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4 Multifunctional acrylic fibers prepared via in-situ formed
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7 silver nanoparticles: Physicochemical, UV radiation
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10 protection, and antistatic properties
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35 **Key-words:** silver nanoparticles; multifunctional acrylic fiber; UV absorption; antistatic;
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37 wash fastness; antibacterial

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41 **Abstract.** A single treatment that makes textiles multifunctional is very attractive to the
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43 textile chemical processors. In this study, multifunctional acrylic fibers were produced by in
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45 situ forming silver (Ag) nanoparticles at various concentrations of Ag and trisodium citrate
46 color with excellent color fastness properties. **Acrylic fiber is also the main precursor for the**
47 (TSC). The exhaustion of silver into acrylic fibers and the reduction of Ag to Ag
48 **manufacturing of carbon fiber, and 50% of the carbon fibers are commercially made from**
49 nanoparticles were carried out at 90 °C, well above the glass transition temperature (T_g) of
50 **extra pure PAN fibers through carbonization [1]. However, the acrylic fibers used for apparel**
51 this fiber in water. The effect of the concentration of Ag, Ag to TSC ratio, pH, and reaction
52 **are not pure PAN fibers and one or more other co-monomers, such as ethylene derivatives,**

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55 **acrylic acid, methacrylic acid, styrene, sulfonic acid and itaconic acid, are added to PAN to**
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62 time on the color strength, ultraviolet (UV) radiation absorption, surface electrical resistance
63 and mechanical properties of the treated fibers were systematically investigated. It was found
64 that if the concentration of Ag was less than 1% on the weight of acrylic fibers or the Ag to
65 TSC ratio was less than 1:2, no color was produced. The color strength and UV radiation
66 absorption capacity of the treated acrylic fibers increased with an increase in the
67 concentration of Ag, and Ag to TSC ratio, and also with a decrease in the pH. On the other
68 hand, the surface resistance of the treated acrylic fibers decreased with an increase in the
69 concentration of Ag and a decrease in the treatment pH. The treated fibers showed excellent
70 antibacterial activity, UV radiation absorption capacity, and also very good antistatic
71 properties along with an excellent colorfastness to washing. Moreover, the developed
72 treatment is highly durable to washing as after 20 washes the treated fibers lost their
73 antibacterial activity only marginally.
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90 **1. Introduction**

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94 Polyacrylonitrile fiber (PAN), more commonly known as acrylic fiber, is a popular fiber
95 for the manufacturing of apparels as well as rugs because of its softness, tactile feeling, low
96 density, adequate elasticity, and excellent thermal insulating properties. They have replaced
97 wool fibers for many applications including knitwear apparel and interior textiles. Acrylic-
98 made fabrics have excellent resistance to pilling, and also the dyed fabric has brilliance in
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121 **enhance their dyeability.** Copolymerization with anionic monomers introduces anionic groups
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123 in the fiber's macromolecular chains and enables dyeing with cationic dyes.
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126 In the past decade, various investigations have been carried out to increase the range of
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128 applications of acrylic fibers in technical textiles. Antistatic property is an important aspect of
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130 technical textiles as acrylic fiber-made apparels are used by the people working in the service
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132 stations and electronic industries. The electrostatic discharge with sparks and shocks can
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134 instigate fire if it occurs in a gasoline service station. Static electricity causes an estimated
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136 US\$5 billion/year worth of damage to electronic devices [2]. A range of treatments, including
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138 metal plating [3], glow-discharge plasma treatment in nitrogen [4] and polyaniline coating by
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140 vapor deposition polymerization [5], have been investigated to improve the poor antistatic
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142 properties of acrylic fibers but the success was very limited. It is also known that UV
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144 radiation can affect human skin, even can cause skin cancer and UV protective textiles can
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146 protect the wearer from the harmful effect of UV radiation.
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150 Antimicrobial properties are another important requirements desired by consumers to have
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152 in their apparel [6], which is not surprising as modern consumers are increasingly concerned
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154 about their health and wellbeing. A range of treatments including the addition of poly(styrene
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156 hydantoin) to the spinning dope of polyacrylonitrile followed by chlorination of the spun
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158 fibers [7], guanidine oligomers to the polyacrylonitrile spinning dope [8], and also the
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160 treatment with copper and zinc sulfates in combination with a direct dye [9], ionic silver
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162 treatment [10], and also the incorporation of silver nanoparticles to the spinning dope [11],
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164 have been investigated with some successes to make acrylic fibers antimicrobial. The
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166 hydantoin-based treatment is unsuitable for the dyed acrylic fibers as the chlorination
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168 treatment may degrade the dyes used for the dyeing.
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171 From ancient time, silver has been used as a broad spectrum antibacterial agent. Silver
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173 ions accumulate inside cells and bind to negatively charged components in proteins and
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180 nucleic acids of the cell causing structural changes in bacterial cell walls, membranes, and
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182 nucleic acids affecting their viability [12]. Silver nanoparticles show antimicrobial activities
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184 by the time-dependent release of silver ions, which is directly related to the constant presence
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186 of free silver ions in the local microbial environment [13].
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189 Silver nanoparticles of various sizes and geometric shapes can show various Plasmon
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191 bands producing different colors ranging from yellow, blue to red, all the trichromatic shades.
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193 The coloration of textiles with noble-metallic nanoparticles including gold and silver has
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195 been investigated to produce various colored fibers [14–17]. There are three types of
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197 coloration methods used for the coloration of textiles with metallic nanoparticles. Colored
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199 nanocomposite fibers are produced by the addition of metallic nanoparticles in the molten
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201 spinning dope of fibers, which is used for only the synthetic fibers. However the interactions
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203 between the polymers and nanoparticles are quite complex, such as the introduction of
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205 nanoparticles into polymers affects the molecular arrangements of the host polymers
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207 changing their flow behavior, orientation, crystallinity, toughness, and mechanical properties
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209 [18]. Similarly, the guest nanoparticles also experience various enthalpic and entropic
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211 interactions that govern their size and spatial distribution [18]. Various capping agents are
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213 used to mediate those interactions [19]. In another method, already formed metallic
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215 nanoparticles are exhausted into the fibers like the dyeing of textiles with pigment dispersion.
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217 However, the penetration of the nanoparticles is limited only to the outer surface or near to
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219 the outer surface of the fibers [20,21]. The other method is the exhaustion of metal ions into
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221 the fibers and in situ formation of metallic nanoparticles within the fibers by using
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223 appropriate reducing agents. Nam et al. formed silver-cotton nanocomposite fibers by
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225 exhausting silver ions into alkali-swollen cotton fibers [22] but the color of the fibers was
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227 only black. Dong and Hinestroza deposited negatively charged metallic nanoparticles of Au,
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229 Pd, and Pt onto positively charged cotton fibers by electrostatic assembly [21] to produce
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239 multicolored fibers. Tang et al. synthesized colloidal silvers of various colors by using TSC
240 and polyvinylpyrrolidone as a stabilizer, and sodium borohydride as a reducing agent to
241 produce multicolored silk fibers [14]. Kelly and Johnston used TSC as a reducing as well as a
242 stabilizing agent to form colored silver nanoparticles in wool fibers [15].
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247 *As the acrylic fibers are anionic, the cationic silver ions (Ag^+) can readily be adsorbed into*
248 *them and silver nanoparticles can be formed in situ, which will make the fibers*
249 *multifunctional, i.e. can make them colored, antibacterial, antistatic, and UV protective, and*
250 *also may improve the durability of the treatment to washing. The effect of AgNO_3*
251 *concentration, pH, and Ag to TSC ratio on the shade formed also has not been investigated*
252 *for the in situ formation of silver nanoparticles in textiles. In this work, we are reporting a*
253 *simple method to make acrylic fibers multifunctional by exhausting Ag^+ into acrylic fibers*
254 *and then converting them into colored silver nanoparticles by the reduction with TSC. The*
255 *effect of changing the concentration of Ag, Ag to TSC ratio, treatment pH and time on the*
256 *shade change, color strength, UV transmission through the fibers, and also the antibacterial*
257 *and antistatic properties of the acrylic fibers are reported here.*
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273 **2. Experimental methods**

274 *2.1 Materials*

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278 Acrylic yarns marketed for knitwear manufacturing were purchased from the Reliance
279 Industries Ltd (India). Silver nitrate, trisodium citrate, acetic acid, and sodium acetate were
280 purchased from Kanto Chemicals (Japan) and were of analytical reagent grade. Sandoclean
281 PC (a non-ionic detergent) and Sandozin MRN (a wetting agent) were purchased from
282 Clariant Chemicals (Switzerland). The standard phosphate-free detergent used for the
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298 assessment of color fastness to washing of the acrylic yarns was purchased from the Society
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300 of Dyers and Colourists (SDC), UK.
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305 *2.2. Coloration with silver nanoparticles*

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309 The supplied acrylic yarns were scoured with 1 g/l Sandoclean PC and 0.25 g/l Sandozin
310 MRN at 90 °C for 30 min to remove any oil and dirt present in them. All Ag nanoparticle
311 treatments were carried out in a Hisaka Circular laboratory dyeing machine (Hisaka Works
312 Ltd., Osaka, Japan) using a 1:40 materials to water ratio. The bath was dosed with the
313 required quantity of AgNO₃ and 0.25 g/l Sandozin MRN. The pH of the bath was set at 3, 5
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315 or 7 with acetic acid and sodium acetate. The temperature of the bath was then raised to 70
316 °C at 2 °C/min, and then to 90 °C at 1 °C/min. It was reported that the dry acrylic fiber had a
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318 T_g of 92 °C, which reduced to 72 °C in wet conditions [23]. Therefore, the peak exhaustion
319 temperature selected is well above the T_g of acrylic fiber. The bath was held at that
320 temperature for 15 minutes. Then the required quantity of TSC was added and held for
321 another 90 minutes. After completion of the treatment, the bath was cooled to 45 °C at 2
322 °C/min, the liquor drained and the treated fiber samples were rinsed with cold water for
323 several times. They were then dried at 60 °C in an oven for 30 min. The multicoloration of
324 PAN fibers were carried out by varying the concentration of silver nitrate in the dyebath on
325 the weight of acrylic yarns (owf) used, the ratio of Ag to TSC, pH, and the dyeing time.
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343 *2.3. Color measurement*

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347 The color measurements of acrylic yarns dyed with various concentrations of Ag
348 nanoparticles were carried out according to a published literature [24]. The reflectance values
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357 and K/S values (at the appropriate wavelength of maximum absorption for each dyeing) of the
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359 dyed samples were measured using a Datacolor Spectraflash 500 spectrophotometer
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361 interfaced to a personal computer. Samples were measured under illuminant D65, using a 10°
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363 standard observer with UV component and specular both excluded. **Yarns were evenly**
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365 **wrapped on a paperboard and four measurements were made at four different places of each**
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367 **sample and the average value is reported here.** The color difference was
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369 spectrophotometrically measured by measuring $CIE L^*$, a^* , b^* color difference (ΔE) between
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371 two different areas of the same sample under illuminant D65, using a 10° standard observer
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373 by a Minolta hand-held spectrophotometer (Konica Minolta Corporation, Japan).
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378 379 *2.4. Mechanical properties*

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383 The tensile strength of the control and silver nanoparticle-treated acrylic yarns were
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385 measured by using an Instron Tensile Testing Machine (Model 4501, Instron Corporation,
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387 Norwood, USA) at 20±2 °C and 65±% relative humidity according to the ASTM Test Method
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389 D2343-02: *Standard Test Method for Tensile Properties of Glass Fiber Strands, Yarns, and*
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391 *Rovings Used in Reinforced Plastics*. The gauge length was 80 mm and the traversing speed
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393 was 50 mm/min. The samples were conditioned at the above-mentioned temperature and
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395 humidity for at least 2 days. At least 10 samples were measured for each treatment and the
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397 averages are reported here. The surface resistance of acrylic yarns was carried out at 20 °C
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399 and 45% relative humidity by a high resistance meter with a two-point probe (Model
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401 MEGARESTA II-A, Shishido Electrostatic, Ltd., Japan) with SSD-A type probe at an
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403 applied voltage of 100 V.
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408 409 *2.5. UV Absorption and colorfastness*

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418 The treated acrylic yarns were uniformly mounted on a cardboard with a big hole. Thermo
419 Scientific UV-VIS Spectrophotometer (Model: Evolution 200, Thermo Fisher Scientific Inc.,
420 Waltham, USA) with a Diffuse Reflectance Measurement attachment was used to assess the
421 percent transmission of light through the acrylic yarns at wavelength intervals up to 5 nm in
422 the 290–400 nm spectral span. The color fastness to washing of the yarns was measured
423 according to the ISO Test Method 105-C03 1987: *Textiles – Tests for colorfastness – Part*
424 *C03: Color fastness to washing: Test 3* by washing in a Gyrowash (Model 415/8) using the
425 phosphate-free standard detergent. In both cases, fastness grades were assessed by comparing
426 with the 3M Grey Scale.
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439 2.6. Fourier transform infrared spectroscopy (FTIR)

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444 The surface of Ag nanoparticle-treated acrylic yarns was characterized by using a
445 Shimadzu FT-IR (Model Prestige 21, Shimadzu Corporation, Japan) with an attenuated total
446 reflectance (ATR) attachment at a resolution of 4 cm⁻¹ in the range from 650 to 4000 cm⁻¹.
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448 The ZnSe crystal was used to record the ATR-FTIR spectra. 64 scans were signal-averaged.
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454 2.7. Assessment of antibacterial activity

