03	55.50	13.51	22.91	12.60
50 °C	0.17	57.29	12.97	22.14	11.64
50 °C	0.5	58.12	11.82	21.31	12.17
80 °C	0.03	51.97	11.43	23.79	10.32
80 °C	0.17	51.66	11.58	24.01	10.57
80 °C	0.5	51.71	11.88	22.38	10.63

APPENDIX XIII

Hunter ColourQuest CIE values for silver composites of merino wool, prepared using merino wool doped with one of either of the halide ions F⁻, Br⁻ or I⁻.

Merino wool doped with:	Ag⁺ Concentration (mg/kg)	pH	L*	a*	b*	475 nm brightness
F ⁻	100	11	60.68	4.14	15.21	20.32
F ⁻	250	11	61.22	5.52	18.47	19.11
F ⁻	500	11	47.65	10.68	22.86	8.34
F ⁻	100	7	71.53	-0.45	5.76	38.63
F ⁻	250	7	68.39	1.18	11.51	30.44
F ⁻	500	7	55.41	5.72	15.59	15.69
F ⁻	100	3	76.88	-0.47	4.58	47.42
F ⁻	250	3	73.56	0.11	7.91	39.70
F ⁻	500	3	69.32	1.21	12.00	29.96

Merino wool doped with:	Ag⁺ Concentration (mg/kg)	pH	L*	a*	b*	475 nm brightness
Br ⁻	100	11	58.63	3.70	14.25	18.95
Br ⁻	250	11	62.43	4.89	18.36	21.04
Br ⁻	500	11	48.08	11.01	21.66	7.21
Br ⁻	100	7	72.65	4.24	12.19	35.14
Br ⁻	250	7	67.16	6.25	17.01	25.53
Br ⁻	500	7	60.35	7.84	17.31	18.88
Br ⁻	100	3	68.50	1.51	4.41	35.49
Br ⁻	250	3	53.84	7.90	2.50	19.90
Br ⁻	500	3	31.96	8.36	3.53	5.88

Merino wool doped with:	Ag⁺ Concentration (mg/kg)	pH	L*	a*	b*	475 nm brightness
I ⁻	100	11	61.04	3.68	14.79	19.17
I ⁻	250	11	62.96	4.77	18.09	20.90
I ⁻	500	11	43.35	9.96	20.77	6.87
I ⁻	100	7	70.20	-0.39	10.77	33.69
I ⁻	250	7	66.28	1.83	14.15	26.73
I ⁻	500	7	62.08	3.87	16.59	21.05
I ⁻	100	3	81.17	-6.61	12.63	47.21
I ⁻	250	3	78.51	-4.45	17.02	45.44
I ⁻	500	3	77.30	-3.48	27.58	33.27

APPENDIX XIV

The uptake of silver ions from solution by 0.1 M HCl pre-treated merino wool.
The concentration of the silver solution and time and temperature of soaking are altered.

100 mg/kg Ag⁺:

Room Temperature

Time (hours)	Residual Ag ⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.03	3.7	96.3	96.3
0.2	2.7	97.4	97.4
0.5	1.8	98.2	98.2
1	0.7	99.3	99.3
2	0.6	99.5	99.5
3	0.2	99.8	99.8
5	0.2	99.8	99.8
16	0.1	99.9	99.9
24	0.1	100.0	100.0
48	0.1	100.0	100.0
72	0.1	99.9	99.9

50 °C

Time (hours)	Residual Ag ⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.03	2.9	97.1	97.1
0.2	1.6	98.4	98.4
0.5	1.2	98.8	98.8
1	1.2	98.9	98.9
2	0.7	99.3	99.3
3	0.6	99.4	99.4
5	0.5	99.5	99.5
16	0.5	99.6	99.6
24	0.5	99.6	99.6
48	0.5	99.6	99.6
72	0.4	99.6	99.6

80 °C

Time (hours)	Residual Ag⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.03	0.3	99.7	99.7
0.2	0.1	99.9	99.9
0.5	0.1	100.0	100.0
1	0.8	99.2	99.2
2	0.6	99.5	99.5
3	0.5	99.5	99.5
5	0.4	99.6	99.6
16	0.4	99.7	99.7
24	0.3	99.7	99.7
48	0.3	99.7	99.7
72	0.1	99.9	99.9

250 mg/kg Ag⁺:**Room Temperature**

Time (hours)	Residual Ag⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.03	2.0	248.0	99.2
0.2	0.9	249.1	99.6
0.5	0.1	249.9	100.0
1	0.5	249.5	99.8
2	0.6	249.4	99.8
3	0.5	249.5	99.8
5	0.6	249.4	99.8
16	0.6	249.4	99.8
24	0.6	249.4	99.8
48	0.6	249.4	99.8
72	0.8	249.2	99.7

