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Biodegradation of silver functionalised cellulose fibres

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ABSTRACT

The efficiency of different chemical forms of silver in protecting cellulose fibres against biodegradation was studied using a soil burial test. Cotton samples were finished using nanopowder of elemental silver with a particle size of 30 nm (Ag-1), dispersion of AgCl (Ag-2), and colloidal silver (Ag-3) of different concentrations. The degree of biodegradation was determined by SEM, colour measurements, tensile strength, degree of polymerization and FT-IR spectroscopy. The results showed that a strong agglomeration of Ag-1 led to its insufficient antimicrobial activity, since it was restricted only to Ag^+ released from the surface of elemental silver by reduction. Despite the agglomeration, a concentration of Ag^+ released by the dissociation of AgCl of the finish Ag-2 in the presence of moisture was high enough to provide excellent protection against fibre biodegradation. The high protective properties of Ag-3 were probably caused by the synergistic action of Ag nanoparticles and Ag^+ cations.

1. Introduction

The durability of textiles produced by the cellulose fibres is directly related to their biodegradation, since they are mainly comprised of cellulose and therefore highly susceptible to bacteria and fungi in water, soil and air, which, in the presence of moisture, heat and dirt, form a biofilm on the surface of the fibres and, during their growth and development, cause depolymerization of the cellulose macromolecules (Allen, Auer, & Pailthorpe, 1995; Clarke, 1997; Desai & Pandey, 1971; Itävaara, Siika-aho, & Viikari, 1999; Montegut, Indictor, & Koestler, 1991; Park, Kang, & Im, 2004; Salerno-Kochan & Szostak-Kotowa, 2001; Szostak-Kotowa, 2004). Although the biodegradability ranks cellulose fibres among environmentally friendly renewable natural materials, biodegradation of the fibres can cause serious functional, aesthetic and hygiene problems of products that are still in use, especially if they are used for protective clothing, textiles for sport and leisure, the military, textiles for the home and decorative textiles. Protection of the cellulose fibres against microorganisms is therefore of great technological importance.

Successful protection of cellulose fibres against biodegradation can be obtained in various ways, which include either worsening the conditions of the microorganisms' growth, or active antimicrobial protection of the fibres. Both forms of protection can be obtained by chemical modification of the cellulose fibres, whereby finishes of various chemical structures can provide active or passive antimicrobial properties to the modified fibres. On this basis, the application of water and oil repellent finishes causes a significant drop of fibre wettability, resulting in a decrease in the amount of moisture required for microbial growth (Montegut et al., 1991; Park et al., 2004; Tomšič, Simončič, Cvijin et al., 2008; Tomšič, Simončič, Orel et al., 2008; Vilčnik et al., 2009). Furthermore, modification of cellulose fibres by durable press finishes causes the formation of covalent bonds between the finish and the cellulose macromolecules, which strengthens the less ordered amorphous regions, resulting in a decrease of fibre swelling (Tomšič, Simončič, Orel, Vilčnik, & Spreizer, 2007). This inhibits the penetration of microorganisms into the fibres, in which biodegradation takes place. However, the most effective protection against fibre biodegradation can certainly be obtained by applying antimicrobial agents that could directly interact with the microorganisms, causing their destruction (Dring, 2003; Purwar & Joshi, 2004; Schindler & Hauser, 2004).

Among modern antimicrobial agents that can be used as antimicrobial finishes for textiles, silver based compounds are of great technological importance (Chen & Schluesener, 2008; Lee, Yeo, & Jeong, 2003; Lok et al., 2006; Mahltig, Fiedler, & Böttcher, 2004; Morones et al., 2005; Rai, Yadav, & Gade, 2009). It has been shown that silver bound on a solid surface, as well as in solution, acts as a very effective biocide. Its advantage over other antimicrobial agents is the biological compatibility and low toxicity toward mammalian cells (Kusnetsov, Iivanainen, Elomaa, Zacheus, & Martikainen, 2001). Commercially available products based on

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silver mostly include the hard to dissolve salt AgCl, an elemental nanosilver in the form of a powder of different particle dimensions and colloidal silver. According to the literature (Adams, Santschi, & Mellencamp, 1999; Ahearn, May, & Gabriel, 1995; Choi et al., 2008; Gorenšek & Recelj, 2007, 2009; Maneerung, Tokura, & Rujiravanit, 2008; Matyjas-Zgondek, Bacciarelli, Rybicki, Szynkowska, & Kołodziejczyk, 2008; Tomšič et al., 2009; Wasif & Laga, 2009; Yeo, Lee, & Jeong, 2003), all three chemical forms of the silver particles have already been successfully applied to textile fibres in order to increase their antimicrobial properties. In our previous research (Tomšič et al., 2009) it was demonstrated that aqueous AgCl applied together with a reactive organic–inorganic binder matrix possesses antimicrobial properties on cotton fabrics and that its antibacterial activity against the bacterium *Escherichia coli* was higher than antifungal activity against the fungi *Aspergillus niger* and *Chaetomium globosum*. Namely, the minimum inhibitory concentration of Ag in the coating providing a sufficient bacterial reduction of 60% was ca 24 mg/kg, but effective antifungal activity was achieved only at Ag concentrations higher than 100 mg/kg. Furthermore, we have also determined (Tomšič, Simončič, Cvijin et al., 2008; Tomšič, Simončič, Orel et al., 2008) that, at the same concentrations on cellulose fibres, the antibacterial activity of aqueous AgCl against bacterium *E. coli* was higher than that of elemental nanosilver of a particle size of 30 nm. On the other hand, Gorenšek and Recelj (2007) determined that application to cotton fibres of silver nanopowder with a particle size of 80 nm, in combination with the reactive dyes by the exhaust dyeing procedure, caused 98% bacterial reduction of the bacteria *Streptococcus feacalis* and *Staphylococcus aureus*, if the concentration of Ag on the fibres was high enough, which proved its excellent antibacterial activity. As can be seen from the literature, most contemporary research work in the field of antimicrobial finishing of cellulose fibres has focused on the application of colloid silver (de Santa Maria et al., 2009; Ilić et al., 2009; Maneerung et al., 2008; Petica, Gavriliu, Lungu, Buruntea, & Panzaru, 2008; Tankhiwale & Bajpai, 2009; Tien, Tseng, Liao, & Tsung, 2009). This research work includes a study of the influence of the mode of production of the Ag nanoparticles, which directly influences the diameter of the nanoparticles, on their biocidal activity, as well as the washing resistance of the finish when present on the fibres. The results of these studies have shown that the antimicrobial activity of Ag nanoparticles strongly increases with a decrease of nanoparticle size, which results in an increase of their specific surface area. At this point, it should be stressed that the antibacterial activity of colloidal silver, mostly against *E. coli*, has been investigated much more intensively than its fungicidal activity.