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459 The antibacterial properties of acrylic yarns treated with Ag nanoparticles at various
460 concentrations were assessed according to the AATCC Test Method 100–1999 (*Antibacterial*
461 *Finishes on Textile Materials: Assessment of*) against *Staphylococcus aureus* (ATCC 6538)
462 and *Klebsiella pneumoniae* (ATCC 4352). A bundle of treated acrylic yarns was placed in
463 individual sterile Petri dishes. The nutrient broth was prepared with 5 g/l peptone and 3 g/l
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475 beef extracts and the pH was adjusted to 6.8 ± 0.1 with 1N sodium hydroxide solution. The
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477 bacterial culture of appropriate type diluted 100 times was transferred to the nutrient by using
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479 a 4 mm inoculating loop and was incubated at 37 ± 2 °C for 24 hours. 1.0 ± 0.1 ml inoculum
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481 was added to the sample in each petri dish. The Petri dishes were then incubated at 37 ± 2 °C
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483 for 48 h. The number of bacteria before and after the incubation is measured by a colony
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485 counter and the reduction in bacteria is measured which is expressed in percentage. This
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487 method provides a quantitative assessment of the antimicrobial performance of antibacterial
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489 textile materials as it provides a percentage of killing of a particular bacteria.
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494 *2.8. Surface morphologies*

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499 The surface morphology of the acrylic yarns coated with in situ formed silver
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501 nanoparticles was investigated by using the field emission scanning electron microscopy
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503 (SEM) technique. The treated yarn surfaces were scanned using a JOEL FESEM (Model:
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505 JSM-7000f, JEOL Ltd., Tokyo, Japan) at an accelerated voltage of 15 kV without any
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507 conductive coating. The elemental analysis of the Ag nanoparticle-treated acrylic yarns was
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509 carried out by an energy dispersive X-ray (EDX) using the same model of JEOL SEM at 15
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511 kV. To examine the cross-sectional surface of acrylic fibers, fiber bundles of straightened
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513 acrylic fibers were coated with a molten polycaprolactone polymer to form a round-shaped
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515 composite strand and then slices of fibers were cut perpendicular to the length of the fibers by
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517 a sharp knife. The cross-sectional area of fibers was scanned by the same FESEM in back-
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519 scattered mode.
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523 **3. Results and discussion**

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3.1 CIE $L^*a^*b^*$ values and color strength

As shown in Fig. 1, the color of the silver nanoparticle-treated acrylic yarns with various Ag concentrations and also at different Ag to TSC ratios is ranged from yellow, greyish green to bluish-black as shown in Fig. 1. Table 1 shows CIE $L^*a^*b^*$ values and color strength of colored acrylic yarns.

3.1.1. Effect of concentration of Ag

The effect of Ag concentration on the shades produced and color strength of acrylic yarns was investigated by varying the concentration of Ag from 0.5 to 3.0% owf using the Ag to TSC ratio of 1:2, as at this ratio stable Ag nanoparticles are formed [25]. Fig. 1 shows the change in color and also the color strength of the acrylic yarns with an increase in the concentration of Ag. The color of the yarns turned from bright white for the 0% Ag to very pale bluish, violet, light yellowish brown to deep yellowish brown for the 2.0% Ag. The color strength of the treated acrylic yarns increased with an increase in the concentration of Ag. Table 1 shows the CIE L^* , a^* and b^* values of acrylic yarns treated with various concentrations of Ag. It is evident that the lightness value (L^*) decreased and the color strength increased with an increase in the applied concentration of Ag. It was found that the minimum concentration of Ag to produce color in acrylic yarns is 2.0% owf as below that concentration produced no color. At 0.5 % Ag, the inherent color of the acrylic fiber was only marginally changed and the produced color strength was only 0.05, which was even, lower than the undyed acrylic fiber. At the silver concentration, 1.0% owf produced color strength only 0.15 and even at 2% Ag concentration, the color strength produced was only 1.32 (Fig. 1), which is considerably lower compared to the color strength produced by

591 synthetic dyes at this level of concentration. The produced color was dull, and the intensity of
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594 the color produced was nowhere near to the color strength of basic dyed acrylic yarns.
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597 The color, shape and the size of Ag nanoparticles depend on the concentration of Ag⁺ in
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599 solution and the size of nanoparticles increases with an increase in the concentration of Ag⁺
600 ions [26,27]. The increase in the concentration of AgNO₃ increases the concentration of Ag
601 nanoparticles and therefore the color strength of the treated fabric increased with an increase
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603 in the concentration of AgNO₃.
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609 610 3.1.2. Effect of Ag to TSC ratios 611

612 To know the effect of the increasing ratio of Ag to TSC on the color of the treated fabrics,
613 we varied the Ag to TSC ratio from 2:1 to 1:8. Fig. 1 shows the change in color and also the
614 color strength of acrylic yarns treated with 2.0% Ag at an increase in the ratio of Ag to TSC
615 from 2:1 to 1:8. The treated yarns using Ag to TSC ratios 2:1 and 1:1 are almost colorless.
616
617 The color of the yarns turned to pale brown, deep yellowish brown and bluish-black with an
618 increase in the ratios of Ag to TSC up to 1:8. It can be seen that the color strength of acrylic
619 yarns treated with 2.0% Ag increased with an increase in the Ag to TSC ratios. The acrylic
620 fibers colored with in situ generated Ag nanoparticles using Ag to TSC ratios 2:1 and 1:1
621 produced very poor color strength and the produced color was not stable as the produced
622 silver nanoparticles were unstable. It can be seen that the value of *L** decreased and the color
623 strength of the acrylic fiber increased with an increase in the Ag to TSC ratio (Table 1). The
624 deepest shade was achieved when the Ag to TSC ratio was 1:8, which is consistent with the
625 reflectance and color strength data. It was found that 1:6 is the optimum Ag to TSC ratio as
626 increasing the ratio more than 1:6 hardly increased the color strength.
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642 Kelly and Johnston found that the conversion of Ag⁺ to Ag nanoparticles are related to the
643 concentration of TSC used as a reducing agent and at low concentrations of TSC only partial
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652 conversion of Ag⁺ to Ag nanoparticles took place and increasing the concentration fully
653 converted into Ag nanoparticles [15]. It is also known that to stabilize the formed Ag
654 nanoparticles, the ratio of Ag to TSC should be at least 1:2. Our results also show that no
655 color was produced when the ratio of Ag to TSC was less than 1:2. The increase in the ratio
656 of Ag to TSC beyond 1:2 changed the color of the treated acrylic fibers from brown to bluish
657 grey indicating that the size of the nanoparticles increased with an increase in the ratio of Ag
658 to TSC. Thottoli and Unni also found that in the case of ZnS nanoparticle formation, the size
659 of the nanoparticles increased with an increase in the concentration of TSC [28].
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672 3.1.3. Effect of pH 673

674 The effect of pH is very important as the pH has an effect on the adsorption of silver into
675 acrylic fibers. The effect of pH on color strength was investigated at acidic to neutral pHs (3,
676 5 and 7) as acrylic fibers have low resistance to alkali. Table 1 shows CIE L*a*b* values and
677 color strength of acrylic fibers colored with silver nanoparticles at various pHs at 2.0% owf
678 Ag for 2 hr at 90 °C. The acrylic yarns treated with 2.0% Ag using Ag to TSC ratio 1:2 at pH
679 3 produced the deepest color and the one treated at pH 7 produced the lightest color. The
680 color strength of the acrylic yarns decreased with an increase in the pH (Fig. 1). It is evident
681 that the lightness values (L*) also increased with an increase in the pH. The color strength of
682 the acrylic fiber dyed at pH 3, was 1.32, which decreased to 1.07 and 0.8 when the treatment
683 pHs was increased to 5 and 7 respectively (Fig. 1). Therefore, pH 3 was the optimum pH for
684 the coloration of acrylic with Ag nanoparticles.
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698 Dong et al. investigated reduction of AgNO₃ to Ag nanoparticle at pH from 5.7 to 11.1
699 and found that the reduction of the silver precursor (Ag⁺) was promoted with an increase in
700 the pH [29]. They also found that at low pH mainly triangle or polygon shaped Ag
701 nanoparticles were formed but at high pH, spherical and rod-like nanoparticles were formed.
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711 Zhang et al. found only spherical shaped Ag nanoparticles were formed at pH 2.5 [30].
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713 However, we found that the fabric sample treated at pH 3 showed the highest color strength.
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715 As the fibers are anionic, most of the applied Ag⁺ should be absorbed into the fiber at that pH
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717 resulting in the in situ formation of Ag nanoparticles. However, the absorption of Ag⁺ into
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719 acrylic fibers decreased with an increase in the pH of the bath resulting in the formation of
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721 Ag nanoparticles outside the fibers, and they did not absorb into the fibers at the increased
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723 pHs. Therefore, the color strength of the treated acrylic yarns decreased with an increase in
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725 the pH.
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731 3.1.4. Effect of reaction time

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733 Fig. 1 shows the effect of the dyeing time on the value of L^* and the color strength of the
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735 acrylic fiber 2.0% Ag using the Ag to TSC ratios and at pH 3 for a different time. It is evident
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737 that the color strength increased with an increase the treatment time. The deepest shade was
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739 achieved when the treatment time was 120 min. It can be seen that even up to 90 min of
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741 treatment time the color strength produced was very low, which considerably increased in the
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743 final 30 min of the treatment. Dong et al. found that at low pH the reduction of AgNO₃ to Ag
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745 nanoparticle is very slow which affects the nucleation and growth of Ag nanoparticles [29].
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747 Therefore, the color strength of the treated fabric increased with an increase in the reaction
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749 time.
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754 3.1.5. Colorfastness to washing

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756 Colorfastness to washing grades of acrylic yarns treated with silver nanoparticles using
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758 various concentrations of Ag, Ag to TSC ratios and treatment pHs are shown in Table 1. It
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760 can be seen that the overall colorfastness to washing is excellent (grade 4–5) only if the
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762 applied Ag concentration is 2.0% owf and above and the Ag to TSC ratio is 1:2 and above.
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770 Overall, the color fastness to washing of the colored acrylic yarns produced by in situ formed
771 silver nanoparticles is reasonably good.
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774 It is known that Ag nanoparticles release Ag⁺ ions in an aqueous media and therefore
775 fastness of the treatment should decrease with multiple times of washing [31]. It can be
776 expected that most of the Ag nanoparticles adsorbed onto the surface of acrylic fibers
777 (especially for the treatment carried out at high pH) would be released during washing.
778 Therefore, the wool fabric treated at pH 3 should better fastness to washing compared to the
779 acrylic fibers treated at pH 5 and 7. Similarly, the fabric treated using Ag to TSC ratio less
780 than 1:2 also showed poor washing fastness due to the formation of unstable Ag
781 nanoparticles. The good wash fastness indicates that the in situ formation of silver into the
782 cationic acrylic fiber enhanced the durability of the treatment to washing.
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796 3.2. UV transmission through the fiber 797

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799 UV radiation levels are divided into three zones, UV-A (320–400 nm), UV-B (290–320
800 nm) and UV-C (200–290 nm). Only UV-A and UV-B reach earth and therefore protection
801 against UV-A and UV-B are important. Fig. 2 shows the effect of applied Ag concentration,
802 Ag to TSC ratio and the pH on the UV transmission through the colored acrylic yarns. It is
803 evident that the treatments with silver nanoparticles considerably reduced the UV
804 transmission through the treated yarns. The UV transmission through the acrylic yarns
805 decreased with an increase in the applied Ag concentration and the highest reduction in UV
806 transmission was observed for the applied Ag concentration 3% owf and **beyond that level,**
807 **no further reduction was observed.** The untreated acrylic fibers show low transmission of
808 UV-B, which was considerably enhanced with the treatment with silver nanoparticles. At 290
809 nm, the undyed acrylic yarns showed UV transmission only 17.72%, which reduced to 8.88%
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829 for the yarns treated with 0.5% Ag. The highest reduction in UV transmission was observed
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831 for the applied Ag concentration 3% as at that concentration the UV transmission reduced to
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833 only 0.6%. Similarly, UV-A transmission also decreased with an increase in the applied
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835 concentration of UV-A and at 340 nm, the UV-A transmission reduced to only 1.9% from
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837 27.2% observed for the control acrylic fiber. It is also evident that the UV-A and UV-B
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839 transmission decreased with an increase in the Ag to TSC ratios. The ratios 2:1 and 1:1
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841 showed low UV transmission as they produced unstable silver nanoparticle but 1:2 and
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843 higher showed an excellent reduction in UV transmission as they produced very stable silver
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845 nanoparticles. The effect of pH of the treatment on the UV transmission showed that the
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847 fibers treated at pH 5 and 7 showed very similar UV-B transmission, which was much higher
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849 compared to the UV transmission observed for the acrylic fibers treated at pH 3. However,
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851 for the UV-A, the transmission decreased with a decrease in the pH of the treatment. The
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853 silver nanoparticle-treated acrylic yarns showed excellent UV protection capability.
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859 *3.3. Surface resistivity*

