

Enhanced colour, hydrophobicity, UV radiation absorption and antistatic properties of wool fabric multifunctionalised with silver nanoparticles

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Key-words: Silver nanoparticles; wool fabric; UV absorption; antistatic; wash fastness; antibacterial

Abstract

In this study, multifunctional wool fabrics were produced by treating them with silver (Ag) nanoparticles in a single-stage treatment using trisodium citrate (TSC) as a reducing and capping agent. The effects of treatment parameters, such as Ag⁺ concentration, pH, temperature and time on the colour strength, antibacterial and antistatic properties, and UV radiation absorption by the treated fabric were carried out. It was found that the wool fabric treated with Ag nanoparticles formed by using Ag⁺ concentration of less than 1.11% on the weight of wool fibres produced very pale shade. The colour strength and UV radiation absorption capacity of the treated wool fibres increased with an increase in the concentration of Ag⁺, and Ag⁺ to citrate anion ratio, and also with a decrease in the treatment pH. The

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treatment temperature had a great effect on the colour strength of the treated fabrics and the size of Ag nanoparticles. The colour strength increased from 1.59 for the fabric treated at 55 °C to 7.74 for the fabric treated at 95 °C. The surface resistance of the treated wool fibres decreased with an increase in the concentration of Ag⁺, while the colour fastness to washing decreased for the fabric treated at a higher pH. The treated fibres showed excellent antibacterial activity, UV radiation absorption capacity, and also very good antistatic properties along with an excellent colourfastness to washing. Moreover, the developed treatment is highly durable to washing as after 20 washes the treated fibres lost their colour and antibacterial activity only marginally.

Key-words: Ag nanoparticles; colour; hydrophobicity; UV radiation absorption; antistatic; antibacterial

1. Introduction

Wool is a niche natural fibre having many attributes including high warmth, and some levels of stain-resistance, flame retardancy, and antistatic properties [1]. Wool fibres are not only used in floor coverings but also in the manufacturing of clothing and suiting. For these applications, the wool fibres are usually dyed with acid and reactive dyes that produce an effluent containing dyes, surfactants, and other textile auxiliaries. The produced effluent needs to be treated before discharging to watercourses. Therefore, the development of alternative colouration of wool fibre that will not produce coloured effluent is the subject of current research.

In the past decade, various investigations have been carried out to increase the range of applications of wool fibres in technical textiles. One of the attributes desired by the

consumers in wool apparel is antistatic property, as hydrophobic fibres have a tendency to cling to the human body due to the formation of static charge, especially in dry conditions. Wool fibres have recently found application in work-wear, but the natural antistatic properties of wool are not enough to utilise them for some applications, i.e. in work-wear that will be used in electronic industry and service stations. A range of treatments, including electroless coating with metals [2], modification of wool fabrics by thiol-epoxy click chemistry [3], corona discharge plasma treatment followed by covalent binding with a quaternary ammonium compound [4], binding Gemini quaternary ammonium salt to the fibre surface [5], and coating with conducting polymers such as polyaniline and polypyrrole [6,7], have been investigated to enhance the antistatic properties of wool fibres; these have had limited success.

UV radiation levels in some countries including New Zealand are high due to the hole in the ozone layer in that region. This high UV radiation not only damages the wool fibre but also affects human skin causing skin cancer. Therefore, the apparel needs to have UV radiation absorption properties to protect our skin from the harmful effect of UV radiation. A range of treatments including the treatment with hydroxyl benzophenone, 2-(2'-hydroxyaryl)-2H-benzothiazole, and benzotriazole, has been investigated to enhance the UV radiation absorption capacity of wool fabrics [8-10]. It was reported that chlorination treatment increased the UV absorption capacity of wool fibre [11]. A treatment with Ag nanoparticles produced by pomegranate peel extract reduction conferred UV absorption capacity to wool fabric [12].

The high volume of articles published in the area of antibacterial textiles indicates that antimicrobial properties are another important requirement desired by consumers to have in their apparel [13,14]. A range of treatments including quaternary ammonium salt [15], polyhexamethylene biguanide [16], tea extract [17], nanosized copper oxide [18], covalent

binding of thioglycolic acid-capped Ag nanoparticles [19], nanosized N-doped ZnO [20], grafting of a quaternary ammonium polymer to wool fibre surface [21], have been investigated with some successes in making wool fibres antimicrobial. Liu et al. investigated the sol-gel coating of wool fabric with capsaicin, which showed good antibacterial activity against *Escherichia coli*, and the developed treatment was quite durable to washing [22]. The hydantoin-based antibacterial treatment is unsuitable for the dyed wool fibres as the chlorination treatment may degrade the dyes used for the dyeing.

Ag nanoparticles are of interest for multi-functionalisation of textiles as several functionalities, such as antibacterial and antistatic properties, protection from UV radiation, and multi-colouration capability, can be introduced in textiles by a single treatment [14]. Metallic Ag has been used as an antibacterial agent for a long time. Its ions accumulate inside cells and bind to negatively charged components in proteins and nucleic acids of the cell causing their death [23]. Ag nanoparticles release Ag ions, which kill bacteria. Therefore, it is necessary to have free Ag ions constantly in the local microbial environment [24].

Ag nanoparticles are produced from Ag salts by the reduction method using various reducing agents including trisodium citrate, sodium borohydride, and natural polyphenols [14,19,25]. The produced Ag nanoparticles are unstable unless they are properly stabilised with various capping agents. The size and shape of the produced nanoparticles vary depending on the concentration and types of Ag salt, reducing agents and their concentrations, and the capping agents used [19,26]. Depending on the size and geometric shape, Ag nanoparticles can produce various Plasmon bands of all the trichromatic shades, such as yellow, blue and red but the produced colours are usually dull. Various metallic nanoparticles, including gold and Ag, have been investigated to produce a range of shade in wool fabrics [27-29]. However, the penetration of the nanoparticles is limited only to the outer surface or near to the outer surface of the fibres [30,31] resulting in poor durability to

washing, especially when the two-stage method is used for the treatment, i.e. fibres are treated with already-formed Ag nanoparticles. The exhaustion of metal ions into the fibres and in-situ formation of metallic nanoparticles within the fibres by using an appropriate reducing agent with Ag nanoparticles of opposite charges of the fibre by a single-stage treatment may improve the durability to washing. However, it is difficult to absorb both the reducing agent and metal ions into the fibre at the same time. Alternatively, small-sized oppositely charged nanoparticles can be formed and absorbed into the fibre.

Dong and Hinestroza synthesised negatively charged metallic nanoparticles of gold, palladium, and platinum, and deposited them onto positively charged cotton fibres by electrostatic assembly [27] but the fabric made from the treated fibres may show poor rubbing fastness. Kelly and Johnston treated the wool fabric with Ag nanoparticles using TSC as a reducing as well as a stabilising agent by the single-stage treatment [26] but did not form Ag nanoparticles in-situ. They did not investigate the effect of processing conditions on the size and shape of Ag nanoparticles, colour strength of the wool fabric, UV radiation absorption, and antistatic properties. Although the absorption of organic dyes into various fibres depends on the treatment conditions, the effect of treatment pH, time, temperature, and the concentrations of Ag^+ and trisodium citrate reducing agent on the physicochemical properties and colour strength of treated wool fibres was not reported. No published literature reported the minimum and the maximum concentration of Ag^+ can be used to produce colour in the textile fibres and also their colourfastness to washing.

In this work, we investigated the effects of processing parameters, such as the concentration of Ag^+ , Ag^+ to citrate anion ratio, treatment pH, temperature and time on the shade change, colour strength, UV transmission through the fibres, and also the antibacterial and antistatic properties of the wool fabrics are reported here. To the best of our knowledge, no published literature reported the effects of the change of Ag^+ concentration, Ag^+ to citrate

anion ratios, and treatment pH and temperature on the size and geometrical shape of the Ag nanoparticles formed, and also various surface properties of wool fibres, such as hydrophobicity and antistatic properties.