To our knowledge, there have been no reports on the influence of silver based compounds on the biodegradation of cellulose fibres. In order to obtain this information, the present research included the chemical modification of cellulose fibres with three commercially available products based on silver, i.e., nanopowder of silver in elemental form with an average particle size of 30 nm, a dispersion of AgCl and colloidal silver of various concentrations. The biodegradability of the finished as well as unfinished cellulose fibres was measured by a soil burial test, in which cotton fabric samples were buried in commercial grade compost for periods of 3 and 12 days. Structural changes after different periods of biodegradation were determined from electron microscopic and spectroscopic analyses, as well as tensile strength and degree of polymerisation measurements. The results of the soil burial test were correlated with the results of the bactericidal and fungicidal activities of the studied finishes determined by ISO 20645:2004 (E) and AATCC 100-1999 and modified DIN 53931 Standard methods. The significance of this research included assessment of the efficiency of different chemical forms of Ag to protect cellulose fibres against biodegradation.

2. Experimental

2.1. Materials

Plain-weave 100% cotton woven fabric with a mass of 145 g/m^2, warp density of 26 threads/cm and weft density of 23 threads/cm was used in the experiments. In pre-treatment processes, the fabric was bleached with H_2O_2 in an alkaline solution followed by neutralization with diluted CH_3COOH solution.

Three antimicrobial finishes based on silver (Ag) were used, i.e., Silver Nano Powder NP-30 (Ames Goldsmith Corp., USA) (Ag-1), which is pure superfine powder of silver in elemental form with an average particle size of 30 nm, iSys AG (CHT, Germany) (Ag-2), which is a water dispersion containing AgCl, and Ionosil (Ion Silver, Sweden), which is a colloidal silver with average particle size smaller than 10 nm (Ag-3). For dispersing and deagglomerating the Ag-1 powder in water, Setamol WS (BASF, Germany) was used as a dispersing agent, and dispersions were exposed to ultrasound before being used in the finishing process.

2.2. Finishing the cotton fabric

The finishes Ag-1, Ag-2 and Ag-3 were applied to cotton fabric at various concentrations by the exhaustion method. Ag-1 was used in concentrations of 0.05%, 0.10%, 0.25% and 0.50% of the weight of fabric (o.w.f.) (concentrations from a to d), Ag-2 in concentrations of 0.15% and 0.30% o.w.f (concentrations a and b) and Ag-3 in a concentration of 0.05%. Cotton fabric samples with a mass of 7 g were immersed in the Ag-1, Ag-2 and Ag-3 dispersions with a ratio of 1:50 and left at room temperature with intensive rotation and stirring of the finishing bath for 30 min in a Launder-ometer. The samples were then wrung and dried at room temperature. Room temperature for drying of the finished cotton samples was chosen, since the results of our previous research work (Tomšič, Simončič, Cvijin et al., 2008; Tomšič, Simončič, Orel et al., 2008) showed that the drying temperature influences neither the samples' physical properties nor the antimicrobial activity of Ag on the finished samples. Four fabric samples were treated with each dispersion, in order to provide a sufficient number of replicate samples for carrying out measurements and statistical analysis.

2.3. Analyses and measurements

2.3.1. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDXS)

The morphology of the cotton fabric finished by the Ag-1, Ag-2 and Ag-3 finishes was determined by a JEOL JSM 5800 scanning electron microscope. The samples were coated with ≈20-nm-thick carbon layer to ensure sufficient electrical conductivity and to avoid charging effects. Analyses were performed using a 10-keV electron beam, 200–500 pA beam current and X-ray spectra acquisition under a 35° take-off angle. SEM micrographs were recorded using both secondary electron (SE) and backscattered electron (BSE) imaging modes. BSE compositional (Z-contrast) imaging was applied to emphasize and expose the difference between the added particles and the cotton fibre–matrix.

A microscopic evaluation of morphological changes occurring during the biodegradation of unfinished and finished cotton samples after 3 and 12 days of exposure to the soil microflora was carried out using a JEOL JSM 6060 LV scanning electron microscope, whereby the samples were coated with carbon and an Au/Pd (90%/10%) alloy in a layer about 10 nm thick before observation.

2.3.2. Inductively coupled plasma mass spectroscopy (ICP-MS)

The concentration of Ag in the finished cotton samples was determined by ICP-MS on a Perkin Elmer SCIED Elan DRC spectrophotometer. A sample of 0.5 g was prepared in a Milestone microwave system by acid decomposition using 65% HNO_3 and 30% H_2O_2. Three measurements were taken for each sample, and the Ag concentration was given as a mean value.

2.3.3. Soil burial test

Determination of the resistance of the unfinished and finished cotton fabrics to the action of soil microflora was carried out by a soil burial test according to ISO 11721-1:2001 and ISO 11721:2003 standards. In this standard process, a container was filled with commercial grade compost. The water content of the soil was 60 ± 5% of its maximum moisture retention capacity. It was held constant during the experiment by spraying with water. The pH of the soil was between 4.0 and 7.5. Cotton fabric samples were buried in the soil for periods of 3 and 12 days. After the defined incubation time, the samples were removed from the soil, lightly rinsed with running tap water and immersed in 70% ethanol for 30 min and dried at room temperature.

2.3.4. Colour measurements

Colour measurements of unfinished and finished cotton samples after different periods of burial time were carried out in the CIELAB colour space with a Datacolor Spectraflash SF 600 Spectrophotometer using D 65/10° light. Twenty colour measurements were taken for every sample. From the measured L^*, a^* and b^* values, the chroma, C^*, was calculated as follows:

$$C^* = \sqrt{(a^*)^2 + (b^*)^2} \tag{1}$$

2.3.5. Breaking strength

The breaking strength of unfinished and finished buried cotton samples was measured with an Instron 6022 dynamometer according to SIST ISO 5081:1996. The relative reduction in breaking strength, q_{red}, of the buried cotton samples compared with the unburied ones was calculated from the mean value of five measurements of the breaking strength for each sample, using the following relationship:

$$q_{\mathrm{red},t} = \frac{F_t}{F_{\mathrm{to}}} \tag{2}$$

where $q_{\mathrm{red},t}$ is the loss of breaking strength of the buried cotton sample after burial time t, F_t is the breaking strength of the buried cotton sample after burial time t, and F_{to} is the breaking strength of the unburied cotton sample. Before testing, the samples were conditioned at 65 ± 2% relative humidity and 20 ± 1 °C temperature for 24 h.

2.3.6. Degree of polymerization (DP)

The DP of the cellulose samples dissolved in Cuoxam, a solution of cupric hydroxide in aqueous ammonia $[Cu(NH_3)_4](OH)_2$, was determined viscosimetrically using an Oswald shear dilution viscometer.

2.3.7. Fourier transform infrared (FT-IR) spectroscopy

FT-IR spectra were obtained on a Brucker IFS 66/S spectrophotometer, equipped with an attenuated total reflection (ATR) cell (SpectraTech) with Ge crystal ($n = 4.0$). The spectra were recorded over the range 4000–600 cm^{-1}, with a resolution of 4 cm^{-1} and averaged over 128 spectra. Before measurement, the studied samples were dried for 5 h at 100 °C.