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863 The antistatic properties of synthetic fibers are quite important as the synthetic fiber-made
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865 fabric has a tendency to stick to the body due to static charge development in the fabric. The
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867 surface resistivity of silver nanoparticle-treated acrylic yarns is shown in Fig. 3. The surface
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869 resistance shown by the untreated acrylic yarn is very high (1200×10^9 Ohm/cm), i.e. it does
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871 not show any antistatic property. On the other hand, acrylic yarns colored with in situ formed
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873 silver nanoparticles using various concentrations of Ag showed considerably lower surface
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875 charge compared to the surface charge shown by the untreated acrylic yarns. The surface
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877 resistivity of the acrylic yarns decreased with an increase in the applied Ag concentration. The
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879 surface resistivity decreased from 1200×10^9 Ohm/cm for the control to 9.2×10^9 Ohm/cm for
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888 the 2% owf concentration of silver. On the other hand, the ratio of Ag to TSC showed mixed
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890 results. The lowest surface resistivity was shown by the acrylic yarn that was treated with
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892 silver nanoparticles with an Ag to TSC ratio 1:2. It is known that when the Ag to TSC ratio is
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894 below 1:2, unstable silver nanoparticles are formed. Increasing the Ag to TSC ratio increased
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896 the surface resistivity. On the other hand, the reaction pH also showed some levels of effect
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898 on the surface resistivity of the acrylic yarns treated with silver nanoparticles. The surface
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900 resistivity of the acrylic yarns treated with Ag nanoparticles decreased with a decrease in the
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902 pH. The isoelectric point of acrylic fiber is 3 [32], i.e. below pH 3 the fiber surface is cationic
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904 and 3 is anionic. Therefore Ag is better absorbed at pH 3 or below compared to the higher
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906 pH. Therefore the yarns treated at pH 3 showed lower surface resistivity compared to the
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908 yarns treated at pH 5 and above.
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911 912 913 *3.4. Elemental analysis by EDX* 914 915

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918 Table 2 shows the elemental analysis of C, O, N, and Ag elements of untreated and silver
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920 nanoparticle-treated acrylic yarns. The EDX spectra and elemental mapping of C, O, N, and
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922 Ag are shown in Figs. S1 and S2 respectively (please see Electronic Supplementary
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924 Material). The control acrylic fibers show no presence of Ag, **which is expected**. On the other
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926 hand, for the acrylic yarns treated with various concentrations of Ag, the elemental Ag %
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928 increased with an increase in the applied concentration of Ag. The highest concentration was
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930 observed for the 3% owf of Ag and the lowest for the 0.5% of Ag.
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934 935 *3.5. Mechanical properties* 936 937 938 939 940 941 942 943 944

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947 The effect of silver nanoparticle treatment on the tensile strength and elongation at peak of
948 unmodified and silver nanoparticle-treated acrylic yarns using various concentrations of Ag,
949 AG to TSC ratios and pHs are shown in Fig. 4. It can be seen that the tensile strength and also
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954 the elongation at peak initially decreased and then increased with an increase in the
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956 concentration of Ag. The strength decreased from 2.80 kgF for the untreated control to 2.12
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958 kgF for the applied concentration of 1.0% Ag. After which the tensile strength started to
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960 increase and reached 2.86 kgF for the 2.0% Ag, which is almost similar to the original
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962 strength of unmodified acrylic fibers. A similar trend was shown also for the elongation at the
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964 peak which decreased from 38.5% to 30.9% and then again increased to 36.2% with an
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966 increase in the concentration of Ag. Probably, Ag nanoparticles formed ionic bonding
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968 between the macromolecular chains of acrylic as the TSC-capped silver nanoparticles are
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970 anionic, which reduced the macromolecular chain mobility resulting in a decrease in the
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972 elongation of acrylic fibers. On the other hand, the increase in the Ag to TSC ratio, the
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974 strength increased to 2.86 kgF for the Ag to TSC ratio 1:2, which is similar to the strength of
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976 control acrylic fiber, which then again started to decrease with an increase in the Ag to TSC
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978 ratio. The elongation at peak also showed a trend consistent with the trend shown for the
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980 tensile strength. On the other hand, the tensile strength decreased with an increase in the pH
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982 of the treatment, although the effect was only marginal. **It is envisaged that the formation of
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984 acrylic/Ag nanoparticle composite fiber caused the reinforcement of the acrylic fiber, which
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986 is consistent with the findings reported by Harifi and Montazer for the polyester fabric treated
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988 with iron-oxide nanoparticles [33].**
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994 *3.6. Antibacterial properties*

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1006 It is known that silver nanoparticle-treated textiles show very good antimicrobial
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1008 performance against a wide range of bacteria [34,35]. Fig. 5 shows the durability of the
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1010 antibacterial performance to multiple washing of acrylic yarns multi-functionalized with
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1012 silver nanoparticles using 2% Ag against *Staphylococcus aureus* and *Klebsiella pneumoniae*.
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1014 It is evident that the treated yarns showed excellent antibacterial activity against both types of
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1016 bacteria and the excellent antimicrobial activity retained even after 20 washes. Before
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1018 washing, the treated yarns showed 99.8 and 99.0% killing of *Staphylococcus aureus* and
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1020 *Klebsiella pneumoniae* respectively. The corresponding values for the 20 washes were 99 and
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1022 98.4% respectively. It can be seen that only marginal reduction of antibacterial activity was
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1024 observed even after 20 times of washing, indicating excellent durability of the treatment.
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1028 It was reported that for textiles treated with Ag nanoparticles unbound or loosely bound to
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1030 textiles by a resin to the fiber surface, sometimes not only silver ions but also silver
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1032 nanoparticles are released into the environment resulting in poor durability to laundering
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1034 [36]. As in the case of acrylic fiber, the Ag nanoparticles were in situ formed and therefore it
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1036 showed better durability to washing compared to non-substantive textiles treated with silver
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1038 nanoparticles.
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1042 3.7. FTIR

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1046 Acrylic fibers used by the textile industry contain at least 85% polyacrylonitrile and the
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1048 rests are other copolymers and additives added to polyacrylonitrile to enable their dyeing
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1050 with conventional dyes [36]. Therefore, the FTIR spectrum of acrylic fiber not only contains
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1052 the typical peaks associated with acrylonitrile but also peaks associated with other additives.
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1054 Fig. 6 shows the ATR-FTIR spectra of undyed acrylic fiber and also acrylic fiber dyed with
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1056 silver nanoparticles. The spectrum of undyed acrylic fiber shows typical acrylic fiber peaks at
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1065 1730 and 2242 cm^{-1} that are associated with nitrile ($\text{C}\equiv\text{N}$) and stretching vibration of ($\text{C}=\text{O}$)
1066 ester linkage respectively [37,38]. The carbonyl peak is coming from the carboxyl-containing
1067 copolymers or additives. The peaks at 1230, 1362, and 1457 cm^{-1} could be associated with
1068 the $-\text{CH}_2$ wagging, C-H in-plane bending, and the $-\text{CH}_2$ bending vibration of the
1069 polyacrylonitrile macromolecular backbone, respectively [39,40]. The small peaks at 1027
1070 and 2927 cm^{-1} are associated with **sulfonate** groups from possibly acryloamidopropane
1071 sulfonic acid additive and $-\text{CH}_2$ stretching vibration of the polyacrylonitrile molecular chains
1072 respectively. The small peaks at 1653 and 1542 cm^{-1} represent the characteristic amide
1073 absorption bands. The Ag nanoparticle treated acrylic yarns also showed similar peaks but the
1074 intensity of the some of the peaks slightly decreased.
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1088 3.8. Surface morphologies

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1093 The surface of untreated and Ag nanoparticle-treated acrylic fibers was characterized by
1094 SEM to observe the assembly of silver nanoparticles formed on the fiber surface. Fig. 7
1095 shows SEM images of acrylic fibers multifunctionalized with in situ generated silver
1096 nanoparticles. As shown in Fig. 7, an assembly of sphere-shaped silver nanoparticles evenly
1097 spread on the fiber surface. It is evident that they are strongly bonded to the fiber surface as
1098 no loosely hold nanoparticle is observed. Some aggregation of silver nanoparticles is evident
1099 on fiber surface at 2% owf of Ag. There is a possibility that nanoparticles may also form
1100 inside the fibers. Therefore, to observe the cross-sectional surface of fibers, the cross-section
1101 of fibers were cut and examined by SEM. **The optical micrographs of the cut surface of the**
1102 **treated fibers are represented in Fig. 8.** It is evident that nanoparticles were mostly formed at
1103 the outer edge of the fibers, which consistent with the findings of other researchers [22].
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1116 However, it is evident not only at the outer edge of the fibers but also inside the fiber
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1124 nanoparticles were formed. The SEM images prove that silver nanoparticles are formed in
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1126 situ in the fibers.
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1129 1130 **4. Conclusions**

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1135 Multifunctional acrylic fibers were produced by treating with silver nanoparticles at
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1137 various Ag concentrations, Ag to TSC ratios, pHs and time. It was found that the colored
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1139 acrylic fibers were produced only if the Ag concentration was at least 1.5% owf and also the
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1141 Ag to TSC ratio 1:2 and the treatment time was 120 min. The produced color varied from
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1143 yellow to brown to bluish black. The color strength increased with an increase in the
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1145 concentration of Ag and also with an increase in the Ag to TSC ratio. The silver nanoparticle-
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1147 treated acrylic yarns showed excellent multifunctional properties as the silver nanoparticle-
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1149 treated yarns showed excellent antimicrobial activity, UV radiation absorption, good
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1151 antistatic property and also produced wash fast colored yarns. The lowest resistance was
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1153 shown by the acrylic fiber dyed with 2.0% Ag with an Ag to TSC ratio 1:2 and treated for
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1155 120 min. The acrylic fibers colored with silver nanoparticles showed excellent antimicrobial
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1157 property against *Staphylococcus aureus*, and *Klebsiella pneumoniae* for at least 100 domestic
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1159 washes. The developed treatment method can be used in textile industry to produce
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1161 multifunctional acrylic fibers.
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1166 1167 **Acknowledgment**

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1183 **References**
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Multifunctional acrylic fibers prepared via in-situ formed silver nanoparticles: Physicochemical, UV radiation protection, and antistatic properties

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Abstract. A single treatment that makes textiles multifunctional is very attractive to the textile chemical processors. In this study, multifunctional acrylic fibers were produced by in situ forming silver (Ag) nanoparticles at various concentrations of Ag and trisodium citrate (TSC). The exhaustion of silver into acrylic fibers and the reduction of Ag to Ag nanoparticles were carried out at 90 °C, well above the glass transition temperature (T_g) of this fiber in water. The effect of the concentration of Ag, Ag to TSC ratio, pH, and reaction

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time on the color strength, ultraviolet (UV) radiation absorption, surface electrical resistance and mechanical properties of the treated fibers were systematically investigated. It was found that if the concentration of Ag was less than 1% on the weight of acrylic fibers or the Ag to TSC ratio was less than 1:2, no color was produced. The color strength and UV radiation absorption capacity of the treated acrylic fibers increased with an increase in the concentration of Ag, and Ag to TSC ratio, and also with a decrease in the pH. On the other hand, the surface resistance of the treated acrylic fibers decreased with an increase in the concentration of Ag and a decrease in the treatment pH. The treated fibers showed excellent antibacterial activity, UV radiation absorption capacity, and also very good antistatic properties along with an excellent colorfastness to washing. Moreover, the developed treatment is highly durable to washing as after 20 washes the treated fibers lost their antibacterial activity only marginally.

1. Introduction

Polyacrylonitrile fiber (PAN), more commonly known as acrylic fiber, is a popular fiber for the manufacturing of apparels as well as rugs because of its softness, tactile feeling, low density, adequate elasticity, and excellent thermal insulating properties. They have replaced wool fibers for many applications including knitwear apparel and interior textiles. Acrylic-made fabrics have excellent resistance to pilling, and also the dyed fabric has brilliance in color with excellent color fastness properties. Acrylic fiber is also the main precursor for the manufacturing of carbon fiber, and 50% of the carbon fibers are commercially made from extra pure PAN fibers through carbonization [1]. However, the acrylic fibers used for apparel are not pure PAN fibers and one or more other co-monomers, such as ethylene derivatives, acrylic acid, methacrylic acid, styrene sulfonic acid and itaconic acid, are added to PAN to

enhance their dyeability. Copolymerization with anionic monomers introduces anionic groups in the fiber's macromolecular chains and enables dyeing with cationic dyes.

In the past decade, various investigations have been carried out to increase the range of applications of acrylic fibers in technical textiles. Antistatic property is an important aspect of technical textiles as acrylic fiber-made apparels are used by the people working in the service stations and electronic industries. The electrostatic discharge with sparks and shocks can instigate fire if it occurs in a gasoline service station. Static electricity causes an estimated US\$5 billion/year worth of damage to electronic devices [2]. A range of treatments, including metal plating [3], glow-discharge plasma treatment in nitrogen [4] and polyaniline coating by vapor deposition polymerization [5], have been investigated to improve the poor antistatic properties of acrylic fibers but the success was very limited. It is also known that UV radiation can affect human skin, even can cause skin cancer and UV protective textiles can protect the wearer from the harmful effect of UV radiation.

Antimicrobial properties are another important requirements desired by consumers to have in their apparel [6], which is not surprising as modern consumers are increasingly concerned about their health and wellbeing. A range of treatments including the addition of poly(styrene hydantoin) to the spinning dope of polyacrylonitrile followed by chlorination of the spun fibers [7], guanidine oligomers to the polyacrylonitrile spinning dope [8], and also the treatment with copper and zinc sulfates in combination with a direct dye [9], ionic silver treatment [10], and also the incorporation of silver nanoparticles to the spinning dope [11], have been investigated with some successes to make acrylic fibers antimicrobial. The hydantoin-based treatment is unsuitable for the dyed acrylic fibers as the chlorination treatment may degrade the dyes used for the dyeing.