2. Experimental methods

2.1 Materials

A plain woven wool fabric of 150 g/m² containing 26 ends/cm and 26 picks/cm made from an average 20 µm diameter merino wool fibres was purchased South Canterbury Textiles, Timaru, New Zealand. Silver nitrate, trisodium citrate, acetic acid, and sodium acetate were purchased from Sigma-Aldrich Chemicals (USA) and were of analytical reagent grade. Teric GN9 and Sandozin MRN were procured from Clariant Chemicals (Switzerland) and Huntsman Chemicals (USA) respectively. The standard phosphate-free detergent used for the assessment of colourfastness to washing was purchased from the American Association of Textile Chemists and Colorists (AATCC). The antibacterial performance of wool fabric treated with Ag nanoparticles was assessed against *Staphylococcus aureus* (ATCC 6538), *Pseudomonas aeruginosa* (ATCC 25619), and *Klebsiella pneumonia* (ATCC 4352) and they were purchased from Environmental Science Research (Porirua, New Zealand).

2.2. Treatment of wool fabrics with Ag nanoparticles

The treatment of wool fabric with Ag nanoparticles was carried out by changing the concentration of silver nitrate in the bath, at various Ag⁺ to citrate anion ratios, pHs, and temperatures. The spinning oil and dirt present in the wool fabric were removed by scouring

1 g/l Teric GN9 (non-ionic detergent) and 0.25 g/l Sandozin MRN (wetting agent) at 50 °C for 30 min. The treatment of wool fabric with Ag nanoparticles was carried out in an Ahiba Turbomat 1000 laboratory dyeing machine (Datacolor International, Switzerland) using Milli-Q water and materials to liquor ratio of 1:40. The treatment bath was prepared with the required quantity of AgNO₃ solution and 0.25 g/l Sandozin MRN. Then 20 g wool fabric sample was introduced into the bath and the pH was set at 3.5, 5.0 and 6.0 with acetic acid/sodium acetate buffer. The temperature of the bath was then raised to a pre-set temperature at 2 °C/min, the required quantity of reducing agent added and held for 90 min. After the completion of the treatment, the bath was cooled to 45 °C at 2 °C/min, the liquor drained, and the treated fibre samples were rinsed with cold water several times, hydro-extracted and dried.

2.3. Measurement of colour strength, CIE L*, a*, b* values, and colourfastness to washing

The measurements of colour strength of wool fabrics treated with various concentrations of Ag nanoparticles were carried out according to the method mentioned in a published literature [24]. The reflectance values at the appropriate wavelength of maximum absorption of the treated samples were measured using a Datacolor spectrophotometer (Model: DC 550, Datacolor International, Switzerland) interfaced to a personal computer and the colour strength was calculated according to the following equation:

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

where K= absorption coefficient, S = scattering coefficient, and R = reflectance value. The measurement was carried out under illuminant D65 using a 10° standard observer with UV component excluded and specular included. The CIE L*, a*, b* colour values were also measured under illuminant D65, using a 10° standard observer by using Mahlo hand-held

spectrophotometer (Colour Eye 45/0, Mahlo GmbH, Germany). The colour fastness to washing of the treated fabrics was measured according to ISO Test Method 105-C03 1987: *Textiles – Tests for colourfastness – Part C03: Colour fastness to washing: Test 3* by washing in a Gyro wash (Model 415/8) using a phosphate-free standard detergent. In both cases, fastness grades were assessed using the Datacolor DC 550 spectrophotometer.

2.4. Measurement of UV Absorption by wool fabric

The percent transmission of UV light through untreated and Ag nanoparticle-treated wool fabric was measured by a Thermo Scientific UV-VIS Spectrophotometer (Model: Evolution 200, Thermo Fisher Scientific Inc., Waltham, USA) in the diffused reflectance mode. The UV-vis spectrophotometer was equipped with integrated (ISA) and the UV transmission was assessed at a wavelength interval of 5 nm in the 290–400 nm spectral spa.

2.5. Dynamic contact angle

The contact angle of water droplet placed on the untreated and treated fabric surface was measured using a KSV Contact Angle Measurement Apparatus (CAM 100, KSV Instruments, Helsinki, Finland) in dynamic mode. The contact angles were quantified by using the Young-Laplace equation. For each treatment, the contact angle was measured at 5 positions and the average contact angle was reported. The first measurement was taken immediately after placing the drop of water, and subsequent measurements were taken at 30 s intervals until 120 s.

2.6. Assessment of antibacterial activity

The antibacterial properties of wool fabrics treated with Ag nanoparticles at various concentrations were assessed according to AATCC Test Method 147–1999 (*Assessment of Textile Materials: Parallel Streak Method*) against three classes of bacteria namely *Staphylococcus aureus*, *Pseudomonas aeruginosa*, and *Klebsiella pneumoniae*. A broth containing bacteria was placed on a fabric sample of size 25 × 50 mm and after 24 h incubation at 37±2 °C, the zone of inhibition was measured. The nutrient broth was prepared with 5 g/l peptone and 3 g/l beef extracts. The pH of the nutrient broth was adjusted to 6.8 ± 0.1 with 1 N sodium hydroxide solution. The bacterial culture was 100 times diluted and five streaks of bacteria were placed on sterilised agar gel in a Petri dish by using a 4 mm inoculating loop. A specimen was gently placed in intimate contact with agar surface and was incubated for 24 h. After incubation, the growth of bacteria along the side and underneath of the test specimen was observed and the average size of the zone of inhibition was measured.

The antibacterial properties of wool fabrics treated with Ag nanoparticles were also quantitatively assessed against two types of bacteria (*Staphylococcus aureus*, and *Klebsiella pneumoniae*) according to the AATCC Test Method 100-1999: *Antibacterial Finishes on Textile Materials: Assessment of*. In this method, a circular shaped sample of 48±1 mm diameter was placed in a sterile Petri dish. The bacterial culture of the appropriate type (100 times diluted) was transferred to the nutrient by using a 4 mm inoculating loop and was incubated at 37±2 °C for 24 hours. 1.0±0.1 mL inoculum was added to the sample in each petri dish. The same nutrient broth that was used in the AATCC Test Method 147-1999, was also used in this method. The Petri dishes were then incubated at 37±2 °C for 48 h. The number of bacteria in Petri dishes before and after the incubation was measured by a colony counter and the % reduction in bacteria was calculated. This method provides a quantitative assessment of a percentage of the killing of a bacterium.

2.7. Fourier transform infrared spectroscopy (FTIR)

The surface of Ag nanoparticle-treated wool fabrics was characterised by using a PerkinElmer FTIR (System 2000, PerkinElmer Inc., USA) with an attenuated total reflectance (ATR) attachment at a resolution of 4 cm^{-1} in the range from 650 to 4000 cm^{-1} . The ZnSe crystal was used to record the ATR-FTIR spectra. 32 scans were signal-averaged.

2.8. Surface morphologies

The surface morphology of the wool fabrics treated with Ag nanoparticles was investigated by using a field emission scanning electron microscope (SEM) in the back-scattered electron imaging mode. The fabric surfaces were scanned using a JOEL FESEM (Model: JSM-7000f, JEOL Ltd., Tokyo, Japan) at an accelerated voltage of 15 kV without any conductive coating. The elemental analysis of the Ag nanoparticle-treated wool fabrics was carried out by energy-dispersive X-ray spectroscopy (EDX) using the same model of JEOL SEM at 15 kV.