3. Results and discussion

The morphological changes and the distribution of Ag particles induced by the application of the finishes Ag-1, Ag-2 and Ag-3 to the cotton fabric can be seen from the SEM micrographs in Fig. 1. Spherically shaped silver particles were observed on samples Ag-1-c and Ag-2-b, with a particle size ranging from 100 to 500 nm, indicating that smaller as well as larger clusters of elemental silver and AgCl are present on the fabric surface as a result of the agglomeration process. At this point, it is important to stress that in the case of finish Ag-1, agglomeration of Ag particles on the cotton fibres could not be prevented despite the presence of the dispersing agent, the use of ultrasound treatment before finishing and by application of the finish by the exhaustion method, which is ensured by intensive rotation and stirring of the finishing bath. Because of the agglomeration process, there are almost no de-agglomerated Ag particles with a size of 30 nm on sample Ag-1-c, since it is decelerated by the producer. In contrast to the finishes Ag-1 and Ag-2, the application of finish Ag-3 from the colloid solution was much more uniform, with a diameter of particles which rarely exceeded 20 nm. On several larger individual particles of the finishes Ag-1 and Ag-2 on the cotton samples, the chemical structure of the Ag particles was determined with the use of qualitative EDXS microanalysis, which clearly showed the characteristic peaks belonging to the family of Ag-Lα spectral lines in the case of the finish Ag-1 and the characteristic peaks of Ag-Lα spectral lines accompanying the Cl-Kα peak in the finish Ag-2, indicating a chemical composition corresponded to the composition of AgCl salt. Unfortunately, the Ag nanoparticles of finish Ag-3 on the cotton sample were too small to be detected by EDXS microanalysis, since the signal of the Ag particle was overshaded by the signal of the cellulose.

The bulk concentration of Ag particles on the cotton samples was determined by ICP-MS analysis (Table 1). The results showed that an increase in the initial concentration of Ag-1 and Ag-2 in dispersion expectedly led to an increase in the Ag concentration on the finished cotton samples. Surprisingly, using the same concentration of the finishes Ag-1 and Ag-3 in the dispersion equal to 0.05% o.w.f., the exhaustion of finish Ag-3 was more than 3.8 times higher than that of finish Ag-1. Furthermore, the exhaustion of finish Ag-3 was also much higher in comparison to that of finish Ag-2, since only 0.05% o.w.f. of finish Ag-3 in the dispersion resulted in 130 mg/kg Ag on the cotton fibres, while a three times higher concentration of finish Ag-2 was needed to obtain a concentration of the adsorbed Ag equal to 120 mg/kg fibres. These results indicate that the concentration of Ag on the cotton fibres was not only influenced by the concentration of the finishing bath, but also by the adsorption affinity of the finish to the cotton fibres. Accordingly, the highest affinity was obtained for finish Ag-3, followed by finish Ag-2 and finish Ag-1. To explain these results, both the chemical form of the silver and its particle size should be taken into account. It is believed that the silver cations in finish Ag-2 which could form attractive electrostatic forces with the anionic charged cotton fibres in the aqueous solution have higher adsorption affinity in comparison to the non-ionic particles of the elemental silver present in the finish Ag-1, which can be adsorbed only by van der Waals forces. On the other hand, the highest adsorption affinity of finish Ag-3 is certainly related to the much smaller silver particles (≈20 nm) with a larger specific surface area, as well as to their cationic character. Finish Ag-3, namely, is decelerated as colloidal silver, which, according to the producer, includes both Ag^+ and Ag NPs in an appropriate proportion. While Ag^+ cations can be exhausted to the anionic cotton fibres to a high degree because of the attractive electrostatic interactions, the high increase of the adsorption ability of Ag NPs caused by the van der Waals forces resulted from the high surface area to volume ratio of these particles.

The efficiency of the studied finishes to protect the cotton fibres against the biodegradation process was studied by a soil burial test. Visual examination of the cotton samples removed from the test soil after different incubation times (Fig. 2) showed that the

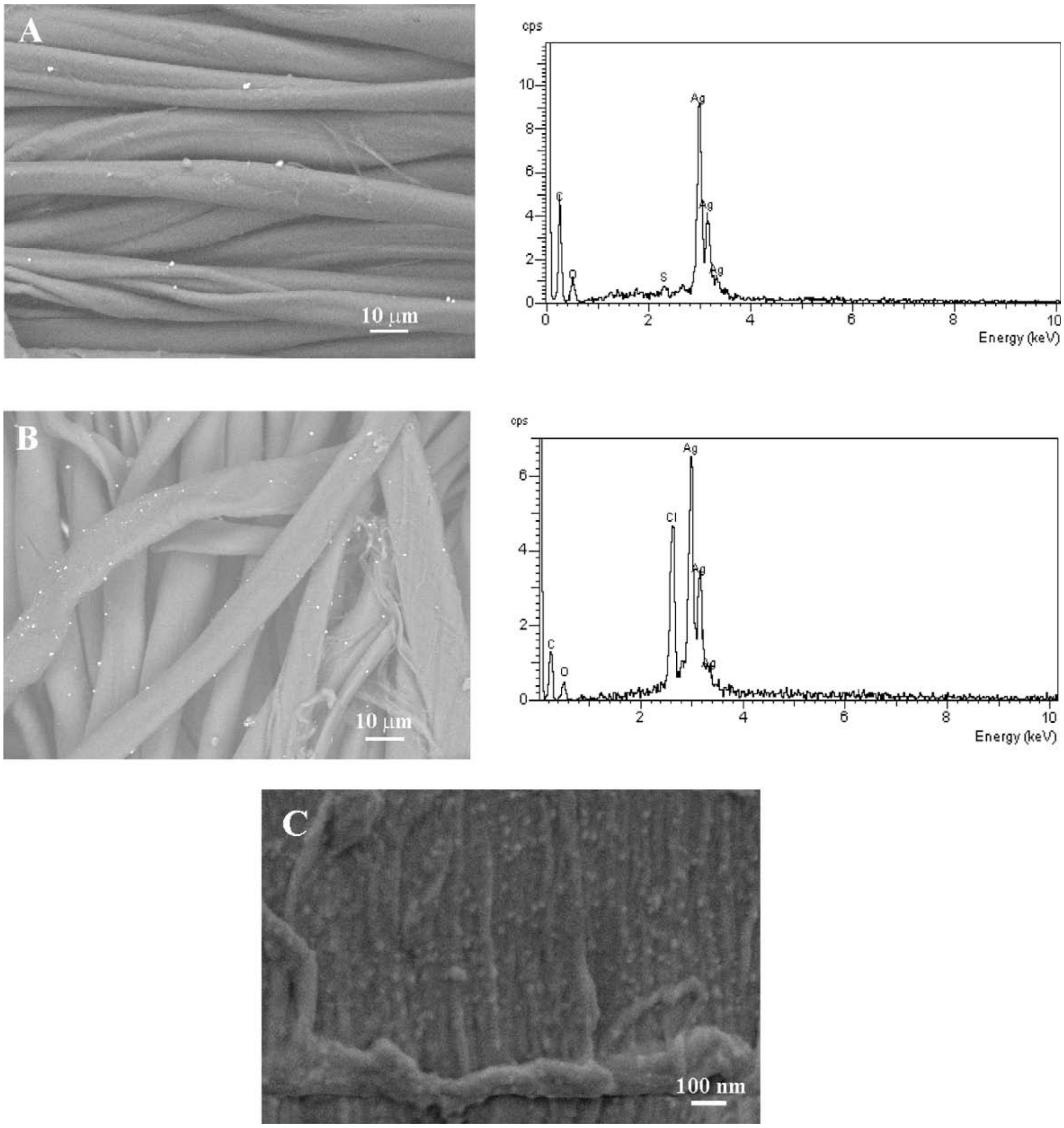

Fig. 1. SEM/BSE micrographs of cotton fabric samples with the corresponding EDXS spectra. (A) Sample Ag-1-c. (B) Sample Ag-2-b. (C) Sample Ag-3 (EDXS spectrum could not be obtained).