From ancient time, silver has been used as a broad spectrum antibacterial agent. Silver ions accumulate inside cells and bind to negatively charged components in proteins and

nucleic acids of the cell causing structural changes in bacterial cell walls, membranes, and nucleic acids affecting their viability [12]. Silver nanoparticles show antimicrobial activities by the time-dependent release of silver ions, which is directly related to the constant presence of free silver ions in the local microbial environment [13].

Silver nanoparticles of various sizes and geometric shapes can show various Plasmon bands producing different colors ranging from yellow, blue to red, all the trichromatic shades. The coloration of textiles with noble-metallic nanoparticles including gold and silver has been investigated to produce various colored fibers [14–17]. There are three types of coloration methods used for the coloration of textiles with metallic nanoparticles. Colored nanocomposite fibers are produced by the addition of metallic nanoparticles in the molten spinning dope of fibers, which is used for only the synthetic fibers. However the interactions between the polymers and nanoparticles are quite complex, such as the introduction of nanoparticles into polymers affects the molecular arrangements of the host polymers changing their flow behavior, orientation, crystallinity, toughness, and mechanical properties [18]. Similarly, the guest nanoparticles also experience various enthalpic and entropic interactions that govern their size and spatial distribution [18]. Various capping agents are used to mediate those interactions [19]. In another method, already formed metallic nanoparticles are exhausted into the fibers like the dyeing of textiles with pigment dispersion. However, the penetration of the nanoparticles is limited only to the outer surface or near to the outer surface of the fibers [20,21]. The other method is the exhaustion of metal ions into the fibers and in situ formation of metallic nanoparticles within the fibers by using appropriate reducing agents. Nam et al. formed silver-cotton nanocomposite fibers by exhausting silver ions into alkali-swollen cotton fibers [22] but the color of the fibers was only black. Dong and Hinestroza deposited negatively charged metallic nanoparticles of Au, Pd, and Pt onto positively charged cotton fibers by electrostatic assembly [21] to produce

multicolored fibers. Tang et al. synthesized colloidal silvers of various colors by using TSC and polyvinylpyrrolidone as a stabilizer, and sodium borohydride as a reducing agent to produce multicolored silk fibers [14]. Kelly and Johnston used TSC as a reducing as well as a stabilizing agent to form colored silver nanoparticles in wool fibers [15].

As the acrylic fibers are anionic, the cationic silver ions (Ag^+) can readily be adsorbed into them and silver nanoparticles can be formed in situ, which will make the fibers multifunctional, i.e. can make them colored, antibacterial, antistatic, and UV protective, and also may improve the durability of the treatment to washing. The effect of AgNO_3 concentration, pH, and Ag to TSC ratio on the shade formed also has not been investigated for the in situ formation of silver nanoparticles in textiles. In this work, we are reporting a simple method to make acrylic fibers multifunctional by exhausting Ag^+ into acrylic fibers and then converting them into colored silver nanoparticles by the reduction with TSC. The effect of changing the concentration of Ag, Ag to TSC ratio, treatment pH and time on the shade change, color strength, UV transmission through the fibers, and also the antibacterial and antistatic properties of the acrylic fibers are reported here.

2. Experimental methods

2.1 Materials

Acrylic yarns marketed for knitwear manufacturing were purchased from the Reliance Industries Ltd (India). Silver nitrate, trisodium citrate, acetic acid, and sodium acetate were purchased from Kanto Chemicals (Japan) and were of analytical reagent grade. Sandoclean PC (a non-ionic detergent) and Sandozin MRN (a wetting agent) were purchased from Clariant Chemicals (Switzerland). The standard phosphate-free detergent used for the

assessment of color fastness to washing of the acrylic yarns was purchased from the Society of Dyers and Colourists (SDC), UK.

2.2. Coloration with silver nanoparticles

The supplied acrylic yarns were scoured with 1 g/l Sandoclean PC and 0.25 g/l Sandozin MRN at 90 °C for 30 min to remove any oil and dirt present in them. All Ag nanoparticle treatments were carried out in a Hisaka Circular laboratory dyeing machine (Hisaka Works Ltd., Osaka, Japan) using a 1:40 materials to water ratio. The bath was dosed with the required quantity of AgNO₃ and 0.25 g/l Sandozin MRN. The pH of the bath was set at 3, 5 or 7 with acetic acid and sodium acetate. The temperature of the bath was then raised to 70 °C at 2 °C/min, and then to 90 °C at 1 °C/min. It was reported that the dry acrylic fiber had a T_g of 92 °C, which reduced to 72 °C in wet conditions [23]. Therefore, the peak exhaustion temperature selected is well above the T_g of acrylic fiber. The bath was held at that temperature for 15 minutes. Then the required quantity of TSC was added and held for another 90 minutes. After completion of the treatment, the bath was cooled to 45 °C at 2 °C/min, the liquor drained and the treated fiber samples were rinsed with cold water for several times. They were then dried at 60 °C in an oven for 30 min. The multicoloration of PAN fibers were carried out by varying the concentration of silver nitrate in the dyebath on the weight of acrylic yarns (owf) used, the ratio of Ag to TSC, pH, and the dyeing time.

2.3. Color measurement

The color measurements of acrylic yarns dyed with various concentrations of Ag nanoparticles were carried out according to a published literature [24]. The reflectance values

and K/S values (at the appropriate wavelength of maximum absorption for each dyeing) of the dyed samples were measured using a Datacolor Spectraflash 500 spectrophotometer interfaced to a personal computer. Samples were measured under illuminant D65, using a 10° standard observer with UV component and specular both excluded. Yarns were evenly wrapped on a paperboard and four measurements were made at four different places of each sample and the average value is reported here. The color difference was spectrophotometrically measured by measuring $CIE L^*$, a^* , b^* color difference (ΔE) between two different areas of the same sample under illuminant D65, using a 10° standard observer by a Minolta hand-held spectrophotometer (Konica Minolta Corporation, Japan).

2.4. Mechanical properties

The tensile strength of the control and silver nanoparticle-treated acrylic yarns were measured by using an Instron Tensile Testing Machine (Model 4501, Instron Corporation, Norwood, USA) at 20 ± 2 °C and $65 \pm$ % relative humidity according to the ASTM Test Method D2343-02: *Standard Test Method for Tensile Properties of Glass Fiber Strands, Yarns, and Rovings Used in Reinforced Plastics*. The gauge length was 80 mm and the traversing speed was 50 mm/min. The samples were conditioned at the above-mentioned temperature and humidity for at least 2 days. At least 10 samples were measured for each treatment and the averages are reported here. The surface resistance of acrylic yarns was carried out at 20 °C and 45% relative humidity by a high resistance meter with a two-point probe (Model MEGARESTA II-A, Shishido Electrostatic, Ltd., Japan) with SSD-A type probe at an applied voltage of 100 V.

2.5. UV Absorption and colorfastness

The treated acrylic yarns were uniformly mounted on a cardboard with a big hole. Thermo Scientific UV-VIS Spectrophotometer (Model: Evolution 200, Thermo Fisher Scientific Inc., Waltham, USA) with a Diffuse Reflectance Measurement attachment was used to assess the percent transmission of light through the acrylic yarns at wavelength intervals up to 5 nm in the 290–400 nm spectral span. The color fastness to washing of the yarns was measured according to the ISO Test Method 105-C03 1987: *Textiles – Tests for colorfastness – Part C03: Color fastness to washing: Test 3* by washing in a Gyrowash (Model 415/8) using the phosphate-free standard detergent. In both cases, fastness grades were assessed by comparing with the 3M Grey Scale.

2.6. Fourier transform infrared spectroscopy (FTIR)

The surface of Ag nanoparticle-treated acrylic yarns was characterized by using a Shimadzu FT-IR (Model Prestige 21, Shimadzu Corporation, Japan) 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. 64 scans were signal-averaged.

2.7. Assessment of antibacterial activity

The antibacterial properties of acrylic yarns treated with Ag nanoparticles at various concentrations were assessed according to the AATCC Test Method 100–1999 (*Antibacterial Finishes on Textile Materials: Assessment of*) against *Staphylococcus aureus* (ATCC 6538) and *Klebsiella pneumoniae* (ATCC 4352). A bundle of treated acrylic yarns was placed in individual sterile Petri dishes. The nutrient broth was prepared with 5 g/l peptone and 3 g/l beef

extracts and the pH was adjusted to 6.8 ± 0.1 with 1N sodium hydroxide solution. The bacterial culture of appropriate type diluted 100 times 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 Petri dishes were then incubated at 37 ± 2 °C for 48 h. The number of bacteria before and after the incubation is measured by a colony counter and the reduction in bacteria is measured which is expressed in percentage. This method provides a quantitative assessment of the antimicrobial performance of antibacterial textile materials as it provides a percentage of killing of a particular bacteria.

2.8. Surface morphologies

The surface morphology of the acrylic yarns coated with in situ formed silver nanoparticles was investigated by using the field emission scanning electron microscopy (SEM) technique. The treated yarn 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 acrylic yarns was carried out by an energy dispersive X-ray (EDX) using the same model of JEOL SEM at 15 kV. To examine the cross-sectional surface of acrylic fibers, fiber bundles of straightened acrylic fibers were coated with a molten polycaprolactone polymer to form a round-shaped composite strand and then slices of fibers were cut perpendicular to the length of the fibers by a sharp knife. The cross-sectional area of fibers was scanned by the same FESEM in back-scattered mode.

3. Results and discussion

3.1 CIE $L^*a^*b^*$ values and color strength

As shown in Fig. 1, the color of the silver nanoparticle-treated acrylic yarns with various Ag concentrations and also at different Ag to TSC ratios is ranged from yellow, greyish green to bluish-black as shown in Fig. 1. Table 1 shows CIE $L^*a^*b^*$ values and color strength of colored acrylic yarns.

3.1.1. Effect of concentration of Ag

The effect of Ag concentration on the shades produced and color strength of acrylic yarns was investigated by varying the concentration of Ag from 0.5 to 3.0% owf using the Ag to TSC ratio of 1:2, as at this ratio stable Ag nanoparticles are formed [25]. Fig. 1 shows the change in color and also the color strength of the acrylic yarns with an increase in the concentration of Ag. The color of the yarns turned from bright white for the 0% Ag to very pale bluish, violet, light yellowish brown to deep yellowish brown for the 2.0% Ag. The color strength of the treated acrylic yarns increased with an increase in the concentration of Ag. Table 1 shows the CIE L^* , a^* and b^* values of acrylic yarns treated with various concentrations of Ag. It is evident that the lightness value (L^*) decreased and the color strength increased with an increase in the applied concentration of Ag. It was found that the minimum concentration of Ag to produce color in acrylic yarns is 2.0% owf as below that concentration produced no color. At 0.5 % Ag, the inherent color of the acrylic fiber was only marginally changed and the produced color strength was only 0.05, which was even, lower than the undyed acrylic fiber. At the silver concentration, 1.0% owf produced color strength only 0.15 and even at 2% Ag concentration, the color strength produced was only 1.32 (Fig. 1), which is considerably lower compared to the color strength produced by

synthetic dyes at this level of concentration. The produced color was dull, and the intensity of the color produced was nowhere near to the color strength of basic dyed acrylic yarns.

The color, shape and the size of Ag nanoparticles depend on 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 AgNO_3 increases the concentration of Ag nanoparticles and therefore the color strength of the treated fabric increased with an increase in the concentration of AgNO_3 .

3.1.2. Effect of Ag to TSC ratios

To know the effect of the increasing ratio of Ag to TSC on the color of the treated fabrics, we varied the Ag to TSC ratio from 2:1 to 1:8. Fig. 1 shows the change in color and also the color strength of acrylic yarns treated with 2.0% Ag at an increase in the ratio of Ag to TSC from 2:1 to 1:8. The treated yarns using Ag to TSC ratios 2:1 and 1:1 are almost colorless. The color of the yarns turned to pale brown, deep yellowish brown and bluish-black with an increase in the ratios of Ag to TSC up to 1:8. It can be seen that the color strength of acrylic yarns treated with 2.0% Ag increased with an increase in the Ag to TSC ratios. The acrylic fibers colored with in situ generated Ag nanoparticles using Ag to TSC ratios 2:1 and 1:1 produced very poor color strength and the produced color was not stable as the produced silver nanoparticles were unstable. It can be seen that the value of L^* decreased and the color strength of the acrylic fiber increased with an increase in the Ag to TSC ratio (Table 1). The deepest shade was achieved when the Ag to TSC ratio was 1:8, which is consistent with the reflectance and color strength data. It was found that 1:6 is the optimum Ag to TSC ratio as increasing the ratio more than 1:6 hardly increased the color strength.

Kelly and Johnston found that the conversion of Ag^+ to Ag nanoparticles are related to the concentration of TSC used as a reducing agent and at low concentrations of TSC only partial

conversion of Ag^+ to Ag nanoparticles took place and increasing the concentration fully converted into Ag nanoparticles [15]. It is also known that to stabilize the formed Ag nanoparticles, the ratio of Ag to TSC should be at least 1:2. Our results also show that no color was produced when the ratio of Ag to TSC was less than 1:2. The increase in the ratio of Ag to TSC beyond 1:2 changed the color of the treated acrylic fibers from brown to bluish grey indicating that the size of the nanoparticles increased with an increase in the ratio of Ag to TSC. Thottoli and Unni also found that in the case of ZnS nanoparticle formation, the size of the nanoparticles increased with an increase in the concentration of TSC [28].