3. Results and discussion

*3.1. Colour produced, and CIE $L^*a^*b^*$ values*

It is necessary to optimise the treatment conditions to produce the deepest colour in the fabric and also to make the colour durable to washing. The effect of pH, treatment temperature, Ag^+ concentration and the ratios of Ag^+ to citrate anion on the shade and colour

strength of the treated wool fabrics was studied. Each of these parameters had a considerable effect on the colour produced and the colour strength of the treated wool fabrics. The colour of the treated fabrics changed from dark brown to light or yellowish-brown with an increase in pH and temperature.

3.1.1. Effect of Ag concentration on colour strength of wool

Fig. 1(a) shows the effect of the applied Ag^+ concentration on the shade produced and colour strength of wool fabric treated with Ag nanoparticles. It is shown that the colour of the fabric turned from light brown to dark brown with an increase in the concentration of Ag^+ . At the lowest concentration of Ag^+ (0.28% owf), hardly any colour was produced and the increase in concentration increased depth and colour strength of the treated fabric. However, the fabric treated with Ag nanoparticles made with the highest concentration of Ag^+ (2.22% owf) had uneven shades with many black spots, which indicates aggregation of Ag nanoparticles on fibre surfaces, suggesting that the depth of colour cannot be increased merely by increasing the concentration of Ag^+ . Similarly, the colour strength of the fabric also increased with an increase in the concentration of Ag^+ , which increases from 1.17 for the fabric treated Ag nanoparticles produced using Ag^+ concentration of 0.28% owf to 3.31 for the Ag^+ concentration of 1.67%. Further increase in Ag^+ concentration produced uneven shade and also only slightly increase the colour strength of the fabric.

Table 1 shows the effect of Ag^+ concentration on the *CIE L*a*b** values. It can be seen the lightness value (L^*) decreased with an increase in the concentration of Ag^+ , i.e. the fabric became darker with the increase in the concentration of Ag^+ . However, the redness of the fabric decreased, and the yellowness of the fabric initially decreased and then started increasing with an increase in the concentration of Ag^+ . The results are consistent with the results observed for the coloration of acrylic fibres with Ag nanoparticles [14]. The colour,

shape and the size of Ag nanoparticles are governed by the concentration of Ag^+ in solution and the size of nanoparticles increases with an increase in the concentration of Ag^+ ions [26,27]. The increase in the concentration of Ag^+ increases the concentration of Ag nanoparticles and therefore the colour strength of the treated fabric increased with an increase in the concentration of Ag^+ .

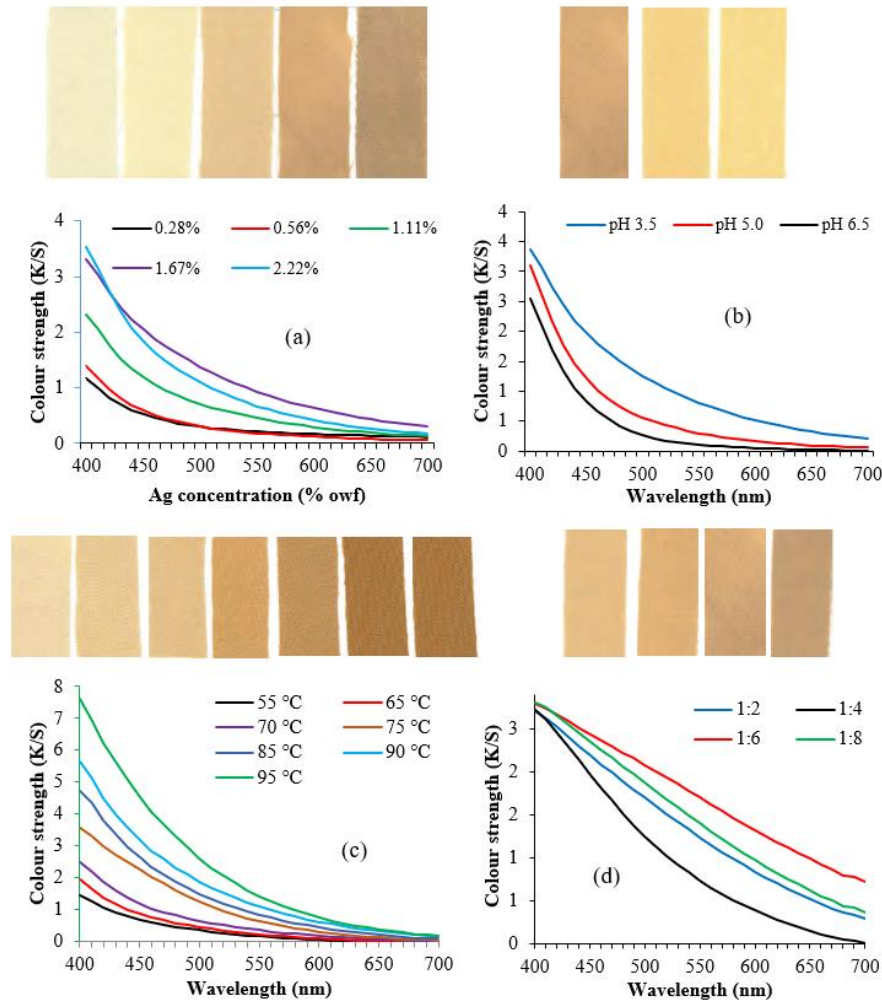


Fig. 1. Effect of Ag concentration (top left), pH (top right), treatment temperature (bottom left), and Ag to TSC ratio (bottom right) on the colour strength of wool fabrics treated with in-situ formed Ag nanoparticles at 75 °C for 90 min.

3.1.2. Effect of pH on colour strength of wool

The effect of pH is very important as the pH has an effect on the adsorption of Ag^+ into wool fibres and also on the size of the formed Ag nanoparticles. The effect of pH on colour strength was investigated at three pH conditions, 3.5, 5.0 and 6.0. No treatment was carried out in alkaline conditions as wool fibres are damaged at high pH, especially at high temperatures. Fig. 1(b) shows the effect of pH on the depth of colour and also the colour strength of Ag-nanoparticle treated wool fabrics. The fabrics treated at pHs below 5 showed higher colour strength compared to the fabrics treated at pH above 5. The colour strength increased with a decrease in pH. The highest colour strength (3.37) was shown by the fabric treated at pH 3.5, while the lowest colour strength (2.54) was shown by the fabric treated at pH 6.0.

Table 1 shows that the value of L^* increased with an increase in the treatment pH, i.e. the fabrics became lighter in colour with an increase in pH. For the fabric treated at pH 3.5 the value of L^* was 64.3, which increased to 83.18 for the wool fabric treated at pH 6.0 with the same concentration of Ag^+ . On the other hand, the redness of the fabric decreased, and the yellowness increased with an increase in the pH, which is consistent with published literature [14].

It is reported that the reduction of the Ag precursor (Ag^+) to Ag nanoparticle is promoted with an increase in the pH [34]. They also found that at low pH mainly triangle or polygon-shaped Ag nanoparticles were formed, but at high pH, spherical and rod-like nanoparticles were formed. Zhang et al. found only spherical shaped Ag nanoparticles are formed at pH 2.5 [35]. However, we found that the fabric sample treated at pH 3.5 showed the highest colour strength. The isoelectric point of wool fibre in water is in between 4.5 and 5.0, i.e. below the isoelectric point wool fibre is cationic and above it wool fibre is anionic. Simpson and Mason found that wool fibres absorbed 0.6 mM/g of Ag at pH 3.0 and at 50 °C compared to almost 1.0 mM/g were absorbed in pH 6.0 [36]. In this work, we found that the highest colour

strength was produced when the treatment was carried out at pH 3.5. It has also been reported that the surfaces of TSC-stabilised Ag nanoparticles are anionic [19]. Therefore, it can be assumed that the majority of the applied Ag^+ , as well as Ag nanoparticles, were adsorbed into the wool fibre at this pH.