Table 1
Concentration of Ag on finished cotton samples determined by ICP-MS.

Antimicrobial finish	Concentration of the finish in dispersion (% o.w.f.)	Concentration of Ag on cotton sample (mg/kg)	Sample designation
Ag-1	0.05	34	Ag-1-a
	0.10	97	Ag-1-b
	0.25	176	Ag-1-c
	0.50	295	Ag-1-d
Ag-2	0.15	120	Ag-2-a
	0.30	195	Ag-2-b
Ag-3	0.05	130	Ag-3

microorganisms in the soil caused the cotton fibre to rot, which resulted in colour changes of the fabric sample surface. A higher rate of rotting was accompanied by greater colour changes. To describe this phenomenon quantitatively, the C^* value of the samples was calculated from the spectrophotometric measurements (Fig. 3). The results showed that the fibre biodegradation process was promoted by an increase of the burial time, whereby the most intensive brownish colour was obtained in the case of the unfinished sample after 12 days of burial. While finish Ag-1 only slightly inhibited fibre biodegradation, the protection by finishes Ag-2 and Ag-3 was much more effective, since insignificant colour change was observed on the finished samples.

Differences in the rotting intensities of the finished samples were also detected by the SEM micrographs (Fig. 4), which showed that the morphological changes obtained on sample Ag-1-d were much greater than those of sample Ag-2-a, in spite of the fact that the concentration of Ag on sample Ag-1-d was more than twice as high as that on sample Ag-2-a (Table 1). The SEM micrograph of sample Ag-3 (Fig. 4D) also revealed that this sample was almost unaffected by the microorganisms in the soil.

In addition, the influence of the Ag finishes on the cotton fabric biodegradation process was investigated by measurements of the

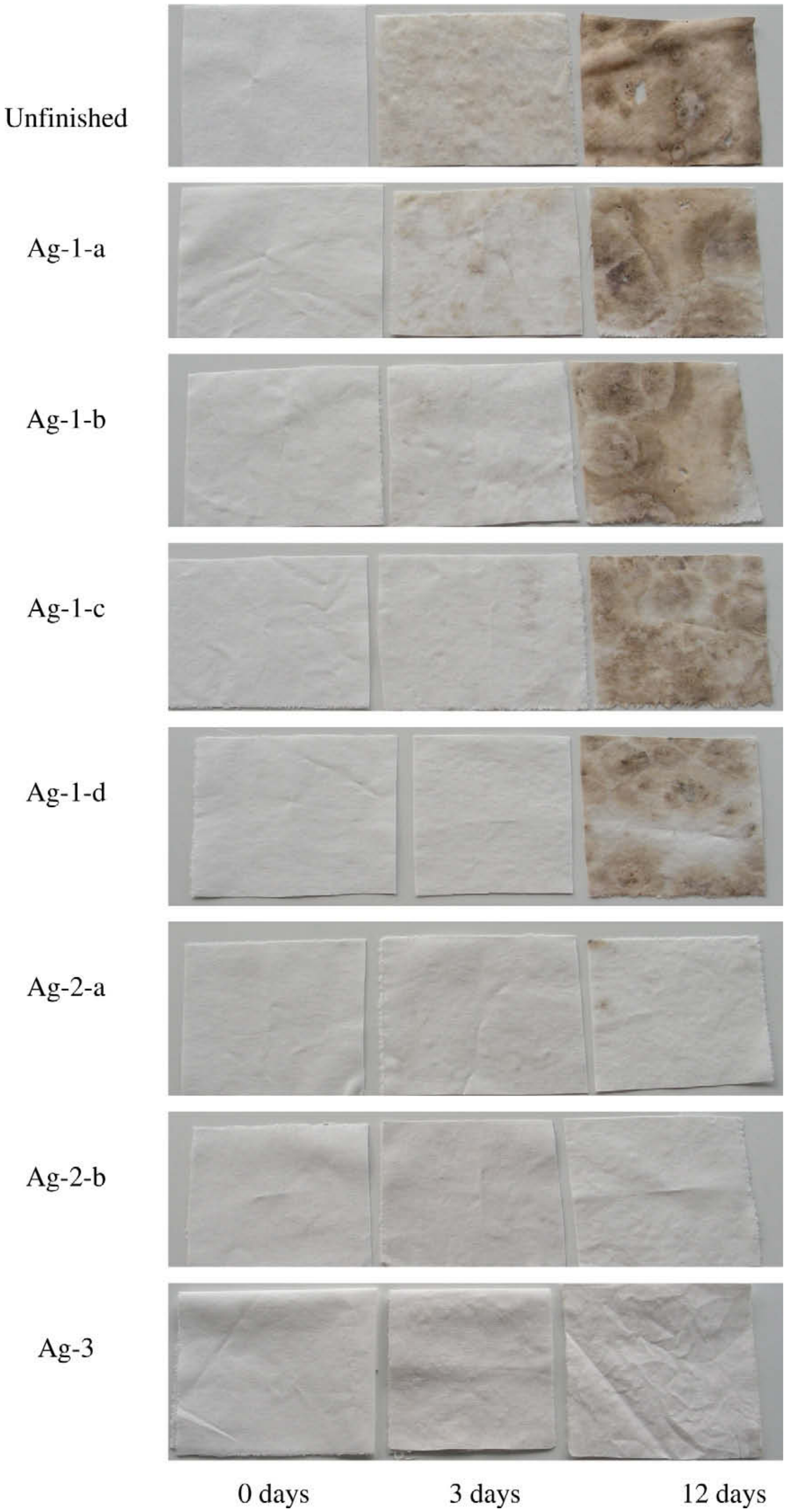

Fig. 2. Photos of unfinished and finished cotton samples before (0 days) and after 3 and 12 days of soil burial.

breaking strength and DP, since these parameters are directly influenced by the degree of sample degradation. As expected, the breaking strength of the unfinished sample greatly decreased after 12 days of soil burial (Fig. 5). The presence of finish Ag-1 in concentrations of Ag higher than 97 mg/kg slightly inhibited the biodegradation process, resulting in a lower drop of the breaking strength in comparison to the unfinished sample. In contrast to finish Ag-1, much more effective inhibition of the biodegradation

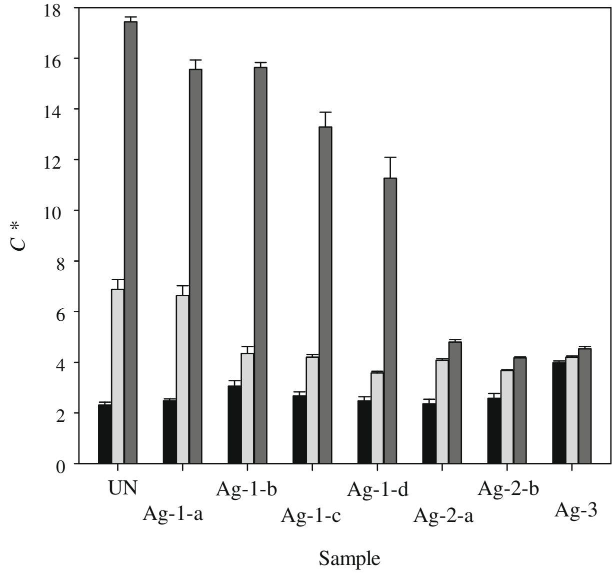

Fig. 3. Chroma, C^*, of cotton samples before (■) and after 3 (□) and 12 (▩) days of soil burial. UN – unfinished sample.