3.1.3. Effect of pH

The effect of pH is very important as the pH has an effect on the adsorption of silver into acrylic fibers. The effect of pH on color strength was investigated at acidic to neutral pHs (3, 5 and 7) as acrylic fibers have low resistance to alkali. Table 1 shows *CIE L*a*b** values and color strength of acrylic fibers colored with silver nanoparticles at various pHs at 2.0% owf Ag for 2 hr at 90 °C. The acrylic yarns treated with 2.0% Ag using Ag to TSC ratio 1:2 at pH 3 produced the deepest color and the one treated at pH 7 produced the lightest color. The color strength of the acrylic yarns decreased with an increase in the pH (Fig. 1). It is evident that the lightness values (L^*) also increased with an increase in the pH. The color strength of the acrylic fiber dyed at pH 3, was 1.32, which decreased to 1.07 and 0.8 when the treatment pHs was increased to 5 and 7 respectively (Fig. 1). Therefore, pH 3 was the optimum pH for the coloration of acrylic with Ag nanoparticles.

Dong et al. investigated reduction of AgNO_3 to Ag nanoparticle at pH from 5.7 to 11.1 and found that the reduction of the silver precursor (Ag^+) was promoted with an increase in the pH [29]. 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 were formed at pH 2.5 [30]. However, we found that the fabric sample treated at pH 3 showed the highest color strength. As the fibers are anionic, most of the applied Ag^+ should be absorbed into the fiber at that pH resulting in the in situ formation of Ag nanoparticles. However, the absorption of Ag^+ into acrylic fibers decreased with an increase in the pH of the bath resulting in the formation of Ag nanoparticles outside the fibers, and they did not absorb into the fibers at the increased pHs. Therefore, the color strength of the treated acrylic yarns decreased with an increase in the pH.

3.1.4. Effect of reaction time

Fig. 1 shows the effect of the dyeing time on the value of L^* and the color strength of the acrylic fiber 2.0% Ag using the Ag to TSC ratios and at pH 3 for a different time. It is evident that the color strength increased with an increase the treatment time. The deepest shade was achieved when the treatment time was 120 min. It can be seen that even up to 90 min of treatment time the color strength produced was very low, which considerably increased in the final 30 min of the treatment. Dong et al. found that at low pH the reduction of AgNO_3 to Ag nanoparticle is very slow which affects the nucleation and growth of Ag nanoparticles [29]. Therefore, the color strength of the treated fabric increased with an increase in the reaction time.

3.1.5. Colorfastness to washing

Colorfastness to washing grades of acrylic yarns treated with silver nanoparticles using various concentrations of Ag, Ag to TSC ratios and treatment pHs are shown in Table 1. It can be seen that the overall colorfastness to washing is excellent (grade 4–5) only if the applied Ag concentration is 2.0% owf and above and the Ag to TSC ratio is 1:2 and above.

Overall, the color fastness to washing of the colored acrylic yarns produced by in situ formed silver nanoparticles is reasonably good.

It is known that Ag nanoparticles release Ag⁺ ions in an aqueous media and therefore fastness of the treatment should decrease with multiple times of washing [31]. It can be expected that most of the Ag nanoparticles adsorbed onto the surface of acrylic fibers (especially for the treatment carried out at high pH) would be released during washing. Therefore, the wool fabric treated at pH 3 should better fastness to washing compared to the acrylic fibers treated at pH 5 and 7. Similarly, the fabric treated using Ag to TSC ratio less than 1:2 also showed poor washing fastness due to the formation of unstable Ag nanoparticles. The good wash fastness indicates that the in situ formation of silver into the cationic acrylic fiber enhanced the durability of the treatment to washing.

3.2. UV transmission through the fiber

UV radiation levels are divided into three zones, UV-A (320–400 nm), UV-B (290–320 nm) and UV-C (200–290 nm). Only UV-A and UV-B reach earth and therefore protection against UV-A and UV-B are important. Fig. 2 shows the effect of applied Ag concentration, Ag to TSC ratio and the pH on the UV transmission through the colored acrylic yarns. It is evident that the treatments with silver nanoparticles considerably reduced the UV transmission through the treated yarns. The UV transmission through the acrylic yarns decreased with an increase in the applied Ag concentration and the highest reduction in UV transmission was observed for the applied Ag concentration 3% owf and beyond that level, no further reduction was observed. The untreated acrylic fibers show low transmission of UV-B, which was considerably enhanced with the treatment with silver nanoparticles. At 290 nm, the undyed acrylic yarns showed UV transmission only 17.72%, which reduced to 8.88%

for the yarns treated with 0.5% Ag. The highest reduction in UV transmission was observed for the applied Ag concentration 3% as at that concentration the UV transmission reduced to only 0.6%. Similarly, UV-A transmission also decreased with an increase in the applied concentration of UV-A and at 340 nm, the UV-A transmission reduced to only 1.9% from 27.2% observed for the control acrylic fiber. It is also evident that the UV-A and UV-B transmission decreased with an increase in the Ag to TSC ratios. The ratios 2:1 and 1:1 showed low UV transmission as they produced unstable silver nanoparticle but 1:2 and higher showed an excellent reduction in UV transmission as they produced very stable silver nanoparticles. The effect of pH of the treatment on the UV transmission showed that the fibers treated at pH 5 and 7 showed very similar UV-B transmission, which was much higher compared to the UV transmission observed for the acrylic fibers treated at pH 3. However, for the UV-A, the transmission decreased with a decrease in the pH of the treatment. The silver nanoparticle-treated acrylic yarns showed excellent UV protection capability.

3.3. Surface resistivity

The antistatic properties of synthetic fibers are quite important as the synthetic fiber-made fabric has a tendency to stick to the body due to static charge development in the fabric. The surface resistivity of silver nanoparticle-treated acrylic yarns is shown in Fig. 3. The surface resistance shown by the untreated acrylic yarn is very high (1200×10^9 Ohm/cm), i.e. it does not show any antistatic property. On the other hand, acrylic yarns colored with in situ formed silver nanoparticles using various concentrations of Ag showed considerably lower surface charge compared to the surface charge shown by the untreated acrylic yarns. The surface resistivity of the acrylic yarns decreased with an increase in the applied Ag concentration. The surface resistivity decreased from 1200×10^9 Ohm/cm for the control to 9.2×10^9 Ohm/cm for

the 2% owf concentration of silver. On the other hand, the ratio of Ag to TSC showed mixed results. The lowest surface resistivity was shown by the acrylic yarn that was treated with silver nanoparticles with an Ag to TSC ratio 1:2. It is known that when the Ag to TSC ratio is below 1:2, unstable silver nanoparticles are formed. Increasing the Ag to TSC ratio increased the surface resistivity. On the other hand, the reaction pH also showed some levels of effect on the surface resistivity of the acrylic yarns treated with silver nanoparticles. The surface resistivity of the acrylic yarns treated with Ag nanoparticles decreased with a decrease in the pH. The isoelectric point of acrylic fiber is 3 [32], i.e. below pH 3 the fiber surface is cationic and 3 is anionic. Therefore Ag is better absorbed at pH 3 or below compared to the higher pH. Therefore the yarns treated at pH 3 showed lower surface resistivity compared to the yarns treated at pH 5 and above.

3.4. Elemental analysis by EDX

Table 2 shows the elemental analysis of C, O, N, and Ag elements of untreated and silver nanoparticle-treated acrylic yarns. The EDX spectra and elemental mapping of C, O, N, and Ag are shown in Figs. S1 and S2 respectively (please see Electronic Supplementary Material). The control acrylic fibers show no presence of Ag, which is expected. On the other hand, for the acrylic yarns treated with various concentrations of Ag, the elemental Ag % increased with an increase in the applied concentration of Ag. The highest concentration was observed for the 3% owf of Ag and the lowest for the 0.5% of Ag.

3.5. Mechanical properties

The effect of silver nanoparticle treatment on the tensile strength and elongation at peak of unmodified and silver nanoparticle-treated acrylic yarns using various concentrations of Ag, AG to TSC ratios and pHs are shown in Fig. 4. It can be seen that the tensile strength and also the elongation at peak initially decreased and then increased with an increase in the concentration of Ag. The strength decreased from 2.80 kgF for the untreated control to 2.12 kgF for the applied concentration of 1.0% Ag. After which the tensile strength started to increase and reached 2.86 kgF for the 2.0% Ag, which is almost similar to the original strength of unmodified acrylic fibers. A similar trend was shown also for the elongation at the peak which decreased from 38.5% to 30.9% and then again increased to 36.2% with an increase in the concentration of Ag. Probably, Ag nanoparticles formed ionic bonding between the macromolecular chains of acrylic as the TSC-capped silver nanoparticles are anionic, which reduced the macromolecular chain mobility resulting in a decrease in the elongation of acrylic fibers. On the other hand, the increase in the Ag to TSC ratio, the strength increased to 2.86 kgF for the Ag to TSC ratio 1:2, which is similar to the strength of control acrylic fiber, which then again started to decrease with an increase in the Ag to TSC ratio. The elongation at peak also showed a trend consistent with the trend shown for the tensile strength. On the other hand, the tensile strength decreased with an increase in the pH of the treatment, although the effect was only marginal. It is envisaged that the formation of acrylic/Ag nanoparticle composite fiber caused the reinforcement of the acrylic fiber, which is consistent with the findings reported by Harifi and Montazer for the polyester fabric treated with iron-oxide nanoparticles [33].

3.6. Antibacterial properties

It is known that silver nanoparticle-treated textiles show very good antimicrobial performance against a wide range of bacteria [34,35]. Fig. 5 shows the durability of the antibacterial performance to multiple washing of acrylic yarns multi-functionalized with silver nanoparticles using 2% Ag against *Staphylococcus aureus* and *Klebsiella pneumoniae*. It is evident that the treated yarns showed excellent antibacterial activity against both types of bacteria and the excellent antimicrobial activity retained even after 20 washes. Before washing, the treated yarns showed 99.8 and 99.0% killing of *Staphylococcus aureus* and *Klebsiella pneumoniae* respectively. The corresponding values for the 20 washes were 99 and 98.4% respectively. It can be seen that only marginal reduction of antibacterial activity was observed even after 20 times of washing, indicating excellent durability of the treatment.

It was reported that for textiles treated with Ag nanoparticles unbound or loosely bound to textiles by a resin to the fiber surface, sometimes not only silver ions but also silver nanoparticles are released into the environment resulting in poor durability to laundering [36]. As in the case of acrylic fiber, the Ag nanoparticles were in situ formed and therefore it showed better durability to washing compared to non-substantive textiles treated with silver nanoparticles.

3.7. FTIR

Acrylic fibers used by the textile industry contain at least 85% polyacrylonitrile and the rests are other copolymers and additives added to polyacrylonitrile to enable their dyeing with conventional dyes [36]. Therefore, the FTIR spectrum of acrylic fiber not only contains the typical peaks associated with acrylonitrile but also peaks associated with other additives. Fig. 6 shows the ATR-FTIR spectra of undyed acrylic fiber and also acrylic fiber dyed with silver nanoparticles. The spectrum of undyed acrylic fiber shows typical acrylic fiber peaks at

1730 and 2242 cm^{-1} that are associated with nitrile ($\text{C}\equiv\text{N}$) and stretching vibration of ($\text{C}=\text{O}$) ester linkage respectively [37,38]. The carbonyl peak is coming from the carboxyl-containing copolymers or additives. The peaks at 1230, 1362, and 1457 cm^{-1} could be associated with the $-\text{CH}_2$ wagging, C-H in-plane bending, and the $-\text{CH}_2$ bending vibration of the polyacrylonitrile macromolecular backbone, respectively [39,40]. The small peaks at 1027 and 2927 cm^{-1} are associated with sulfonate groups from possibly acryloamidopropane sulfonic acid additive and $-\text{CH}_2$ stretching vibration of the polyacrylonitrile molecular chains respectively. The small peaks at 1653 and 1542 cm^{-1} represent the characteristic amide absorption bands. The Ag nanoparticle treated acrylic yarns also showed similar peaks but the intensity of the some of the peaks slightly decreased.

3.8. Surface morphologies

The surface of untreated and Ag nanoparticle-treated acrylic fibers was characterized by SEM to observe the assembly of silver nanoparticles formed on the fiber surface. Fig. 7 shows SEM images of acrylic fibers multifunctionalized with in situ generated silver nanoparticles. As shown in Fig. 7, an assembly of sphere-shaped silver nanoparticles evenly spread on the fiber surface. It is evident that they are strongly bonded to the fiber surface as no loosely hold nanoparticle is observed. Some aggregation of silver nanoparticles is evident on fiber surface at 2% owf of Ag. There is a possibility that nanoparticles may also form inside the fibers. Therefore, to observe the cross-sectional surface of fibers, the cross-section of fibers were cut and examined by SEM. The optical micrographs of the cut surface of the treated fibers are represented in Fig. 8. It is evident that nanoparticles were mostly formed at the outer edge of the fibers, which consistent with the findings of other researchers [22]. However, it is evident not only at the outer edge of the fibers but also inside the fiber

nanoparticles were formed. The SEM images prove that silver nanoparticles are formed in situ in the fibers.

4. Conclusions

Multifunctional acrylic fibers were produced by treating with silver nanoparticles at various Ag concentrations, Ag to TSC ratios, pHs and time. It was found that the colored acrylic fibers were produced only if the Ag concentration was at least 1.5% owf and also the Ag to TSC ratio 1:2 and the treatment time was 120 min. The produced color varied from yellow to brown to bluish black. The color strength increased with an increase in the concentration of Ag and also with an increase in the Ag to TSC ratio. The silver nanoparticle-treated acrylic yarns showed excellent multifunctional properties as the silver nanoparticle-treated yarns showed excellent antimicrobial activity, UV radiation absorption, good antistatic property and also produced wash fast colored yarns. The lowest resistance was shown by the acrylic fiber dyed with 2.0% Ag with an Ag to TSC ratio 1:2 and treated for 120 min. The acrylic fibers colored with silver nanoparticles showed excellent antimicrobial property against *Staphylococcus aureus*, and *Klebsiella pneumoniae* for at least 100 domestic washes. The developed treatment method can be used in textile industry to produce multifunctional acrylic fibers.