3.1.3. Effect of temperature on colour strength of wool

It is necessary to study the effect of temperature as the adsorption of Ag^+ ions into wool fibre as well as the size and shape of the formed Ag nanoparticles are influenced by temperature. In this work, we varied the treatment temperature from 55 to 95 °C while keeping the treatment pH, the concentration of Ag^+ , the Ag^+ to citrate anion ratio, and the treatment time constant. It is evident that the treatment temperature had a large effect on the shade produced (Fig. 1c) and also on the colour strength of the treated fabric, which increased with the increasing temperature. The deepest colour was produced by the fabric treated at 90 °C and the lowest colour strength was produced by the fabric treated at the lowest temperature (55 °C). The colour strength increased from 1.59 for the fabric treated at 55 °C to 7.74 for the fabric treated at 95 °C. Similarly, the value of L^* decreased with an increase in the treatment temperature. The value of L^* for the fabric treated at 55 °C was 76.68, which decreased to 55.14 for the fabric treated at 95 °C. It is generally accepted that the nucleation of Ag^+ is favoured by high temperature while low temperature promotes the growth of nanoparticles, i.e. the nanoparticles grow better and larger at lower temperatures [37]. The nucleation rate constant increases and the growth rate constant of Ag nanoparticles decreases with an increase in reaction temperature. The increase in the color strength of wool fibers treated with Ag nanoparticles at high temperatures suggests that the increase in temperature considerably decreased the size of the formed Ag nanoparticle and they absorbed into wool

fibre, especially at temperatures higher than 75 °C. The results achieved are consistent with the results published by other researchers [35,38].

3.1.4 Effect of Ag⁺ to citrate anion ratio on colour strength of wool

To observe the effect of Ag⁺ to citrate anion ratio on the shade and colour strength of the treated fabrics, the Ag⁺ to citrate anion ratio was varied from 1:2 to 1:8. No ratios lower than 1:2 were tested as ratios lower than 1:2 produce unstable Ag nanoparticles [19]. The concentration of Ag⁺, pH, temperature and time were kept fixed at 1.67% owf, 3.5, 75 °C and 90 min respectively. The colour of the wool fabric turned from pale yellow to dark brown with an increase in the ratio of Ag⁺ to citrate anion. However, the increase in the Ag⁺ to citrate anion ratio showed a comparatively lower effect than the effect shown by the change of Ag⁺ concentration, pH and temperature. The colour strength of the treated fabric increased slightly, from 3.0 for an Ag⁺ to citrate anion ratio of 1:2 to 3.54 for an Ag⁺ to citrate anion ratio of 1:8 (Fig. 1d).

It can be seen that the value of L^* of the treated wool fabrics decreased with an increase in the Ag⁺ to citrate anion ratio (Table 1), i.e., the treated fabrics became slightly darker with an increase in the Ag⁺ to citrate anion ratio. Our previous work reported that in the case of colouration of acrylic fibres with in-situ formed Ag nanoparticles, the change in Ag⁺ to citrate anion ratio showed a greater effect compared to the effect observed for the colouration of wool fibres with Ag nanoparticles [14]. The optimum Ag⁺ to citrate anion ratio is 1:6 as beyond that level little increase in the colour strength was achieved. The effect of the Ag⁺ to citrate anion ratio was less pronounced during this treatment of wool fabric than it was in our previous work that investigated the colouration of acrylic fibres with in-situ formed Ag nanoparticles.

Table 1. CIE $L^*a^*b^*$ values and colourfastness to washing of wool fabrics multi-functionalised with Ag nanoparticles at various conditions.

| Sample ID | Conc. of Ag ⁺ (% owf) | Time (min) | Temp . (°C) | Ag ⁺ to citrate ratio | pH | CIE | | | Colour strength (K/S) | Colour fastness to washing grades |
|--|----------------------------------|------------|-------------|----------------------------------|-----|------------|------------|------------|-----------------------|-----------------------------------|
| | | | | | | L* | a* | b* | | |
| <u>At various Ag⁺ conc.</u> | | | | | | | | | | |
| A1 | 0.28 | 90 | 75 | 1:4 | 3.5 | 83.18±0.27 | 2.96±0.22 | 34.57±0.07 | 1.17 | 2-3 |
| A2 | 0.56 | 90 | 75 | 1:4 | 3.5 | 82.81±33 | 3.00±0.21 | 21.61±0.09 | 1.39 | 3 |
| A3 | 1.11 | 90 | 75 | 1:4 | 3.5 | 73.06±0.07 | 5.76±0.06 | 23.09±0.05 | 2.32 | 4 |
| A4 | 1.67 | 90 | 75 | 1:4 | 3.5 | 66.95±0.53 | 7.74±0.09 | 25.8±0.25 | 3.31 | 4 |
| A5 | 2.22 | 90 | 75 | 1:4 | 3.5 | 62.61±0.16 | 7.14±0.02 | 20.58±0.17 | 3.52 | 4 |
| <u>At different Ag⁺ to citrate anion ratios</u> | | | | | | | | | | |
| B1 | 1.67 | 90 | 75 | 1:2 | 3.5 | 71.37±0.43 | 7.53±0.01 | 26.96±0.27 | 3.00 | 4 |
| B2 | 1.67 | 90 | 75 | 1:4 | 3.5 | 65.61±0.22 | 10.24±0.07 | 29.92±0.13 | 3.23 | 4 |
| B3 | 1.67 | 90 | 75 | 1:6 | 3.5 | 64.55±0.44 | 7.83±0.01 | 22.87±0.25 | 3.44 | 4 |
| B4 | 1.67 | 90 | 75 | 1:8 | 3.5 | 69.04±0.33 | 8.27±0.04 | 27.64±0.04 | 3.54 | 4 |
| <u>At different pHs</u> | | | | | | | | | | |
| C1 | 1.67 | 90 | 75 | 1:4 | 3.5 | 64.31±0.12 | 10.23±0.08 | 29.70±0.11 | 3.37 | 4 |
| C2 | 1.67 | 90 | 75 | 1:4 | 5.0 | 77.51±0.14 | 6.09±0.11 | 30.58±11 | 3.11 | 3-4 |
| C3 | 1.67 | 90 | 75 | 1:4 | 6.5 | 83.18±0.27 | 2.96±0.22 | 34.57±0.07 | 2.54 | 3 |
| <u>At different temperatures</u> | | | | | | | | | | |
| D1 | 1.67 | 90 | 55 | 1:4 | 3.5 | 76.68±0.55 | 5.47±0.03 | 21.26±23 | 1.59 | 3-4 |
| D2 | 1.67 | 90 | 65 | 1:4 | 3.5 | 75.64±0.22 | 5.58±0.11 | 23.47±0.05 | 2.07 | 3-4 |
| D3 | 1.67 | 90 | 70 | 1:4 | 3.5 | 71.62±0.31 | 6.18±0.04 | 24.56±0.06 | 2.62 | 3-4 |
| D4 | 1.67 | 90 | 75 | 1:4 | 3.5 | 65.61±0.22 | 10.24±0.07 | 29.92±0.13 | 3.70 | 4 |
| D5 | 1.67 | 90 | 85 | 1:4 | 3.5 | 62.23±0.22 | 9.44±0.08 | 27.86±0.22 | 4.88 | 4 |
| D6 | 1.67 | 90 | 90 | 1:4 | 3.5 | 59.38±0.19 | 9.53±0.05 | 26.99±0.06 | 5.80 | 4 |
| D7 | 1.67 | 90 | 95 | 1:4 | 3.5 | 55.14±0.21 | 11.90±0.11 | 30.21±0.12 | 7.74 | 4 |

3.1.5. Colourfastness to washing

The colourfastness to washing grades of wool fabrics treated with Ag nanoparticles using various concentrations of Ag⁺, Ag⁺ to citrate anion ratios, pHs and temperatures are shown in Table 1. The colourfastness to washing was excellent as the colourfastness grade was 4 when the Ag⁺ concentration is 1.67% owf and above, the Ag⁺ to citrate anion ratio is 1:2 and above, the treatment pH is 3.5, and the treatment temperature is 75 °C or higher. Overall, the

colourfastness to washing of the coloured wool fabrics produced by in situ formed Ag nanoparticles was reasonably good. It is known that Ag nanoparticles release Ag^+ ions in an aqueous media and therefore fastness of the treatment to washing may decrease with successive washing [33] due to the loss of Ag^+ ions and Ag nanoparticles. It can be expected that most of the Ag nanoparticles adsorbed onto the surface of wool fibres would be released during washing, especially for the treatment carried out at high pH. Hence, the wool fabric treated at pH 3.5 showed better fastness to washing compared to the wool fabrics treated at pH 5.0 and 6.0.