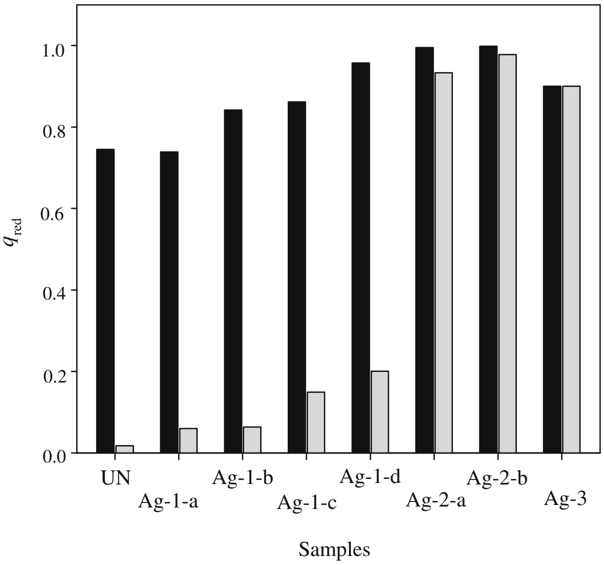

Fig. 5. The loss of breaking strength, $q_{red,t}$, of cotton samples after 3 (■) and 12 (□) days of soil burial. UN – unfinished sample.

process was observed for samples treated with finishes Ag-2 and Ag-3 (Fig. 5). In spite of the fact that the concentration of Ag on the samples Ag-1-c and Ag-1-d was higher in comparison to samples Ag-2-a and Ag-2-b, the breaking strengths of the first two samples were much lower than those of the latter ones. The values of $q_{red,t}$ equal to 0.97 and 0.90 obtained for samples Ag-2-b and Ag-3 after 12 days of soil burial indicated that the mechanical properties of these samples did not significantly decrease during exposure to the microorganisms. The results of DP (Fig. 6) were in accordance with the results of the breaking strength. Since the degree of polymerization of all measured samples decreased with increasing time of burial, the drop of DP was directly influenced by the structure and the concentration of the Ag finishes. These results showed that the highest DP drop, of about 15%, was obtained for the unfinished cotton sample after 12 days of incubation, and the lowest for samples Ag-2-b and Ag-3, which was less than 1.5%.

According to the results of our previous study (Tomšič et al., 2007), important information about the progress of the cotton fibre biodegradation process can be obtained by FTIR analysis, in which the intensity of the bands at 1640 and 1548 cm^{-1}, belonging to the Amides I and II groups (Socrates, 2001; Vince et al., 2006), resulting from the presence of protein production by microbial growth (Socrates, 2001) on fibres, should be inspected. A higher degree of fibre biodegradation is accompanied by a greater growth of

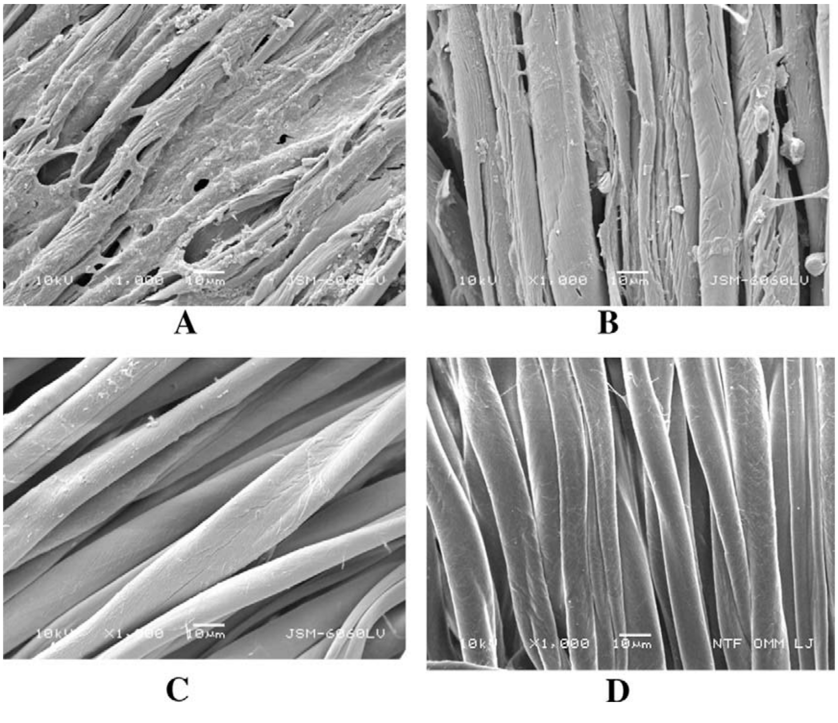

Fig. 4. SEM micrographs of unfinished cotton sample (A) and finished cotton samples Ag-1-d (B), Ag-2-a (C) and Ag-3 (D) after 12 days of soil burial.

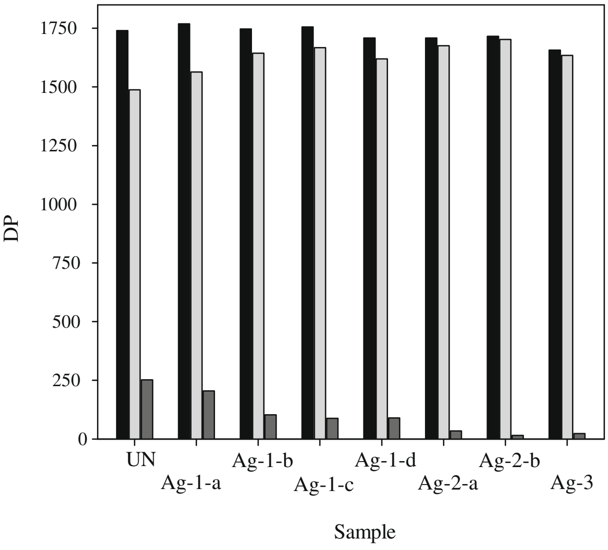

Fig. 6. DP of cotton samples before (■) and after 12 (□) days of soil burial, as well as the differences of DP (▨). UN – unfinished sample.