50 °C

Time (hours)	Residual Ag⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.03	21.3	228.7	91.5
0.2	5.2	244.8	97.9
0.5	0.7	249.3	99.7
1	0.6	249.4	99.8
2	0.3	249.7	99.9
3	0.2	249.8	99.9
5	0.1	249.9	100.0
16	0.2	249.8	99.9
24	0.1	249.9	100.0
48	0.0	250.0	100.0
72	0.2	249.8	99.9

80 °C

Time (hours)	Residual Ag⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.03	6.7	243.3	97.3
0.2	6.0	244.0	97.6
0.5	4.3	245.8	98.3
1	2.1	247.9	99.1
2	1.6	248.4	99.4
3	1.8	248.2	99.3
5	0.9	249.1	99.6
16	0.7	249.3	99.7
24	0.4	249.6	99.9
48	0.2	249.8	99.9
72	0.2	249.8	99.9

500 mg/kg Ag⁺:**Room Temperature**

Time (hours)	Residual Ag⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.03	178.0	322.0	64.4
0.2	99.2	400.8	80.2
0.5	73.2	426.8	85.4
1	1.2	498.8	99.8
2	1.0	499.0	99.8
3	1.0	499.0	99.8
5	1.2	498.8	99.8
16	1.2	498.8	99.8
24	1.4	498.6	99.7
48	1.2	498.8	99.8
72	1.4	498.6	99.7

50 °C

Time (hours)	Residual Ag⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.03	69.2	430.8	86.2
0.2	39.6	460.4	92.1
0.5	19.0	481.0	96.2
1	6.4	493.6	98.7
2	4.8	495.2	99.0
3	1.2	498.8	99.8
5	1.0	499.0	99.8
16	0.6	499.4	99.9
24	0.6	499.4	99.9
48	0.4	499.6	99.9
72	0.2	499.8	100.0

80 °C

Time (hours)	Residual Ag⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.03	71.5	428.5	85.7
0.2	55.5	444.5	88.9
0.5	51.0	449.0	89.8
1	49.0	451.0	90.2
2	43.6	456.4	91.3
3	25.6	474.4	94.9
5	22.5	477.5	95.5
16	15.0	485.0	97.0
24	13.5	486.5	97.3
48	7.9	492.1	98.4
72	7.7	492.3	98.5

APPENDIX XV

The uptake of silver ions from solution by 0.001 M HCl pre-treated merino wool.
The concentration of the silver solution and time and temperature of soaking are altered.

100 mg/kg Ag⁺:

Room Temperature

Time (hours)	Residual Ag ⁺	Amount Uptaken	% Uptake
0	0	0	0
0.03	67.9	32.1	32.1
0.2	66.4	33.6	33.6
0.5	57.4	42.6	42.6
1	53.4	46.6	46.6
2	51.9	48.1	48.1
3	49.3	50.7	50.7
5	45.4	54.6	54.6
16	34.7	65.3	65.3
24	31.4	68.6	68.6
48	28.3	71.7	71.7
72	25.1	74.9	74.9

50 °C

Time (hours)	Residual Ag ⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.03	41.4	58.6	58.6
0.2	35.8	64.2	64.2
0.5	34.8	65.2	65.2
1	33.2	66.8	66.8
2	29.6	70.4	70.4
3	26.1	73.9	73.9
5	23.4	76.6	76.6
16	17.9	82.1	82.1
24	14.0	86.0	86.0
48	6.4	93.6	93.6
72	4.9	95.1	95.1

80 °C

Time (hours)	Residual Ag⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.03	57.6	42.4	42.4
0.2	32.2	67.8	67.8
0.5	29.0	71.0	71.0
1	24.5	75.5	75.5
2	12.6	87.4	87.4
3	11.6	88.4	88.4
5	6.8	93.2	93.2
16	0.8	99.2	99.2
24	0.2	99.8	99.8
48	0.0	100.0	100.0
72	0.0	100.0	100.0

250 mg/kg Ag⁺:**Room Temperature**

Time (hours)	Residual Ag⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.03	218.6	31.4	12.6
0.2	190.8	59.2	23.7
0.5	167.8	82.2	32.9
1	146.0	104.0	41.6
2	145.0	105.0	42.0
3	138.6	111.4	44.6
5	131.4	118.6	47.4
16	129.0	121.0	48.4
24	113.4	136.6	54.6
48	102.8	147.2	58.9
72	91.0	159.0	63.6