The change in Ag^+ to citrate anion ratio did not change the colourfastness to washing as it is known that the ratio of 1:2 and above produced stable Ag nanoparticles. Similarly, the fabrics treated at 70 °C and below showed slightly poorer washing fastness than the fabrics treated at 75 °C and above. The excellent wash fastness shown by the Ag nanoparticle-treated fabrics suggests that in-situ formed anionic TSC-stabilised Ag nanoparticles were absorbed into cationic wool fibres rather than adsorbed onto the surface of fibre, resulting in enhanced durability of the treatment to washing.

3.2. Elemental analysis

Table 2 shows EDX elemental analysis of C, N, O, S, and Ag in untreated and multi-functionalised wool fabrics with Ag nanoparticles using various concentrations of Ag. For the untreated wool fabric, the elemental composition of C, N, O, and S was 47.48, 20.60, 29.25 and 2.67% respectively. As expected, the Ag content for the untreated wool fabric was zero. However, the elemental content of C, N, O, and S changed for the wool fabrics treated with various concentrations of Ag. The Ag content of wool fabrics increased with an increase in the concentration of Ag. The Ag content of the fabrics proportionally increased with an

increase in the concentration of Ag. The elemental mapping of C, N, O, S, and Ag of wool fabrics treated with Ag nanoparticles formed by using various concentrations of Ag are shown in Fig. S1 (Supplementary Content).

Table 2. EDX elemental analysis of wool fabric treated with various concentrations of Ag⁺ to form Ag nanoparticles in the fibre.

| Concentration of Ag ⁺ (% owf) | Mass of elements (%) | | | | |
|---|----------------------|-------|-------|------|------|
| | C | N | O | S | Ag |
| 0 | 47.48 | 20.60 | 29.25 | 2.67 | 0 |
| 0.55 | 46.78 | 19.39 | 29.31 | 2.93 | 1.59 |
| 1.11 | 45.79 | 18.89 | 29.79 | 3.14 | 2.39 |
| 1.67 | 44.19 | 19.43 | 30.03 | 3.37 | 2.98 |
| 2.22 | 44.92 | 18.61 | 29.24 | 3.76 | 3.47 |

3.3. UV radiation absorption

The level of damage to human skin caused by solar UV radiation depends on the levels and intensity of the radiation. The high UV transmission through the fabric means that most of the UV radiation will reach our skin through the apparel. Therefore, a fabric having no or low UV transmission through the fabric is beneficial to protect human skin from the damaging effect of UV radiation, which can cause skin cancer. Fig. 2 shows the effect of Ag⁺ concentration, Ag⁺ to citrate anion ratio, treatment temperature, and the pH on the UV transmission through the treated wool fabrics. It is evident that the untreated wool fabric had poor UV protection as the transmission of UV through the fabric was high. On the other hand, the wool fabric samples treated with Ag nanoparticles had much lower UV

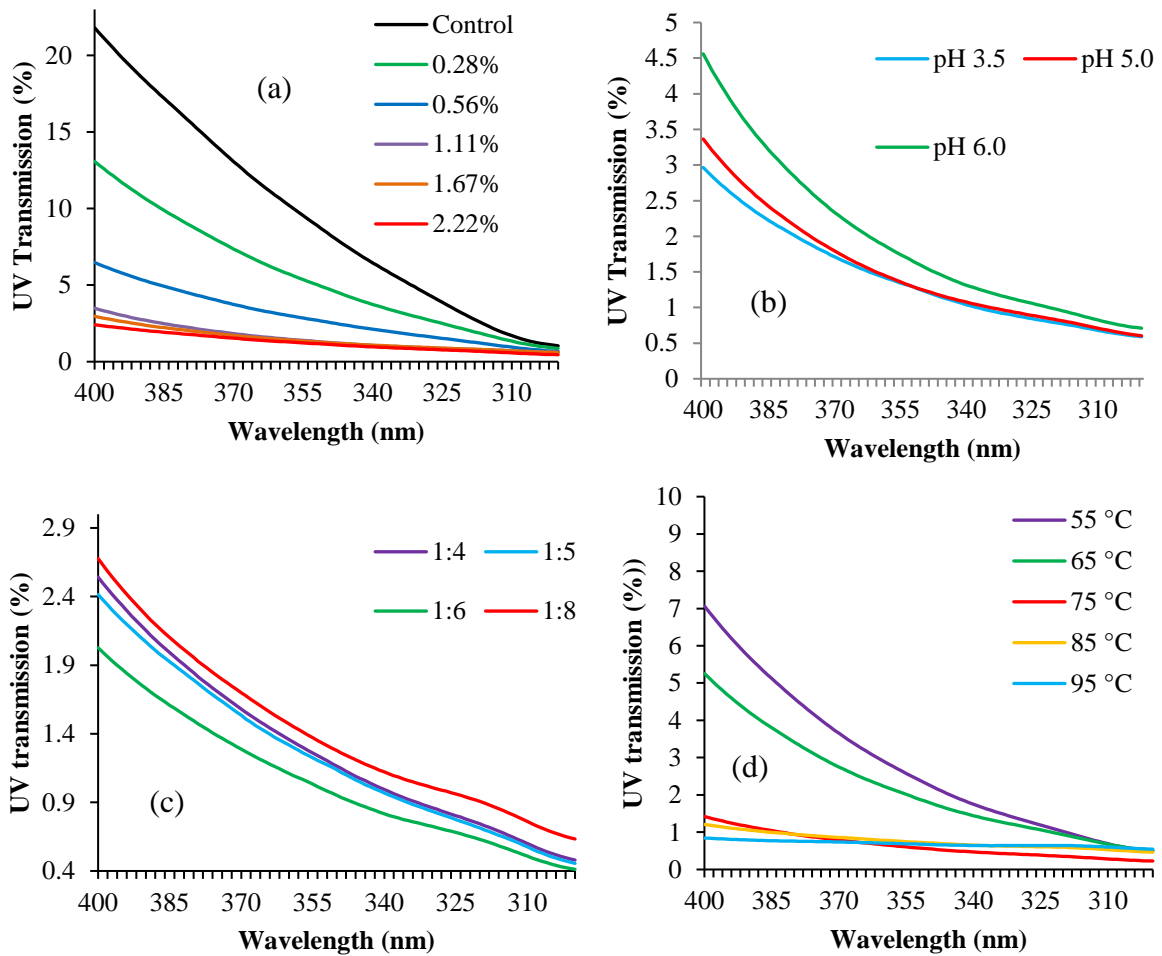


Fig. 2. Effect of Ag concentration (top left), pH (top right), Ag to TSC ratio (bottom left), and treatment temperature (bottom right) on the UV transmission through the Ag nanoparticle-treated wool fabrics.

transmissions, inferring excellent UV radiation absorption. The increase in the concentration of Ag increased the UV radiation absorption by the treated fabrics as the surface coverage by Ag nanoparticles increases with an increase in the concentration of Ag. The untreated wool fibres show high transmission of UV-B (290–320 nm), which was considerably decreased with the treatment with Ag nanoparticles. At 320 nm, the undyed wool fabrics had a UV transmission of 3.72%, which reduced to 0.71% for the fabrics treated with 2.22% Ag⁺ (Fig. 2a). The highest reduction in UV transmission was observed for the applied Ag⁺ concentration of 2.22%; at that concentration, the UV transmission reduced to 0.71%.