microorganisms on the fibres, reflected in the larger increase of the bands at 1640 and 1548 cm^{-1}. At this point, it should be stressed that silver particles present on the finished cotton samples are not chemically bonded to the cotton fibres and cannot therefore be detected by FTIR analysis. Inspection of the measured ATR spectra of unfinished and finished cotton samples (Fig. 7) revealed that, irrespective of the presence of the finish, bands that are characteristic of cellulose fibres (Hulleman, van Hazendonk, & van Dam, 1994; Kačuráková & Wilson, 2001; Langkilde & Svantesson, 1995) occur at 3340 cm^{-1} due to OH stretching, at 2918 and 2853 cm^{-1} due to CH and CH_2 stretching and at 1456, 1429, 1370, 1336, 1318, 1280, 1160, 1105, 1053 and 1029 cm^{-1} due to C–C and C–O stretching vibrations, skeletal vibrations and ring vibrations in the cellulose fingerprint region. The band at 1640 cm^{-1} due to deformation vibration of the absorbed water molecules also appeared in the spectra (Hofstetter, Hinterstoisser, & Salmen, 2006; Kondo, 1997; Łojewska, Miśkowiec, Łojewski, & Proniewicz, 2005). As was demonstrated in our previous research (Tomšič et al., 2007), the intensity of this band decreased on degraded cellulose fibres, indicating that the ability to adsorb water decreases after a period of biodegradation. However, the location of this band coincides with the band related to Amide I, the intensity of which increased with an increase in the degree of biodegradation. This phenomenon is clearly seen in the spectra of unfinished cotton samples after different period of soil burial (Fig. 8). Moreover, in addition to the increased band at 1640 cm^{-1}, a characteristic band at 1548 cm^{-1} related to Amide II was also visible in the spectrum of the degraded fibres after 12 days of burial.

Examination of the band intensities at 1640 and 1548 cm^{-1} in the spectra of the finished cotton samples after 12 days of soil burial (Fig. 9) showed that, irrespective to the concentration of the finish, a greater increase of the bands at 1640 and 1548 cm^{-1} was observed in spectra of cotton samples Ag-1-a to Ag-1-d than Ag-2-a, Ag-2-b and Ag-3. This indicated that the growth of microorganisms was greater on the former than on the latter samples. The ineffective protection of cellulose fibres against biodegradation in the presence of finish Ag-1 was not a surprise, since insufficient antibacterial activity with a reduction of the bacteria *E. coli* not higher than 60% was obtained even when the concentration of Ag-1 was raised to 350 mg/kg (Tomšič, Simončič, Cvijin et al., 2008). In contrast to finish Ag-1, finish Ag-2 caused excellent, 100% bacterial reduction of the bacteria *E. coli*, as well as sufficient fungicidal activity against the fungi *C. globosum* and *A. niger*, at concentrations higher than 100 mg/kg (Tomšič et al., 2009).

To explain why the efficiencies of finishes Ag-1, Ag-2 and Ag-3 in protecting the cotton fibres against biodegradation differ, both the chemical form and the particle size of the silver on the fibres should be discussed. It has already been established that the antimicrobial activity of silver based compounds is related to the activity of the silver nanoparticles (Ag NPs) as well as to the silver cations (Ag$^+$). Namely, both Ag NPs and Ag$^+$ can form attractive interactions with microorganisms. Due to their small size, they can also penetrate the microbial cell, where they bond to the thiol groups of enzymes or nucleic acid (Akkopru & Durucan, 2007; Feng et al., 2000; Matsumura, Yoshikata, Kunisaki, & Tsuchido, 2003; Monteiro et al., 2009; Morones et al., 2005; Sharma, Yngard, & Lin, 2009; Sondi & Salopek-Sondi, 2004) causing inhibition of the cellular metabolism and final eradication of the microorganisms.

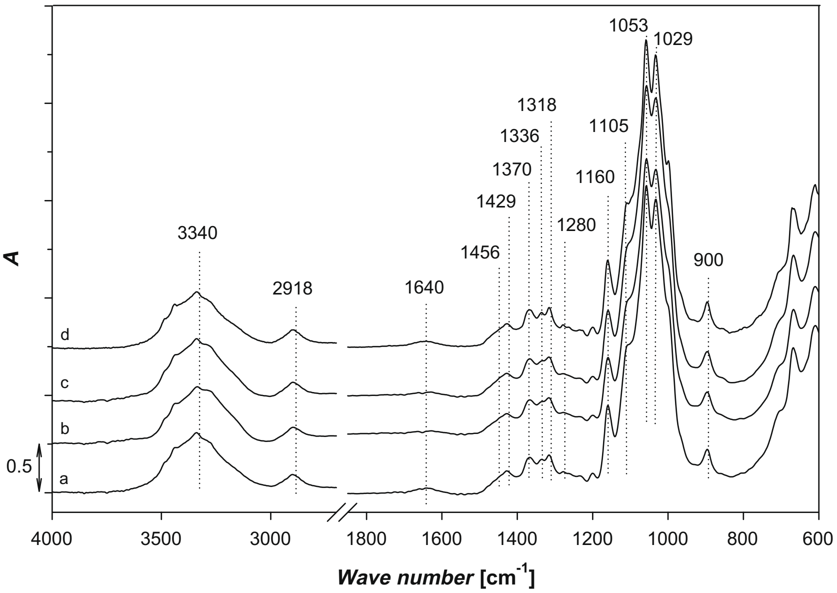

Fig. 7. Measured infrared ATR spectra of unfinished (a) and finished cotton samples Ag-1-d (b), Ag-2-b (c) and Ag-3 (d).

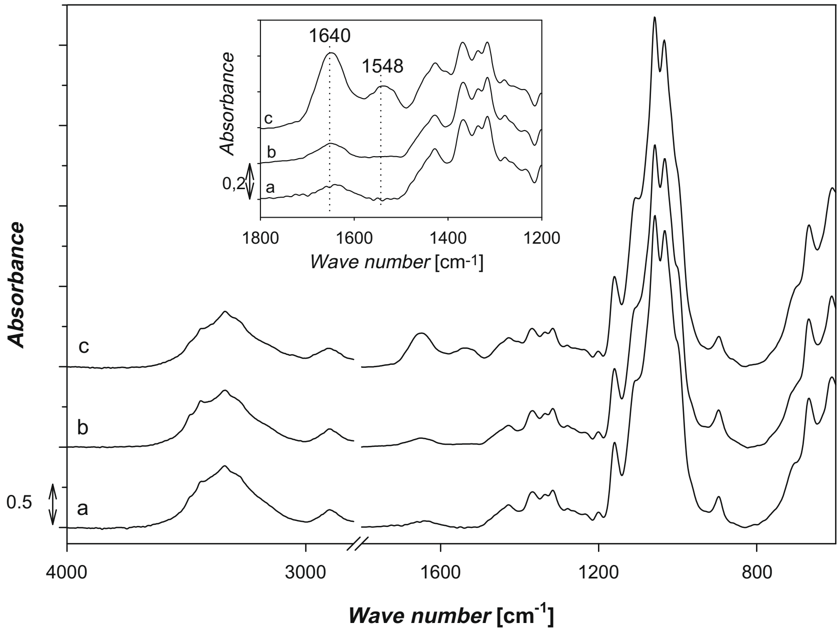

Fig. 8. Measured infrared ATR spectra of unfinished cotton samples before (a) and after 3 (b) and 12 (c) days of soil burial.