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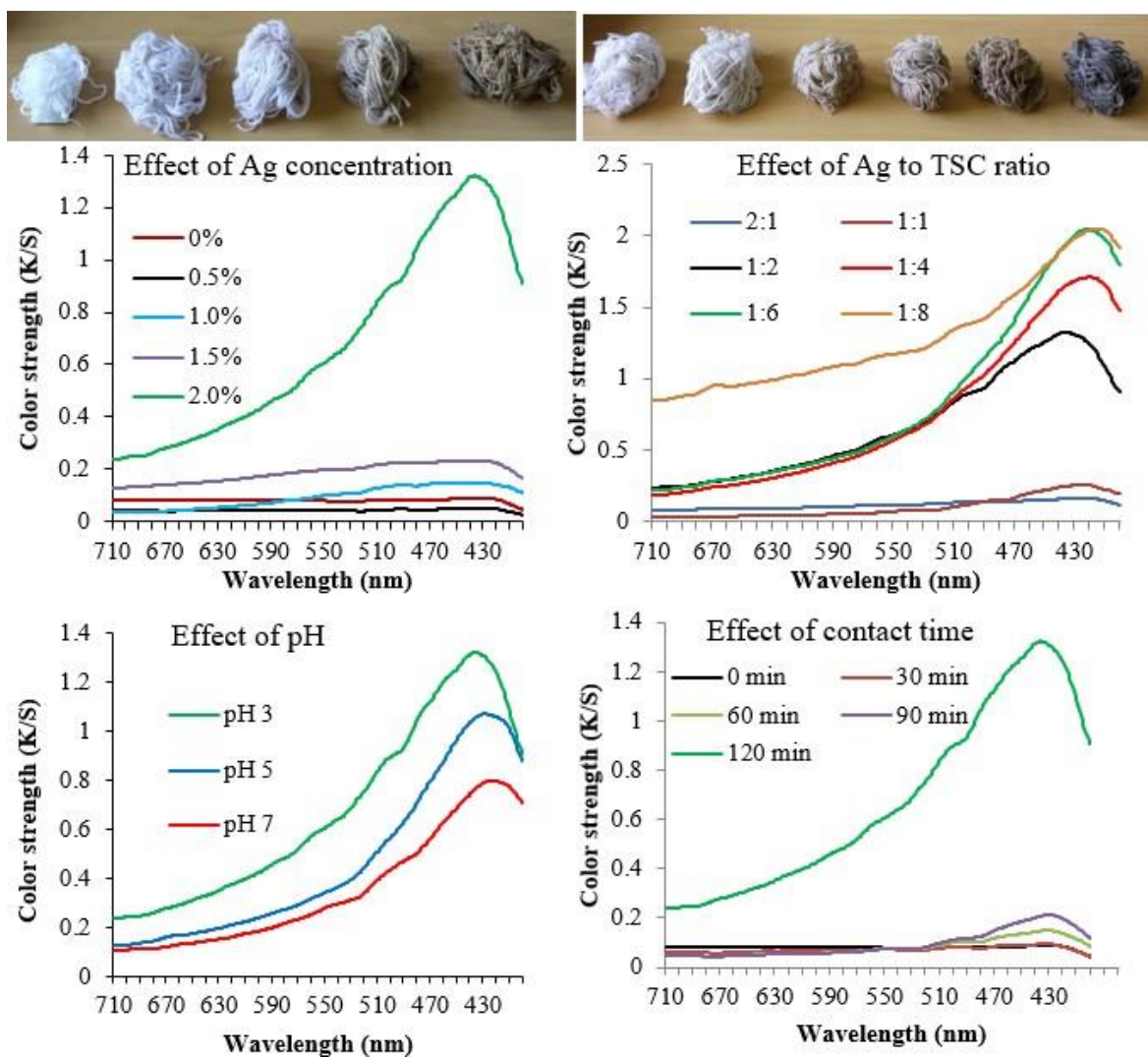


Fig. 1. The effect of the applied concentration of Ag, Ag to TSC ratio, pH, and treatment time on the color strength of acrylic fiber multi-functionalized with silver nanoparticles. Ag conc. = 2.0% owf; Ag to TSC ratio = 1:2; pH = 3; and treatment time = 120 min.

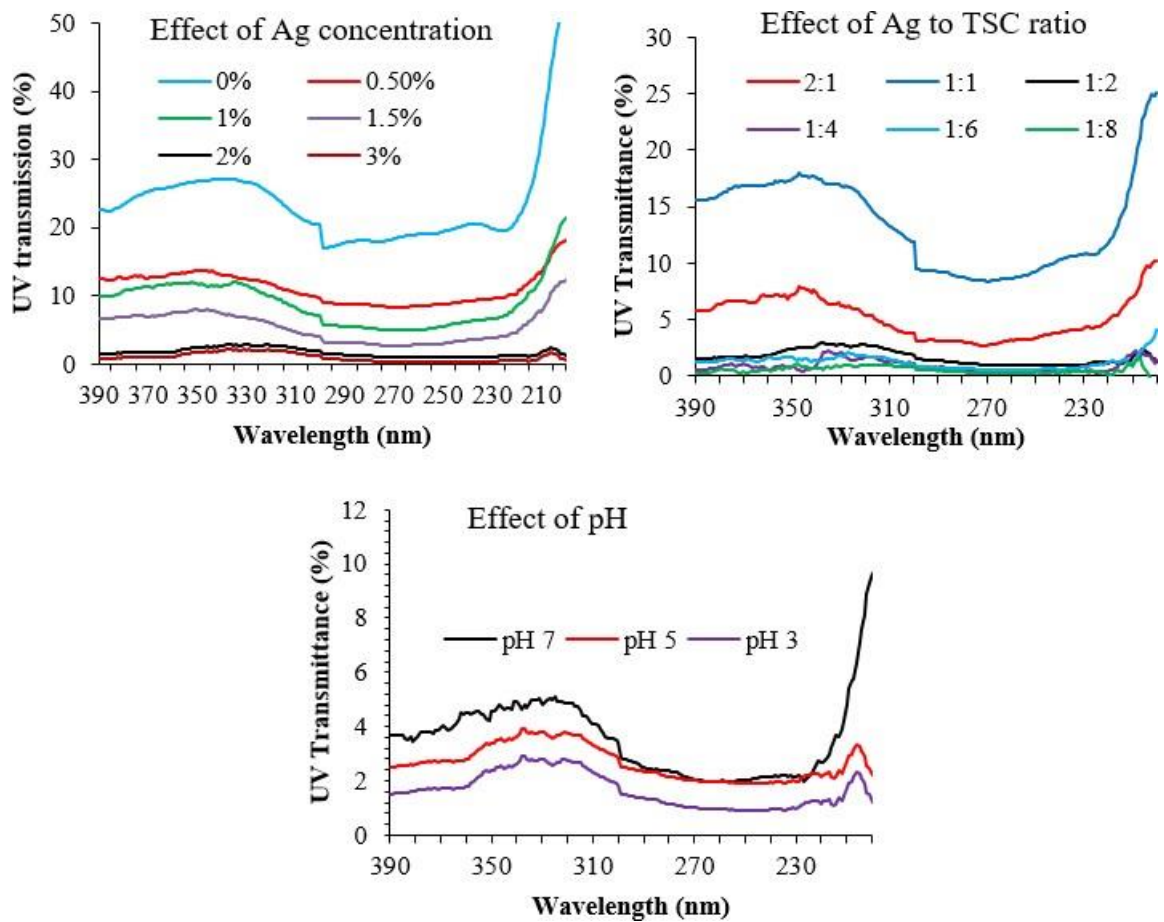


Fig.2. The effect of the concentration of Ag, Ag to TSC ratio, and pH on the UV transmission through the acrylic yarns multifunctionalized with silver nanoparticles. Ag conc. = 2.0% owf; Ag to TSC ratio = 1:2; pH = 3; and treatment time = 120 min.

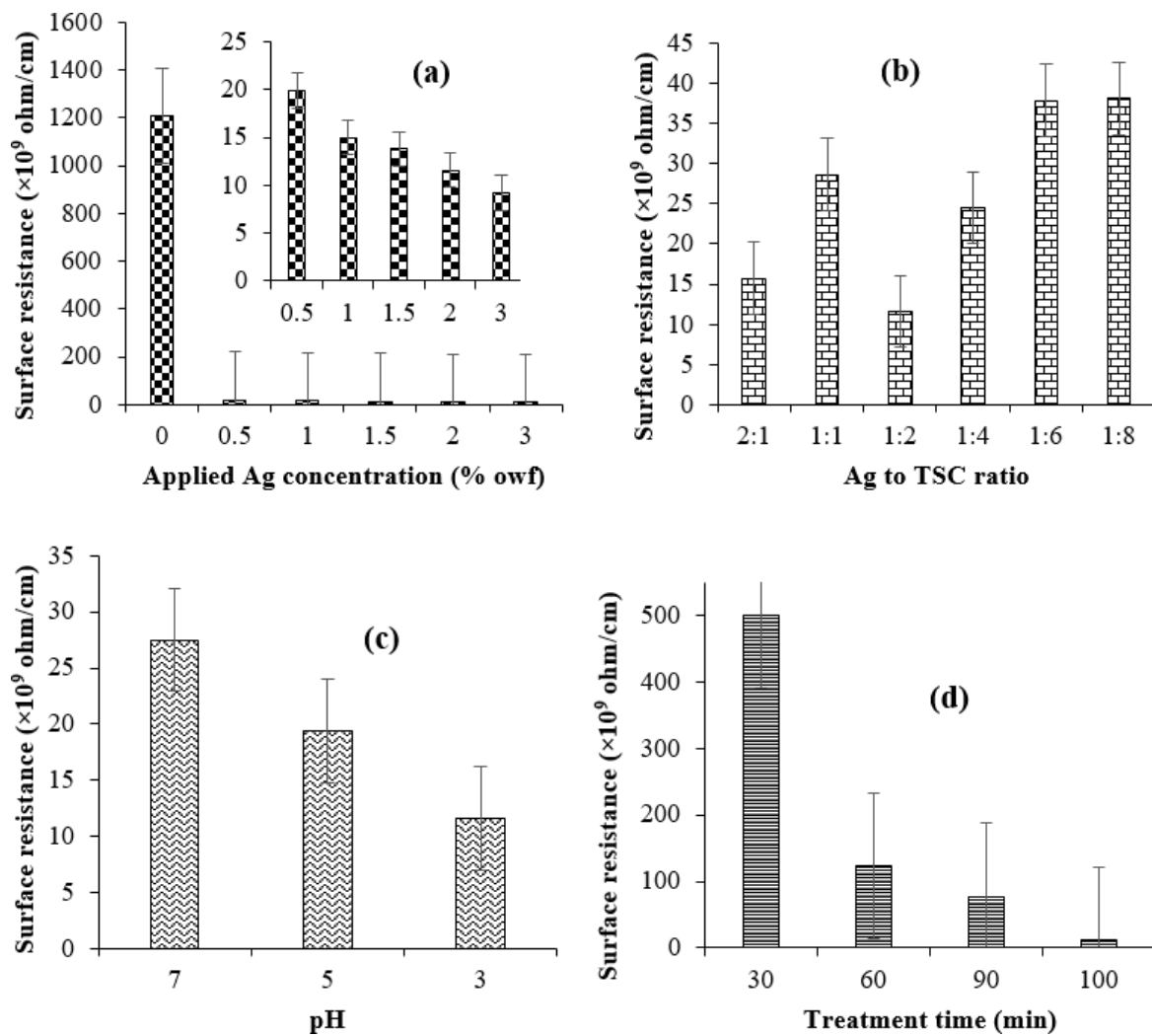


Fig. 3. Effect of the applied concentration of Ag (a), Ag to TSC ratio (b), pH (c) and treatment time (d) on the surface resistance of acrylic fiber multifunctionalized with silver nanoparticles. Ag conc. = 2.0% owf; Ag to TSC ratio = 1:2; pH = 3; and treatment time = 120 min.