Similarly, UV-A (320–400 nm) transmission also decreased with an increase in the applied concentration of Ag nanoparticles. At 360 nm, the UV-A transmission reduced from 10.64% to 1.31%. The decrease in the treatment pH also showed a positive effect on the reduction of UV transmission through the wool fabric (Fig. 2b). The UV transmission at 320 and 360 nm reduced from 0.98 and 1.91% respectively for the fabric treated at pH 6.0 to 0.79 and 1.45% respectively for the fabric treated at pH 3.5.

It is also evident that the UV-A and UV-B transmission decreased with an increase in the Ag^+ to citrate anion ratios. The wool fabric treated with 1.67% Ag^+ using Ag^+ to citrate anion ratio of 1:2 showed 0.74 and 1.36% of UV transmission through wool fabric at 320 and 360 nm respectively which decreased to 0.63 and 1.11% respectively for the fabric treated with Ag nanoparticles using Ag^+ to citrate anion ratio 1:6 (Fig. 2c). However, further increasing the Ag^+ to citrate anion ratio increased the UV transmission through the fabric. Fig. 2d showed the effect of the treatment temperature on the UV transmission through wool fabric treated with 1.67% owf Ag^+ using Ag^+ to citrate anion ratio of 1:6. The wool fabric treated at 55 °C had high UV transmission but the wool fabrics treated at 75 °C and above showed very low transmission of UV radiation providing excellent protection against solar UV radiation. The UV transmission at 320 nm decreased from 3.05% for the fabric treated at 55 °C to 0.91% for the fabric sample treated at 95 °C. Similarly, the UV transmission at 360 nm decreased from 10.64% for the fabric treated at 55 °C to 1.45% for the fabric treated at 95 °C. The results obtained show that the processing parameters have great effects on UV transmission through the wool fabric treated with in situ formed Ag nanoparticles.

3.4. Antibacterial properties

The antibacterial activity of Ag nanoparticle-treated textiles against a wide range of Gram-positive and Gram-negative bacteria is quite well known, therefore, in this work we mainly focused on the durability of the antibacterial activity after multiple washing [36,37]. The fabrics were washed according to the Woolmark 7A wash protocol for 5, 10, 15 and 20 washing cycles (wet-on-wet basis without drying in-between washing cycles); this test is more severe than domestic washing. Table S1 (Supplementary content) shows the antibacterial activity of untreated and Ag nanoparticle-treated wool fabric after 20 washes against three types of bacteria, *Staphylococcus aureus*, *Klebsiella pneumoniae*, and *Pseudomonas aeruginosa* evaluated according to the AATCC Test Method 147-1999. As expected, the control fabric did not show at all any antibacterial activity against any type of bacteria and no zone of inhibition was observed. Moreover, very strong growth of bacteria was observed underneath the control fabric. On the other hand, the Ag nanoparticle-treated showed moderate to strong antibacterial activity against the tested bacteria. The best antibacterial activity was observed against *Staphylococcus aureus* and *Pseudomonas aeruginosa*, and moderate activity against *Klebsiella pneumoniae*. No growth of bacteria was observed under the treated fabric. In the case of *Staphylococcus aureus* and *Pseudomonas aeruginosa*, the average size of the zone of inhibition was 7.5 and 3 mm respectively but in the case of the size of zone inhibition dropped to 0.5 mm only.

Fig. 3 shows the durability of the antibacterial activity to multiple washing of wool fabrics multi-functionalised with Ag nanoparticles using 1.67% owf Ag⁺ against *Staphylococcus aureus* and *Klebsiella pneumoniae* assessed according to the AATCC Test Method 100-1998. It is evident that the treated fabrics showed excellent antibacterial activity against both types of bacteria and the antimicrobial activity was retained even after 20 washes. Before washing, the treated fabrics showed 99.1 and 98.4% killing of *Staphylococcus aureus* and *Klebsiella pneumoniae* respectively. The corresponding values for the 20 washes were 98.9 and 98.2%

respectively. Only marginal reduction of antibacterial activity was observed after 20 cycles of washing (equivalent to 80 domestic washings), indicating excellent durability of the treatment. Textile fabrics treated with Ag nanoparticles, that are unbound or loosely bound to the fibre surface by a resin, could be dangerous because of the possible release of Ag⁺ ions and Ag nanoparticles into the environment during washing [38]. This was not the case for the wool fibre/fabrics used in this study as the Ag nanoparticles were formed in situ and therefore the treated fabric had better durability to washing when compared to non-substantive textiles treated with Ag nanoparticles.

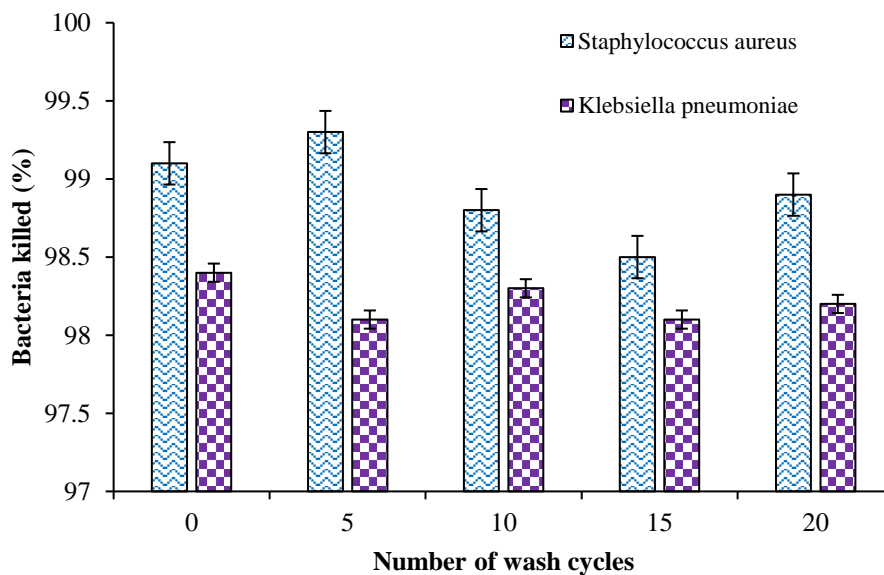


Fig. 3. The effect of multiple washing on the antibacterial activity of wool fabrics treated with in situ formed Ag nanoparticles using 1.67% owf Ag, Ag to TSC ratio 1:4, pH 3.5, and 75 °C for 90 min.

3.6. Surface resistivity of treated wool fabrics

The surface resistivity of wool fabrics treated with Ag nanoparticle using various concentrations of Ag⁺ is shown in Table 3. The surface resistance shown by the untreated

wool fabric was very high (13.6×10^{11} Ohm/cm), whereas the wool fabrics treated with in situ formed Ag nanoparticles had considerably lower surface charges. The surface resistivity of the wool fabrics decreased with an increase in the applied Ag^+ concentration. The surface resistivity decreased from 12×10^{11} Ohm/cm for the control to 3.3×10^{11} Ohm/cm for the wool fabric treated with 0.56% owf Ag^+ . Increasing the Ag^+ concentration further decreased the surface resistivity. The lowest surface resistivity was shown by the fabric treated with 1.67% owf Ag^+ . A further increase in the Ag^+ concentration (to 2.22%) slightly increased the surface resistance; this was likely to have been caused by uneven treatment.