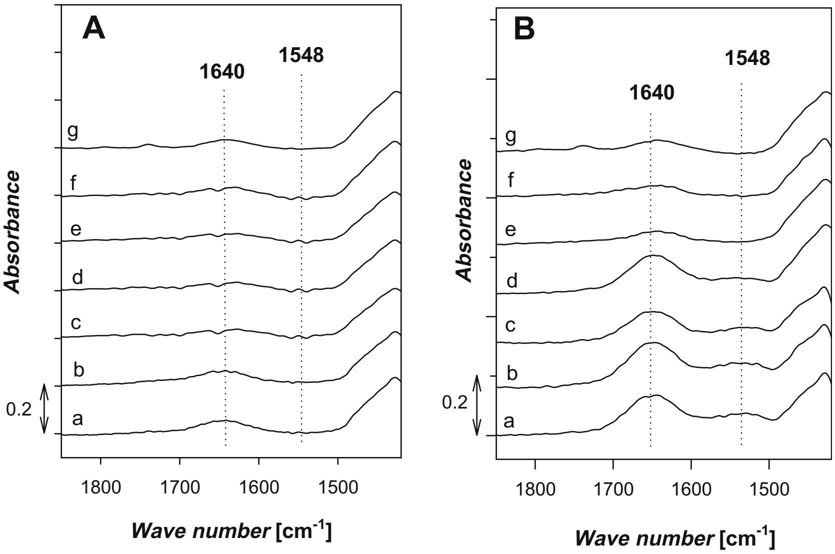

Fig. 9. Measured infrared ATR spectra of the finished cotton samples before (A) and after 12 days of soil burial (B) in the 1850–1450 cm^{-1} spectral region: a, Ag-1-a; b, Ag-1-b; c, Ag-1-c; d, Ag-1-d; e, Ag-2-a; f, Ag-2-b; g, Ag-3.

Furthermore, the antimicrobial properties of Ag NPs are size dependent, since particles with a smaller size have a larger specific surface area with which they can form interactions and therefore higher antimicrobial activity. Moreover, it has been determined that only Ag NPs smaller than 10 nm can directly interact with microorganisms (Morones et al., 2005).

According to the SEM micrographs on Fig. 1A, Ag NPs of finish Ag-1 strongly agglomerated on the cellulose fibres and therefore largely exceeded a diameter of 30 nm indicating that the Ag NPs agglomeration strongly decreased their antimicrobial activity. Because no de-agglomerated Ag particles could be seen on the cellulose fibres, we believe that the antimicrobial properties of finish Ag-1 were influenced only by the release of Ag^+ ions from the surface of the elemental silver, which can occur in an oxidation reaction in the presence of water and oxygen (Damm, Münstedt, & Rösch, 2008; Hoskins, Karanfil, & Serkiz, 2002). The inadequate antimicrobial protection of the cellulose fibres by finish Ag-1, irrespective to its concentration, indicated that the rate of silver ion release from the finish was too slow and therefore the concentration of Ag^+ too low to reach the critical concentration of inhibition at which fibre biodegradation is prevented. This assumption was confirmed by the SEM/BSE micrograph of cotton fabric sample Ag-1-d after 12 days of soil burial (Fig. 10), in which highly degraded parts of the fibres were present in the immediate vicinity of Ag NPs agglomerates.

In contrast to finish Ag-1, finish Ag-2 contains AgCl and its antimicrobial activity is related to the concentration of Ag^+ released from the surface of the crystals by dissociation of the silver salt in water. In spite of the fact that the SEM micrographs also indicated the growth of AgCl into large crystals on the cellulose fibres

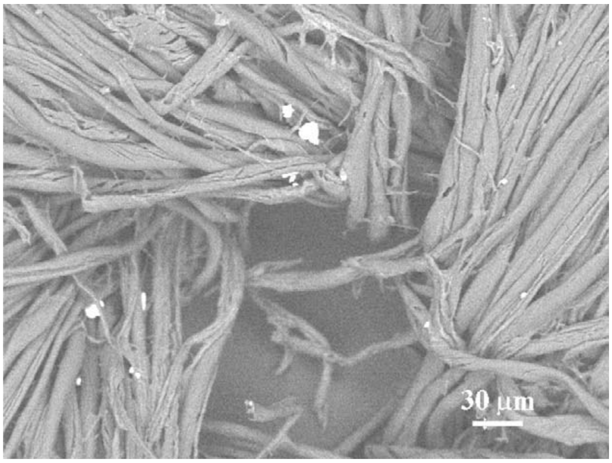

Fig. 10. SEM/BSE micrograph of the cotton fabric sample Ag-1-d after 12 days of soil burial.

(Fig. 1B), the water content in the soil was high enough to ensure dissolution of the salt crystals and provide a sufficient amount of Ag^+ cations to inhibit cellulose fibre biodegradation. The much more effective protection of the cellulose fibres by finish Ag-2 than finish Ag-1 of similar concentration and the particle size also confirmed that, under the same conditions, the rate of the reaction of salt dissociation is much higher than the reaction of silver oxidation.

It is believed that excellent antimicrobial properties of finish Ag-3, which were comparable with finish Ag-2 and much better than those of finish Ag-1, were caused by the synergistic action of Ag NPs and Ag^+ present on the finished cellulose fibres. Namely, in addition to the direct antimicrobial activity of the Ag NPs, the large specific surface area of these particles enabled a high increase of the concentration of released silver cations from the particle surface, which resulted in the rise of the biocidal activity of the finish.

Comparison of the protective properties against cellulose biodegradation and the antibacterial activity (Tomšič, Simončič, Cvijin et al., 2008; Tomšič, Simončič, Orel et al., 2008; Tomšič et al., 2009) of the studied finishes revealed that these two properties are in good correlation. While in the case of finish Ag-1 insufficient protection of the fibres against rotting was accompanied by a low bacterial reduction, which did not exceed 60%, excellent protection against microorganisms in the soil as well as against bacteria, higher than 99%, was determined for finishes Ag-2 and Ag-3. These results differed from those obtained for the biostatic activity of the QAS, for which excellent bacterial reduction was obtained for bacteria *E. coli*, *S. faecalis*, *Pseudomonas aeruginosa* and *S. aureus* but, at the same time, the presence of Si-QAC had no affect on the activity of the cellulose, which allowed the biodegradation process of the cellulose fibres (Tomšič & Simončič, 2005, 2009).

4. Conclusion

To conclude, the chemical form and particle size of silver directly influence the rate and the degree of cellulose biodegradation. It was found that the use of Ag NPs for fibre functionalisation does not necessarily lead to adequate protection against microorganisms. Because the agglomeration of Ag NPs strongly decreases their antimicrobial activity, it is limited only to the release of a small amount of Ag^+ cations from the surface of the agglomerates occurring in the oxidation reaction in the presence of water and oxygen. In this case, Ag NPs are much less effective than AgCl, with which the concentration of Ag^+, released from the surface of the crystals by dissociation of the silver salt in the presence of moisture in the soil, is high enough to inhibit fibre biodegradation. Only in the case of mostly de-agglomerated Ag NPs, could their antimicrobial activity be caused by the synergistic action of Ag NPs and Ag^+ cations.

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References

Adams, A. P., Santschi, E. M., & Mellencamp, M. A. (1999). Antibacterial properties of a silver chloride-coated nylon wound dressing. *Veterinary Surgery, 28*(4), 219–225.

Ahearn, D. G., May, L. L., & Gabriel, M. M. (1995). Adherence of organisms to silver-coated surfaces. *Journal of Industrial Microbiology, 15*(4), 372–376.

Akkopru, B., & Durucan, C. (2007). Preparation and microstructure of sol–gel derived silver-doped silica. *Journal of Sol–Gel Science and Technology, 43*(2), 227–236.