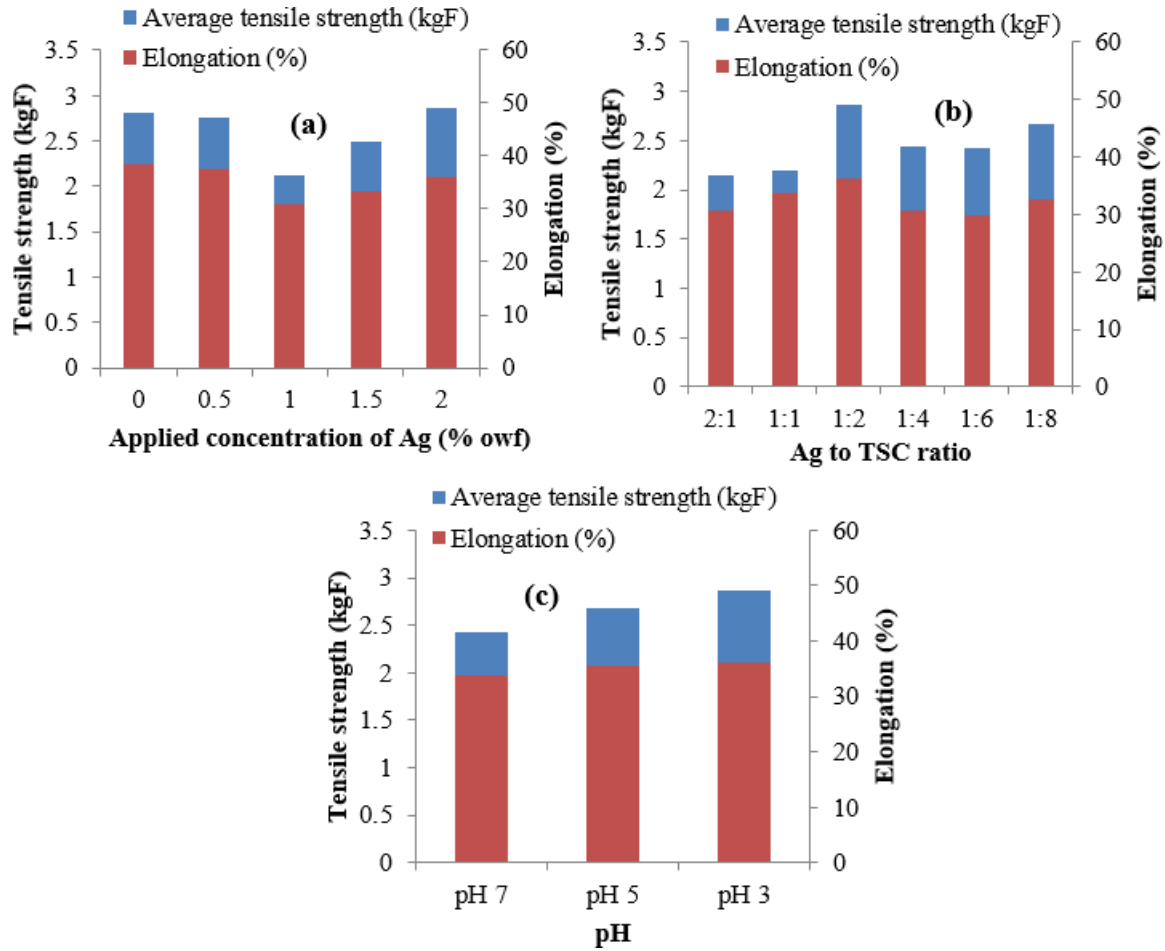


Fig. 4. Effect of the applied concentration of Ag (a), Ag to TSC ratio (b), and pH on the tensile strength and elongation at peak of the acrylic yarns multifunctionalized with silver nanoparticles.

Ag conc. = 2.0% owf; Ag to TSC ratio = 1:2; pH = 3; and treatment time = 120 min.

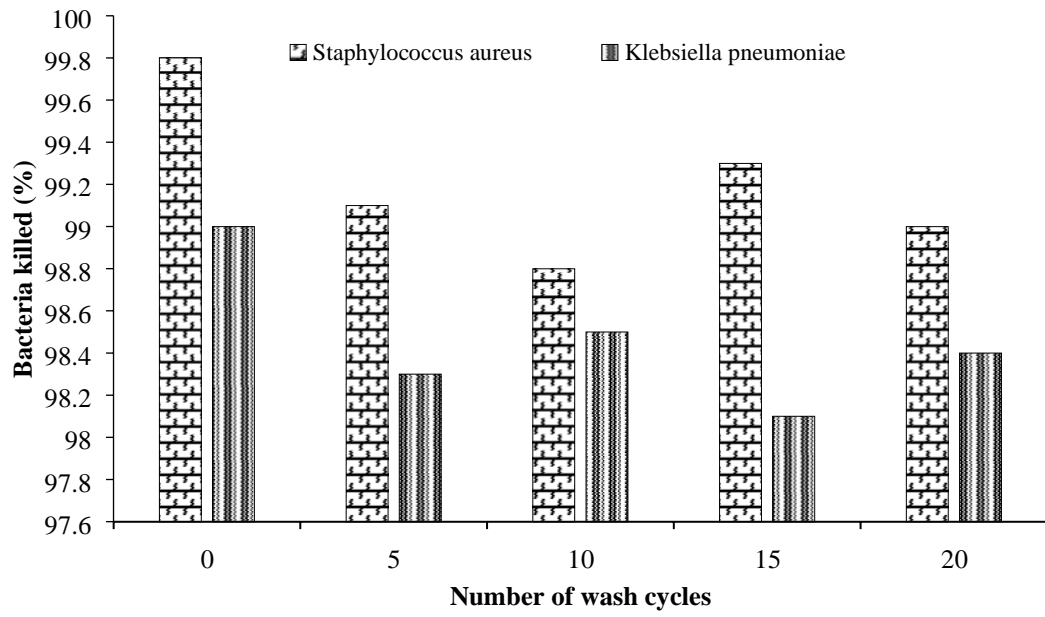


Fig. 5. The effect of multiple washing on the antibacterial activity of acrylic yarns multi-functionalized by treating with 2% owf Ag using Ag to TSC ratio 1:2 at pH for 120 min.

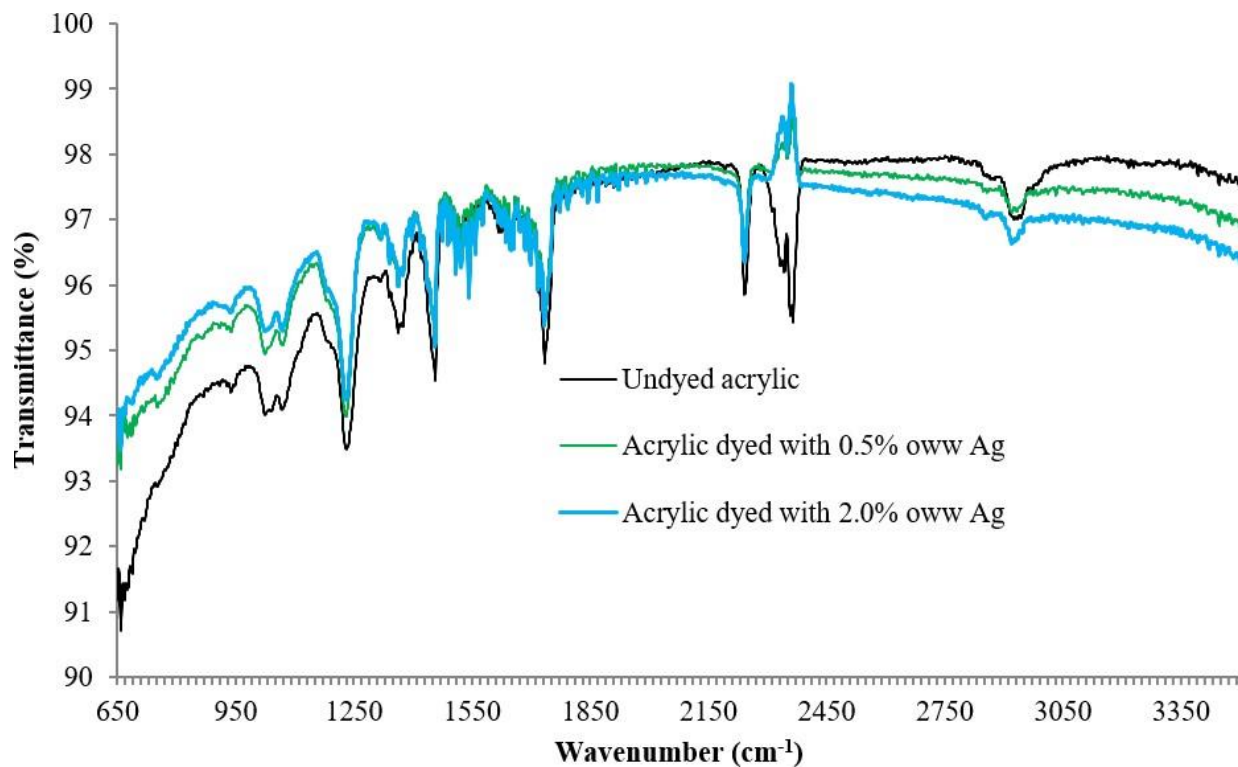


Fig. 6. ATR-FTIR spectra of untreated acrylic yarns and also acrylic yarns multifunctionalized with silver nanoparticles (0.5 and 2.0% owf of Ag) for 120 min using Ag to TSC ratio 1:2 at pH 3.

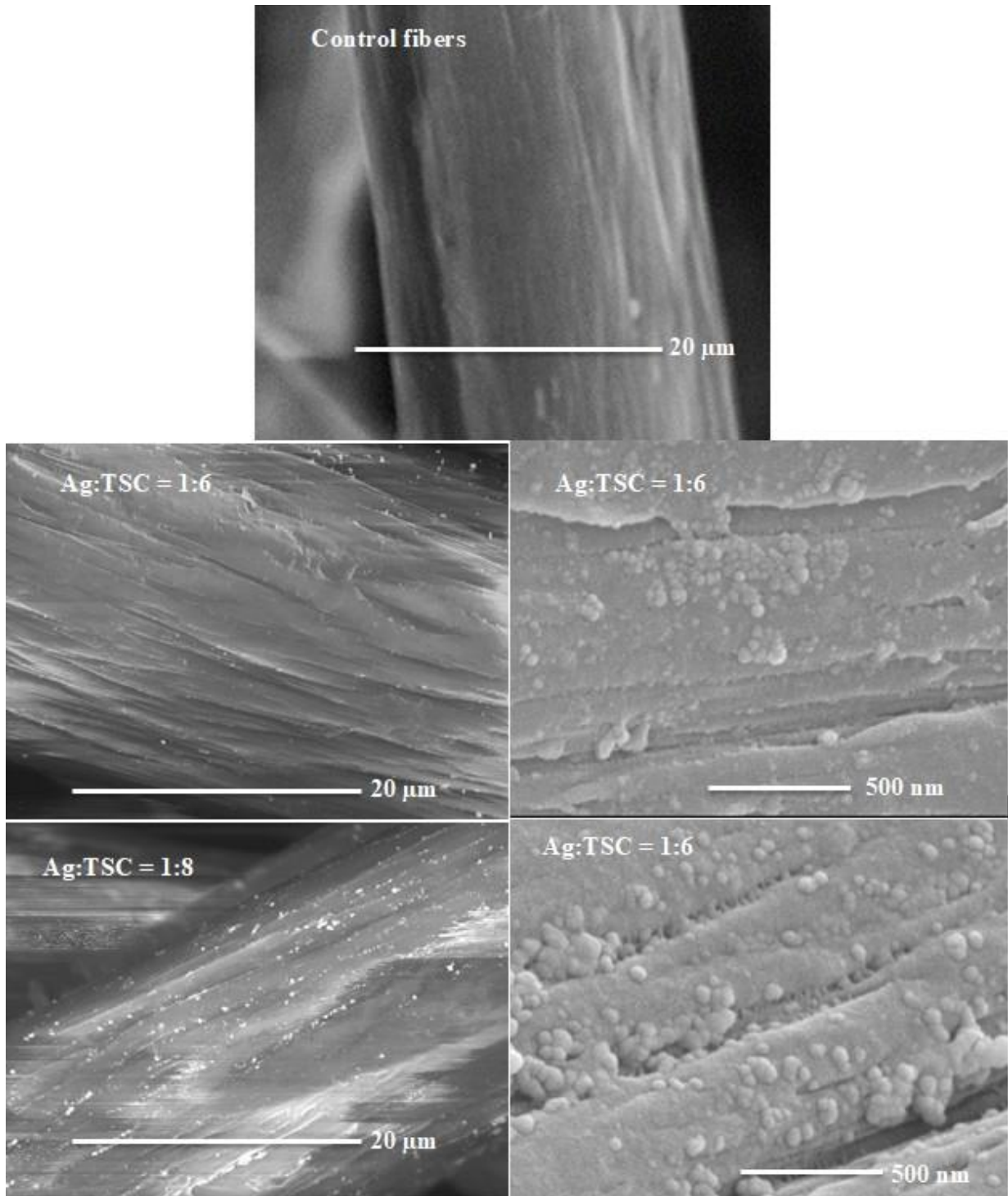


Fig. 7. FESEM images of control acrylic yarns (top) and also acrylic yarns treated with 2.0% owf of Ag using Ag to TSC ratios of 1:6 (middle) and 1:8 (bottom) at pH 3 for 120 min.