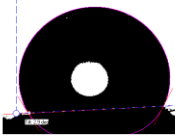
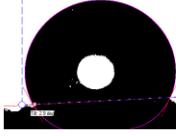
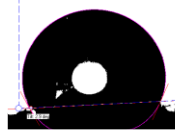
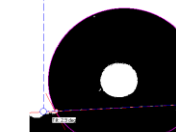
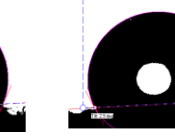



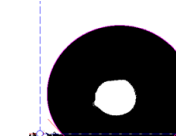


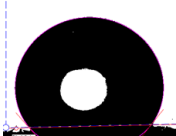
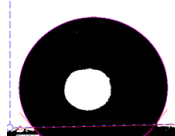




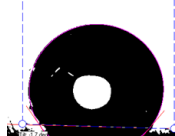
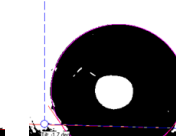

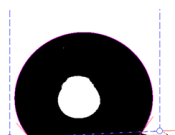
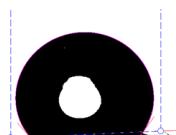

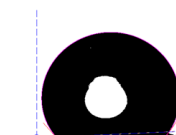

Table 3. Antistatic properties of wool fabric treated with various concentration of silver nanoparticles.

| Concentration of Ag^+ (% owf) | Surface resistance ($\times 10^{11}$ Ohm/cm) | | | | | |
|--|---|--------|--------|--------|--------|---------|
| | Test 1 | Test 2 | Test 3 | Test 4 | Test 5 | Average |
| 0 | 11.0 | 13.4 | 13.0 | 13.9 | 16.5 | 13.6 |
| 0.56 | 3.24 | 3.14 | 3.23 | 3.0 | 3.65 | 3.3 |
| 1.11 | 2.86 | 2.74 | 2.78 | 2.72 | 2.87 | 2.8 |
| 1.67 | 2.25 | 2.43 | 2.46 | 2.37 | 2.5 | 2.4 |
| 2.22 | 2.62 | 2.48 | 2.47 | 2.34 | 2.42 | 2.5 |

3.7 Dynamic contact angle

It is known that the nano-indentation and the deposition of micro to nano-sized particles on the surface of textile fibres considerably increase their surface hydrophobicity and can

Table 4. The dynamic contact angle of untreated and Ag nanoparticle-treated wool fabrics at various times.

| Concentration of Ag ⁺ (% owf). | Average contact angle (°) at | | | | |
|--|---|---|---|--|---|
| | 0 s | 30 s | 60 s | 90 s | 120 s |
| 0 |  119.5 |  117.3 |  116.6 |  116.0 |  115.9 |
| 0.56 |  129.53 |  128.53 |  126.9 |  124.6 |  123.1 |
| 1.11 |  131.29 |  131.10 |  131.0 |  130.8 |  130.7 |
| 1.67 |  133.10 |  132.9 |  132.95 |  133.05 |  133.10 |
| 2.22 |  131.49 |  131.49 |  131.35 |  131.15 |  131.10 |

make the textiles super-hydrophobic [39-41]. Therefore, it was envisaged that the deposition of Ag nanoparticles onto wool fabric may enhance the hydrophobicity of the treated fabric.

Table 4 shows the dynamic contact angle of wool fabric surfaces at various time intervals. The low contact angle means the fabric is hydrophilic and high contact angle means the

fabric is hydrophobic. The untreated fabric showed some levels of hydrophobicity because of the presence of 18-methyleicosanoic acid (18-MEA) which is bonded to the fibre surface through thioester bonds. 18-MEA forms a polyethylene-like layer on the surface of the fibre, which provides it some hydrophobicity. The untreated wool fabric surface showed a contact angle of 119.5° at 0 s, which gradually decreased to 115.9° after 120 s. The wool fabric treated with Ag nanoparticles using an Ag^+ concentration of 0.56% owf showed better hydrophobicity (higher contact angle, 129.3°) than the untreated fabric but the contact angle slowly decreased to 123.1° after 120 s. The contact angle and the stability of the hydrophobicity increased after a further increase of the Ag^+ concentration as the contact angle at 0 s shown by the fabric treated with Ag nanoparticles using Ag^+ concentration of 1.11% owf was 131.29 which reduced to only 130.7 after 120 s of placing the water droplet. The highest contact angle was shown by the fabric treated using 1.67% owf Ag^+ (133.10°), which was stable and did not diminish even after 120 s.

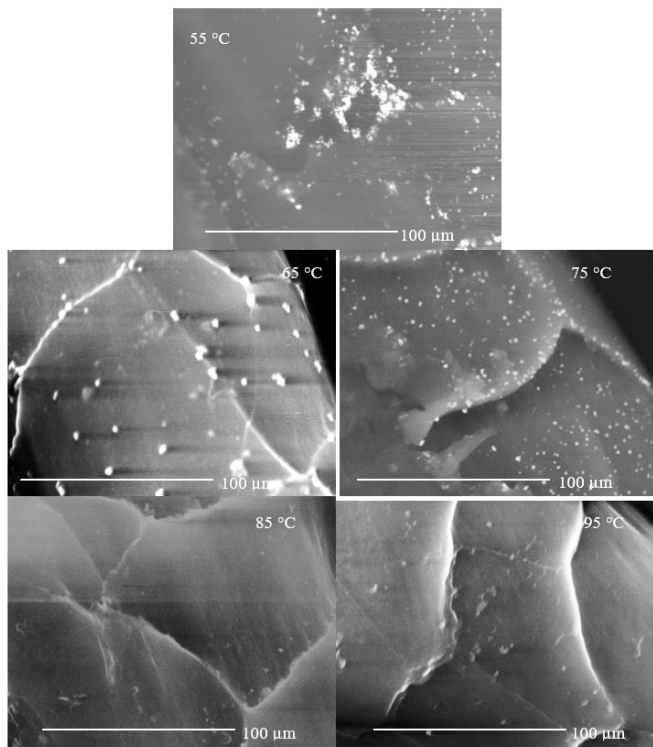


Fig. 4. SEM micrographs wool fabric treated with silver nanoparticles using 1.67% owf Ag and Ag to TSC ratio 1:4 at pH 3.5 at 55, 65, 75, 85 and 95 °C.

3.8. Surface morphologies

The surfaces of wool fabrics treated with 1.67% owf Ag^+ at 55, 65, 75, 85 and 95 °C was characterised by SEM to observe the assembly of Ag nanoparticles formed on the fibre surfaces, and also to look at the shape and size of the Ag nanoparticles formed. Fig. 4 shows the SEM micrographs of the surface of wool fabrics treated at various temperatures. The treatment temperature showed an interesting effect on the shape and size of Ag nanoparticles produced. The surface of wool fabric treated at 55 °C showed large agglomeration of Ag nanoparticles but the size of the formed Ag nanoparticles was small. Increasing the treatment temperature to 65 °C considerably reduced the agglomeration of Ag nanoparticles and the size of the nanoparticles also decreased. However, for the fabrics treated at 75 °C, no agglomeration of Ag nanoparticles was evident, and the nanoparticles were uniformly distributed on the surface of the fibre. The size of Ag nanoparticles decreased with this temperature increase, and it looks like this was also the case for treatment temperatures of 85 °C and above as very few nanoparticles are shown on the surface of these fibres. It is probable that at these higher temperatures most of the Ag nanoparticles absorbed into the fibre.