50 °C

Time (hours)	Residual Ag⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.03	184.6	65.4	26.2
0.2	167.8	82.2	32.9
0.5	152.0	98.0	39.2
1	148.0	102.0	40.8
2	143.6	106.4	42.6
3	135.2	114.8	45.9
5	128.4	121.6	48.6
16	113.0	137.0	54.8
24	94.8	155.2	62.1
48	74.7	175.3	70.0
72	66.0	184.0	73.6

80 °C

Time (hours)	Residual Ag⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.03	189.6	60.4	24.2
0.2	148.0	102.0	40.8
0.5	125.6	124.4	49.8
1	95.9	154.1	61.6
2	79.5	170.5	68.2
3	72.6	177.4	71.0
5	59.4	190.6	76.2
16	22.2	227.8	91.1
24	5.9	244.1	97.6
48	1.0	249.0	99.6
72	0.0	250.0	100.0

500 mg/kg Ag⁺:**Room Temperature**

Time (hours)	Residual Ag⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.03	478.5	21.5	4.3
0.2	435.5	64.5	12.9
0.5	419.5	70.5	14.1
1	415.5	84.5	16.9
2	406.0	94.0	18.8
3	404.5	95.5	19.1
5	398.5	101.5	20.3
16	368.0	132.0	26.4
24	353.0	147.0	29.4
48	334.5	165.5	33.1
72	313.5	186.5	37.3

50 °C

Time (hours)	Residual Ag⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.03	454.5	45.5	9.1
0.2	409.5	90.5	18.1
0.5	391.0	109.0	21.8
1	362.5	137.5	27.5
2	357.5	142.5	28.5
3	350.0	150.0	30.0
5	336.5	163.5	32.7
16	312.0	188.0	37.6
24	288.5	211.5	42.3
48	264.5	235.5	47.1
72	238.0	262.0	52.4

80 °C

Time (hours)	Residual Ag⁺	Amount Uptaken	% Uptake
0	0.0	0.0	0.0
0.03	431.6	68.4	13.7
0.2	378.8	121.2	24.2
0.5	316.0	184.0	36.8
1	300.8	199.2	39.8
2	264.4	235.6	47.1
3	257.6	242.4	48.5
5	203.6	296.4	59.3
16	137.6	362.4	72.5
24	83.4	416.6	83.3
48	28.4	471.6	94.3
72	0.6	499.4	99.9

APPENDIX XVI

Hunter ColourQuest CIE values for merino wool - silver chloride nanoparticle composites prepared using merino wool doped with either sodium chloride, potassium chloride or magnesium chloride, altering the pH of the chlorine solution during soaking.

pH = 3:

Dopant	Ag ⁺ Concentration (mg/kg)	L*	a*	b*	475 nm brightness
NaCl	500	38.66	10.19	5.02	8.98
KCl	500	39.32	10.78	4.92	9.15
MgCl ₂	500	36.87	11.14	4.33	7.22
NaCl	250	54.28	9.97	4.52	19.47
KCl	250	54.77	9.98	4.27	20.06
MgCl ₂	250	54.25	9.41	4.25	19.62
NaCl	100	72.11	3.30	4.00	40.36
KCl	100	69.72	4.37	4.33	39.78
MgCl ₂	100	62.70	2.98	3.37	28.84

pH = 6:

Dopant	Ag ⁺ Concentration (mg/kg)	L*	a*	b*	475 nm brightness
NaCl	500	36.18	10.84	9.24	7.88
KCl	500	36.17	10.92	9.91	7.35
MgCl ₂	500	32.16	11.48	5.87	5.59
NaCl	250	41.35	10.39	7.83	9.38
KCl	250	45.20	11.61	7.96	10.50
MgCl ₂	250	36.66	12.31	8.12	6.98
NaCl	100	48.12	8.82	5.84	14.24
KCl	100	50.49	8.72	5.53	16.04
MgCl ₂	100	52.13	6.78	4.06	18.09

pH = 9:

Dopant	Ag⁺ Concentration (mg/kg)	L*	a*	b*	475 nm brightness
NaCl	500	59.84	5.13	12.39	20.90
KCl	500	58.78	6.34	12.41	20.72
MgCl ₂	500	44.18	13.63	14.86	8.74
NaCl	250	63.75	6.35	16.90	22.23
KCl	250	63.12	6.97	17.75	23.00
MgCl ₂	250	50.50	14.16	11.95	13.44
NaCl	100	68.84	3.69	8.77	32.83
KCl	100	69.21	4.14	9.11	33.67
MgCl ₂	100	55.01	12.38	8.70	18.28

pH = 11:

Dopant	Ag⁺ Concentration (mg/kg)	L*	a*	b*	475 nm brightness
NaCl	500	58.13	4.74	16.99	17.24
KCl	500	57.01	4.88	16.24	16.99
MgCl ₂	500	61.28	6.60	16.10	20.32
NaCl	250	65.75	5.30	19.05	23.01
KCl	250	66.14	6.08	18.96	23.88
MgCl ₂	250	66.03	6.93	16.95	24.41
NaCl	100	71.11	3.38	15.82	30.77
KCl	100	73.22	5.12	13.96	31.49
MgCl ₂	100	67.01	7.22	15.40	26.29

APPENDIX XVII

XPS spectra relating to silver composites of merino wool, prepared using fluoride-doped merino wool as the base material. Comparisons are made between those composites prepared with fibres with an acidic pH and that of an alkaline pH.