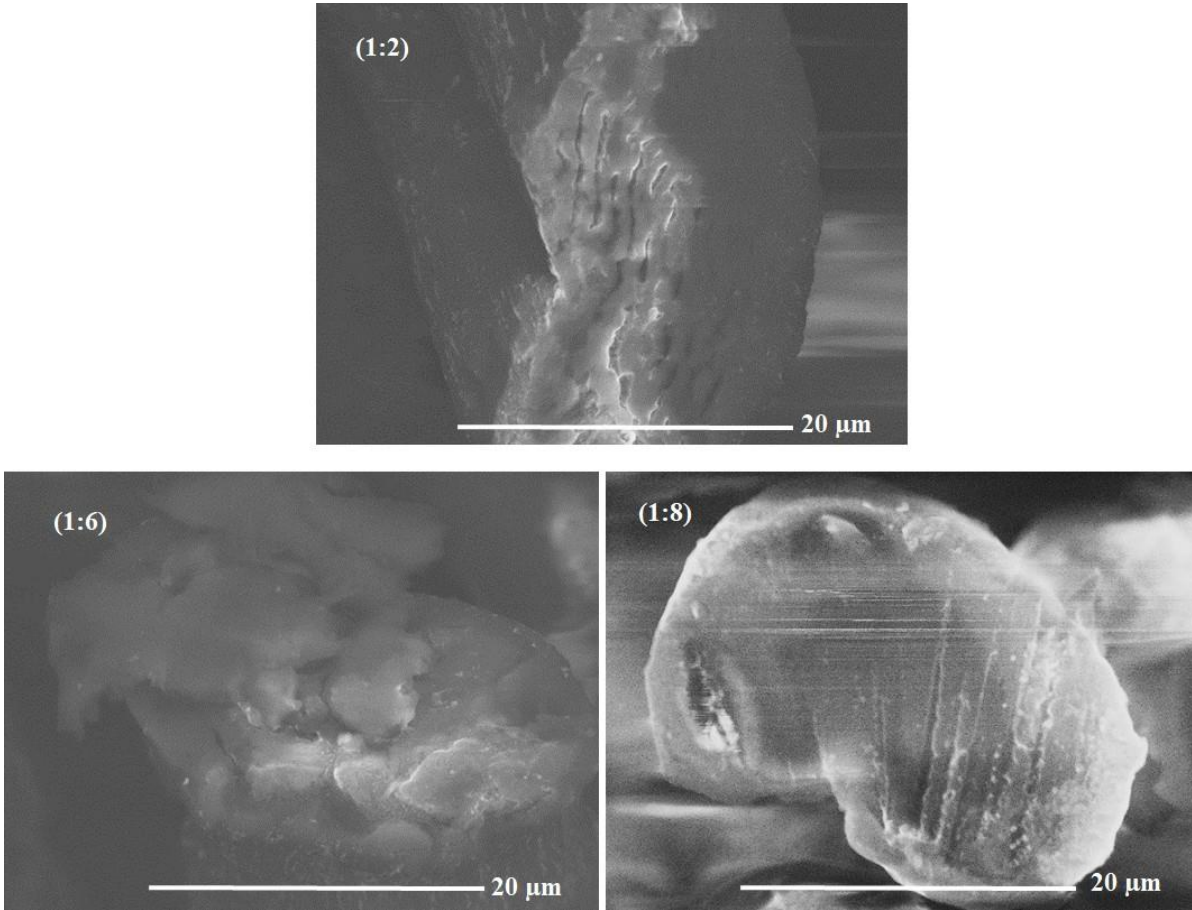


Fig. 8. Back-scattered cross-sectional SEM images of in situ formed silver nanoparticles inside wool fibers using the Ag concentration of 2.0% (owf) at Ag to TSC ratios 1:2, 1:4, and 1:8 at pH 3 for 120 min.

Table 1.

*CIE L*a*b** values and colorfastness to washing of acrylic yarns multifunctionalized with Ag nanoparticles at various conditions.

Sample ID	Concentration of Ag (% owf)	Concentration of Ag (owf)	Treatment time (min)	Ratio of Ag to TSC	pH	L*	a*	b*	Colorfastness to washing ratings
Control	2.0	2	120	-	-	80.68	1.92	1.95	0
<u>At different Ag concentrations</u>									
Sam A	0.5	0.5	120	1:2	3	80.96	1.57	3.56	4
Sam B	1.0	1	120	1:2	3	72.65	5.89	10.05	4
Sam C	1.5	1.5	120	1:2	3	62.55	3.63	5.11	4
Sam D	2.0	2	120	1:2	3	49.4	7.31	19.65	4-5
	3.0	3	120	1:2	3				
<u>At different TSC concentrations</u>									
Sam E	2.0	2	120	2:1	3	76.24	3.3	6.6	2-3
Sam F	2.0	2	120	1:1	3	72.37	4.1	15.77	2-3
Sam G	2.0	2	120	1:2	3	52.51	5.91	18.14	4-5
Sam H	2.0	2	120	1:4	3	49.4	7.31	19.65	4-5
Sam I	2.0	2	120	1:6	3	46.43	5.84	21.98	4-5
Sam J	2.0	2	120	1:8	3	38.53	2.56	9.11	4-5
<u>At different pH</u>									
Sam K	2.0	2	120	1:2	3	49.4	7.31	19.65	4-5
Sam L	2.0	2	120	1:2	5	57.16	5.28	17.61	4
Sam M	2.0	2	120	1:2	7	60.31	5.28	18.18	4
<u>At different reaction time (min)</u>									
Sam N	2.0	2	30	1:2	3	79.6	1.90	1.93	Not measured
Sam O	2.0	2	60	1:2	3	73.45	4.76	3.50	Not measured
Sam P	2.0	2	90	1:2	3	64.30	4.21	8.90	Not measured
Sam Q	2.0	2	120	1:2	3	62.70	3.82	5.45	Not measured

Table 2.

EDX elemental analysis of untreated and multifunctionalized acrylic yarns with Ag nanoparticles using various concentrations of Ag.

Concentration of silver (% owf)	Mass of elements (%)			
	C	N	O	Ag
0	63.03	30.9	4.85	0
0.5	62.31	34.01	3.43	0.25
1.0	61.66	35.51	2.45	0.38
1.5	61.31	32.96	5.25	0.54
2.0	62.58	32.87	3.61	0.93
3.0	61.93	32.3	4.45	1.32

Multifunctional acrylic fibers prepared via in-situ formed
silver nanoparticles: Physicochemical, UV radiation
protection and antistatic properties

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Electronic Supplementary Material

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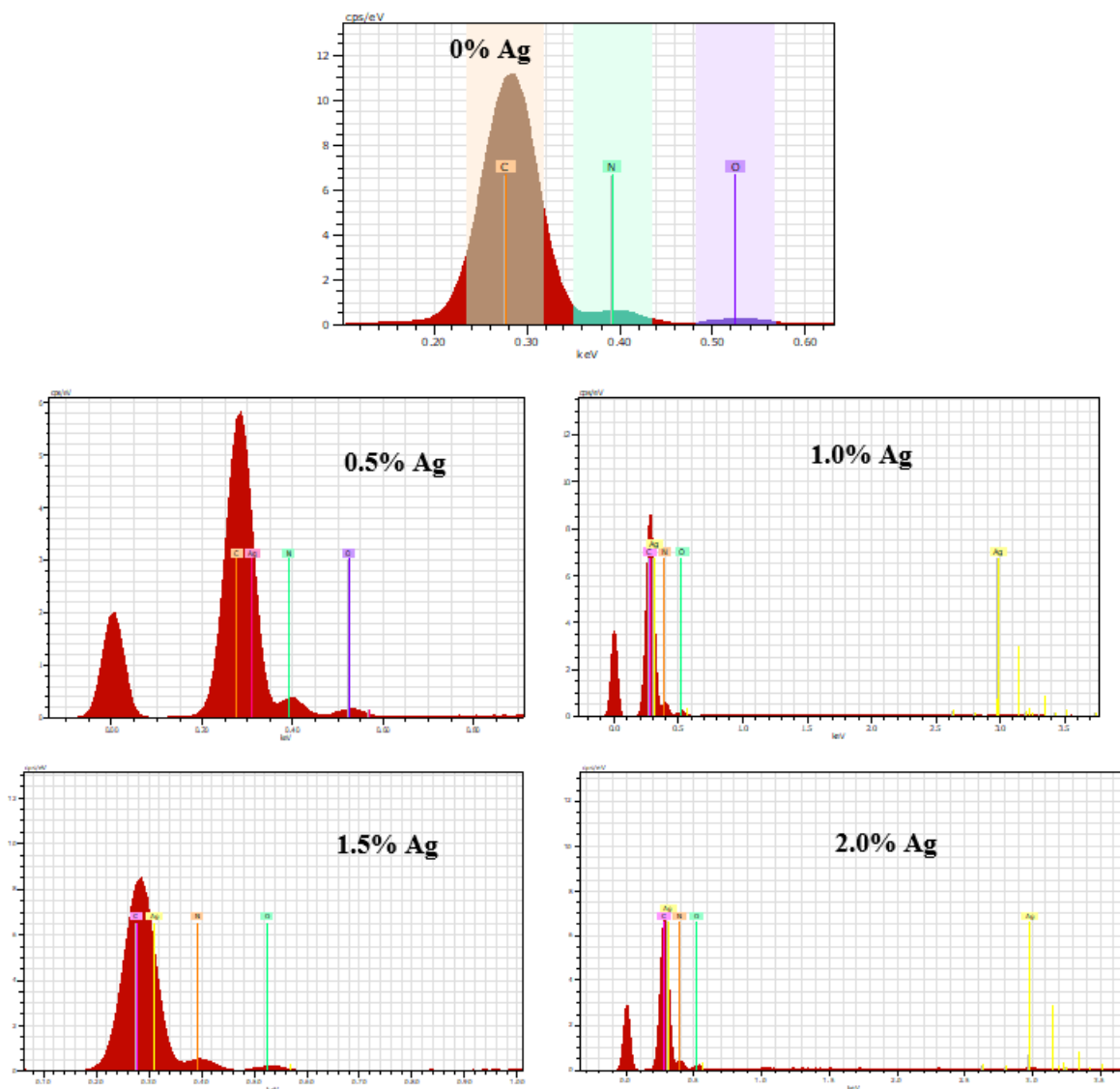


Fig. S1. EDX spectra of undyed acrylic yarns and also acrylic yarns treated with various concentration of Ag (% owf) using the Ag to TSC ratio of 1:2 for 120 min at pH 3.

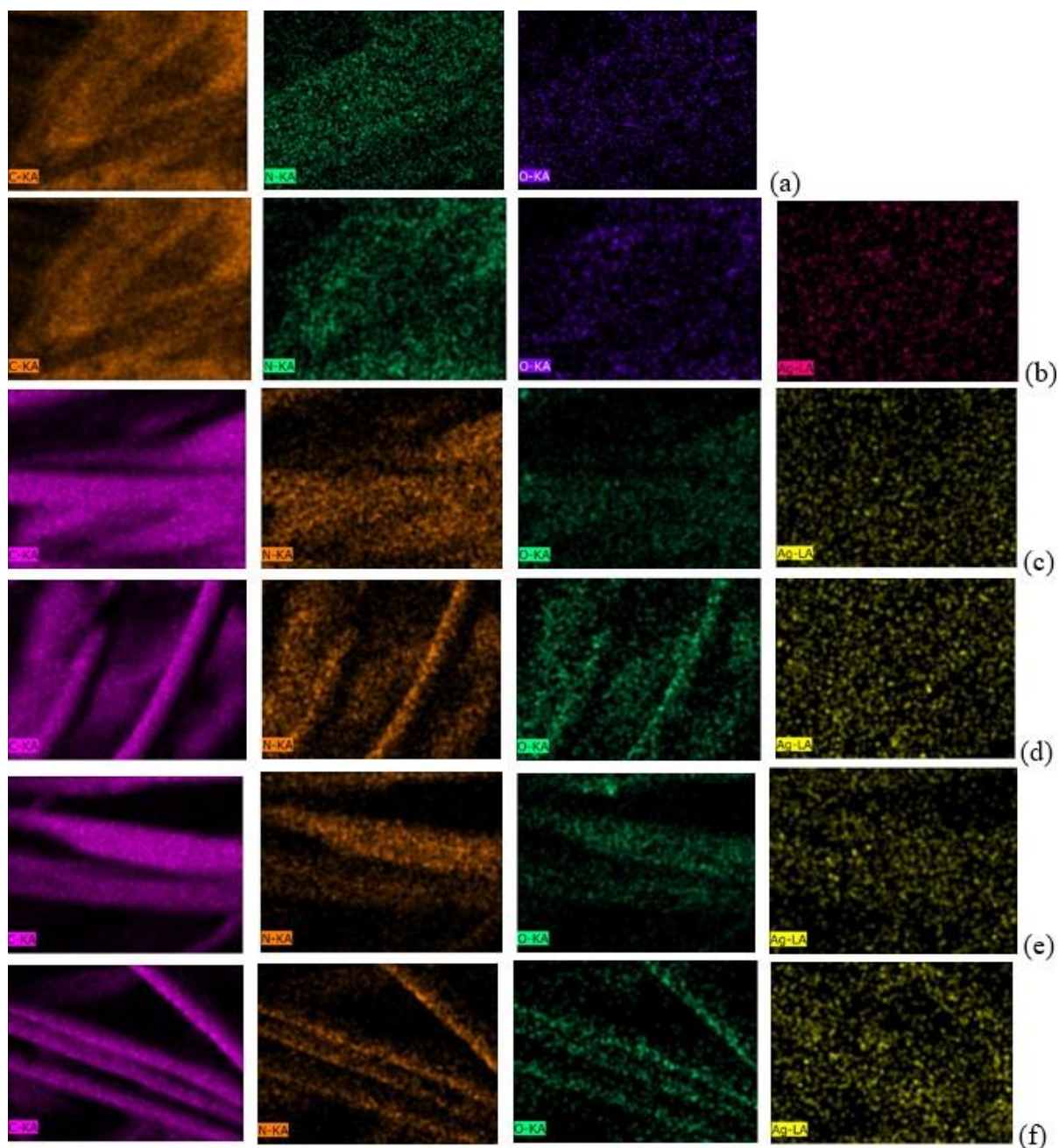


Fig. S2. Elemental distribution of C, N, O, and Ag in the acrylic yarns multifunctionalized by treating with 0 (a), 0.5 (b), 1.0 (c), 1.5 (d), 2.0 (e) and 3.0% (f) of Ag using Ag to TSC ratio 1:2 for 120 min.