Fig. 5 shows the SEM micrographs of the surface of wool fabrics treated with Ag nanoparticles using 1.11, 1.67, and 2.22% owf Ag^+ . It can be seen that in the case of Ag^+ concentration of 1.11% owf, the number of nanoparticles per unit area of the Ag nanoparticles is quite low and the size of the nanoparticles are comparatively big. The nanoparticles are mostly cube-shaped and the length and width of the nanoparticles are 300 to 375 nm. Increasing the concentration of Ag^+ to 1.67% produced much smaller (47 to 80 nm), sphere-shaped, Ag nanoparticles. However, further increasing the concentration of Ag did not

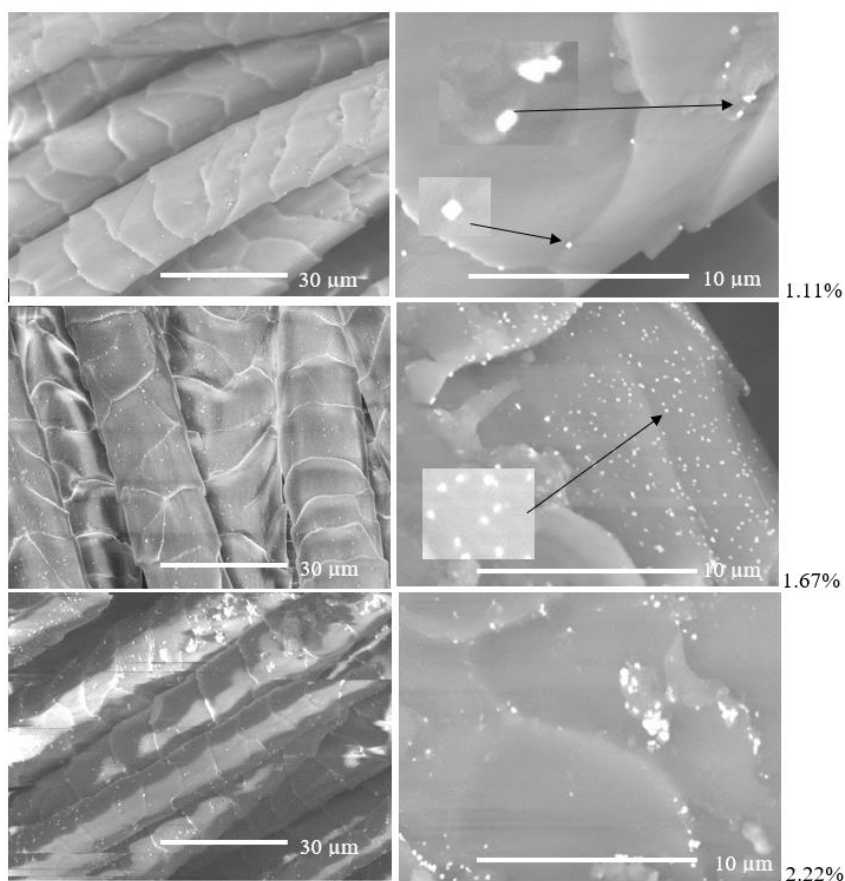


Fig. 5. SEM micrographs of wool fabrics treated with Ag nanoparticles using Ag concentrations of 1.11, 1.67 and 2.22% owf using Ag^+ to citrate anion ratio of 1:4.

change the size or shape of the Ag nanoparticles but did cause agglomeration. A few micron-sized aggregates of Ag nanoparticles are visible on the surface of fibre from the fabric treated with 2.22% owf Ag^+ ; these aggregates produced black spots and uneven colour on the fabric as shown in Fig. 1(a). Therefore, it is evident that the intensity of the colour of wool fabric formed by Ag nanoparticle treatment cannot be increased simply by increasing the concentration of Ag^+ as increasing the concentration of Ag^+ beyond 1.67% owf forms uneven colour shade due to the agglomeration of the Ag nanoparticles. Therefore, for the treatment method used in this study, 1.67% owf Ag is the optimum concentration for the colouration of wool fabric by Ag nanoparticles.

3.9. ATR-FTIR

The ATR-FTIR spectral analysis was used to find out the interactions between the fibre and the Ag nanoparticles. The spectrum of wool fibre shows typical IR bands at 1039, 1230, 1383, 1446, 1514, 1633, and 3254 cm^{-1} . The IR bands at 1227, 1350, 1540, and 1635 cm^{-1} are associated with the amide III, amide II and amide I respectively as shown in Fig. S2 (Supplementary Content). The narrow bands at 2866 and 2964 cm^{-1} could be attributed to the symmetric and asymmetric C-H stretching vibrations. The broad peak shown at 3254 cm^{-1} could be attributed to hydroxyl groups attached to carboxyl groups through H bonding. On the other hand, the spectra of wool fabric samples treated with Ag-nanoparticle formed by various concentration of Ag^+ show a new band at 1260 cm^{-1} , which is related to the stretching vibration of carboxylic acid and its intensity decreased with an increase in the Ag^+ concentration. The Ag nanoparticles are stabilised by TSC and this band could be attributed to the carboxyl groups of TSC. It is also evident that the intensity of hydroxyl peak at 3254 cm^{-1} slightly decreased with for fabric treated with Ag nanoparticles but no change in the intensity of hydroxyl peak observed with an increase in the applied Ag^+ concentration. Similarly, the intensity of amide bands decreased for the Ag nanoparticle-treated fabrics compared to the untreated control fabric suggesting interaction between Ag nanoparticles and wool fabrics.

4. Conclusions

In this study, we demonstrated that wool fabrics can be made multi-functional by Ag nanoparticle-treatment, which not only produces colour in the fabric but also makes them antibacterial, antistatic and hydrophobic along with excellent durability of the treatment to

washing. We also demonstrated that the various processing parameters, such as the concentration of Ag^+ , Ag^+ to citrate anion ratio, treatment pH, and treatment temperature had significant effects on the functional properties of wool fabric. It was found that the coloured wool fibres were produced only if the Ag^+ concentration was at least 0.56% owf and the Ag^+ to citrate anion ratio was 1:2 and the treatment temperature was 75 °C or above. The produced colour varied from yellow to dark brown to blackish brown. The colour strength and UV radiation absorption capability of the treated fabric increased with an increase in the concentration of Ag^+ , Ag^+ to citrate anion ratio and treatment temperature, or a decrease in the treatment pH. The treatment method developed in this study could be used in the textile industry to produce multifunctional wool fibres.

Acknowledgment

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Caption of Figures

Fig. 1. Effect of Ag^+ concentration (a), pH (b), treatment temperature (c), and Ag^+ to citrate anions ratio (d) on the colour strength of wool fabrics treated with in-situ formed Ag nanoparticles at 75 °C for 90 min.

Fig. 2. Effect of Ag^+ concentration (a), pH (b), Ag to citrate anions ratio (c), and treatment temperature (d) on the UV transmission of wool fabrics treated with Ag nanoparticles.

Fig. 3. The effect of multiple washing on the antibacterial activity of wool fabrics treated with in situ formed Ag nanoparticles using 1.67% owf Ag^+ , Ag^+ to citrate anions ratio 1:4, pH 3.5, and 75 °C for 90 min.

Fig. 4. SEM micrographs wool fabric treated with silver nanoparticles using 1.67% owf Ag⁺ and Ag⁺ to citrate anions ratio 1:4 at 55, 65, 75, 85 and 95 °C.

Fig. 5. SEM micrographs of wool fabrics treated with Ag nanoparticles using Ag concentrations of 1.11, 1.67 and 2.22% owf using Ag⁺ to citrate anions ratio of 1:4.

Caption of Tables

Table 1. *CIE L*a*b** values and colourfastness to washing of wool fabrics multi-functionalised with Ag nanoparticles at various conditions.

Table 2. EDX elemental analysis of wool fabric treated with Ag nanoparticles by using various concentrations of Ag⁺.

Table 3. Antistatic properties of wool fabric treated with Ag nanoparticles made with various concentration of Ag⁺.

Table 4. The dynamic contact angle of untreated and Ag nanoparticle-treated wool fabrics at various times.