Figure 8.3: S 2p XPS spectra for composites of merino wool, prepared using fluoride-doped merino wool as the base material under: a) acidic conditions (pH = 3); and b) alkaline conditions (pH = 11).

Figure 8.4: Ag 3d XPS spectra for composites of merino wool, prepared using fluoride-doped merino wool as the base material under: a) acidic conditions (pH = 3); and b) alkaline conditions (pH = 11).

Figure 8.5: F 1s XPS spectra for composites of merino wool, prepared using fluoride-doped merino wool as the base material under: a) acidic conditions (pH = 3); and b) alkaline conditions (pH = 11).

APPENDIX XVIII

XPS spectra relating to silver composites of merino wool, prepared using chloride-doped merino wool as the base material. Comparisons are made between those composites prepared with fibres with an acidic pH and that of an alkaline pH.

Figure 8.6: S 2p XPS spectra for composites of merino wool, prepared using chloride-doped merino wool as the base material under: a) acidic conditions (pH = 3); and b) alkaline conditions (pH = 11).

Figure 8.7: Ag 3d XPS spectra for composites of merino wool, prepared using chloride-doped merino wool as the base material under: a) acidic conditions (pH = 3); and b) alkaline conditions (pH = 11).

Figure 8.8: Cl 2p XPS spectra for composites of merino wool, prepared using chloride-doped merino wool as the base material under: a) acidic conditions (pH = 3); and b) alkaline conditions (pH = 11).

APPENDIX XIX

XPS spectra relating to silver composites of merino wool, prepared using bromide-doped merino wool as the base material. Comparisons are made between those composites prepared with fibres with an acidic pH and that of an alkaline pH.

Figure 8.9: S 2p XPS spectra for composites of merino wool, prepared using bromide-doped merino wool as the base material under: a) acidic conditions (pH = 3); and b) alkaline conditions (pH = 11).

Figure 8.10: Ag 3d XPS spectra for composites of merino wool, prepared using bromide-doped merino wool as the base material under: a) acidic conditions (pH = 3); and b) alkaline conditions (pH = 11).

Figure 8.11: Br 3d XPS spectra for composites of merino wool, prepared using bromide-doped merino wool as the base material under: a) acidic conditions (pH = 3); and b) alkaline conditions (pH = 11).

APPENDIX XXI

XPS spectra relating to silver composites of merino wool, prepared using iodide-doped merino wool as the base material. Comparisons are made between those composites prepared with fibres with an acidic pH and that of an alkaline pH.

Figure 8.12: S 2p XPS spectra for composites of merino wool, prepared using iodide-doped merino wool as the base material under: a) acidic conditions (pH = 3); and b) alkaline conditions (pH = 11).

Figure 8.13: Ag 3d XPS spectra for composites of merino wool, prepared using iodide-doped merino wool as the base material under: a) acidic conditions (pH = 3); and b) alkaline conditions (pH = 11).

Figure 8.14: I 3d XPS spectra for composites of merino wool, prepared using iodide-doped merino wool as the base material under: a) acidic conditions (pH = 3); and b) alkaline conditions (pH = 11).

APPENDIX XXII

XPS spectra comparing merino wool - silver iodide nanoparticle composites kept in the dark or natural light over a 13 week period.

Figure 8.15: S 2p XPS spectra for a merino wool - silver iodide nanoparticle composite kept in: a) dark; b) natural light for 13 weeks.

Figure 8.16: C 1s XPS spectra for a merino wool - silver iodide nanoparticle composite kept in: a) dark; b) natural light for 13 weeks.

Figure 8.17: Ag 3d XPS spectra for a merino wool - silver iodide nanoparticle composite kept in: a) dark; b) natural light for 13 weeks.

Figure 8.18: N 1s XPS spectra for a merino wool - silver iodide nanoparticle composite kept in: a) dark; b) natural light for 13 weeks.

Figure 8.19: O 1s XPS spectra for a merino wool - silver iodide nanoparticle composite kept in: a) dark; b) natural light for 13 weeks.

Figure 8.20: I 3d XPS spectra for a merino wool - silver iodide nanoparticle composite kept in: a) dark; b) natural light for 13 weeks.