Allen, S. J., Auer, P. D., & Pailthorpe, M. T. (1995). Microbial damage to cotton. *Textile Research Journal, 65*(7), 379–385.

Chen, X., & Schluesener, H. J. (2008). Nanosilver: A nanoproduct in medical application. *Toxicology Letters, 176*(1), 1–12.

Choi, O., Deng, K. K., Kim, N.-J., Ross, L., Jr., Surampallli, R. Y., & Hu, Z. (2008). The inhibitory effects of silver nanoparticles, silver ions, and silver chloride colloids on microbial growth. *Water Research, 42*(12), 3066–3074.

Clarke, A. J. (1997). *Biodegradation of cellulose: Enzymology and biotechnology*. Lancaster: Technomic Publishing Co.. p. 272.

Damm, C., Münstedt, H., & Rösch, A. (2008). The antimicrobial efficacy of polyamide 6/silver-nano- and microcomposites. *Materials Chemistry and Physics, 108*(1), 61–66.

de Santa Maria, L. C., Santos, A. L. C., Oliveira, P. C., Barud, H. S., Messaddeq, Y., & Ribeiro, S. J. L. (2009). Synthesis and characterization of silver nanoparticles impregnated into bacterial cellulose. *Materials Letters, 63*(9–10), 797–799.

Desai, A. J., & Pandey, S. N. (1971). Microbial degradation of cellulosic textiles. *Journal of Scientific and Industrial Research, 30*, 598–610.

Dring, I. (2003). Anti-microbial, rot proofing and hygiene finishes. In D. Heywood (Ed.), *Textile finishing* (pp. 351–371). Bradford: Society of Dyers and Colourists.

Feng, Q. L., Wu, J., Chen, G. Q., Cui, F. Z., Kim, T. N., & Kim, J. O. (2000). A mechanistic study of the antibacterial effect of silver ions on *Escherichia coli* and *Staphylococcus aureus*. *Journal of Biomedical Materials Research, 52*(4), 662–668.

Gorenšek, M., & Recelj, P. (2007). Nanosilver functionalized cotton fabric. *Textile Research Journal, 77*(3), 138–141.

Gorenšek, M., & Recelj, P. (2009). Reactive dyes and nano-silver on PA6 micro knitted goods. *Textile Research Journal, 79*(2), 138–146.

Hofstetter, K., Hinterstoisser, B., & Salmen, L. (2006). Moisture uptake in native cellulose—The roles of different hydrogen bonds: A dynamic FT-IR study using Deuterium exchange. *Cellulose, 13*(2), 131–145.

Hoskins, J. S., Karanfil, T., & Serkiz, S. M. (2002). Removal and sequestration of iodide using silver-impregnated activated carbon. *Environmental Science and Technology, 36*(4), 784–789.

Hulleman, S. H. D., van Hazendonk, J. M., & van Dam, J. E. G. (1994). Determination of crystallinity in native cellulose from higher-plants with diffuse-reflectance Fourier-transform infrared-spectroscopy. *Carbohydrate Research, 261*(1), 163–172.

Ilić, V., Šaponjić, Z., Vodnik, V., Potkonjak, B., Jovančić, P., Nedeljković, J., et al. (2009). The influence of silver content on antimicrobial activity and color of cotton fabrics functionalized with Ag nanoparticles. *Carbohydrate Polymers, 78*(3), 564–569.

Itävaara, M., Siika-aho, M., & Viikari, L. (1999). Enzymatic degradation of cellulose-based materials. *Journal of Environmental Polymer Degradation, 7*(2), 67–73.

Kačuráková, M., & Wilson, R. H. (2001). Development in mid-infrared FT-IR spectroscopy of selected carbohydrates. *Carbohydrate Polymers, 44*(4), 291–303.

Kondo, T. (1997). The assignment of IR absorption bands due to the free hydroxyl groups in cellulose. *Cellulose, 4*(4), 281–292.

Kusnetsov, J., Iivanainen, E., Elomaa, N., Zacheus, O., & Martikainen, P. J. (2001). Copper and silver ions more effective against legionellae than against mycobacteria in a hospital warm water system. *Water Research, 35*(17), 4217–4225.

Langkilde, F. W., & Svantesson, A. (1995). Indentification of celluloses with Fourier-Transform (FT) mid-infrared, FT-Raman and near-infrared spectrometry. *Journal of Pharmaceutical & Biomedical Analysis, 13*(4/5), 409–414.

Lee, H. J., Yeo, S. Y., & Jeong, S. H. (2003). Antibacterial effect of nanosized silver colloidal solution on textile fabrics. *Journal of Materials Science, 38*(10), 2199–2204.

Łojewska, J., Miśkowiec, P., Łojewski, T., & Proniewicz, L. M. (2005). Cellulose oxidative and hydrolytic degradation: In situ FTIR approach. *Polymer Degradation and Stability, 88*(3), 512–520.

Lok, C.-N., Ho, C.-M., Chen, R., He, Q.-Y., Yu, W.-Y., Sun, H., et al. (2006). Proteomic analysis of the mode of antibacterial action of silver nanoparticles. *Journal of Proteome Research, 5*(4), 916–924.

Mahltig, B., Fiedler, D., & Böttcher, H. (2004). Antimicrobial sol–gel coatings. *Journal of Sol–Gel Science and Technology, 32*(1–4), 219–222.

Maneerung, T., Tokura, S., & Rujiravanit, R. (2008). Impregnation of silver nanoparticles into bacterial cellulose for antimicrobial wound dressing. *Carbohydrate Polymers, 72*(1), 43–51.

Matsumura, Y., Yoshikata, K., Kunisaki, S., & Tsuchido, T. (2003). Mode of bactericidal action of silver zeolite and its comparison with that of silver nitrate. *Applied and Environmental Microbiology, 69*(7), 4278–4281.

Matyjas-Zgondek, E., Bacciarelli, A., Rybicki, E., Szynkowska, M. I., & Kołodziejczyk, M. (2008). Antibacterial properties of silver-finished textiles. *Fibres & Textiles in Eastern Europe, 16*(January/December), 101–107.

Montegut, D., Indictor, N., & Koestler, R. J. (1991). Fungal deterioration of cellulosic textiles: A review. *International Biodeterioration, 28*(1–4), 209–226.

Monteiro, D. R., Gorup, L. F., Takamiya, A. S., Ruvollo-Filho, A. C., de Camargo, E. R., & Barbosa, D. B. (2009). The growing importance of materials that prevent microbial adhesion: Antimicrobial effect of medical devices containing silver. *International Journal of Antimicrobial Agents, 34*(2), 103–110.

Morones, J. R., Elechiguerra, J. L., Camacho, A., Holt, K., Kouri, J. B., Ramírez, J. T., et al. (2005). The bactericidal effect of silver nanoparticles. *Nanotechnology, 16*(10), 2346–2353.

Park, C. H., Kang, Y. K., & Im, S. S. (2004). Biodegradability of cellulose fabrics. *Journal of Applied Polymer Science, 94*(1), 248–253.

Petica, A., Gavriliu, S., Lungu, M., Buruntea, N., & Panzaru, C. (2008). Colloidal silver solutions with antimicrobial properties. *Materials Science and Engineering B – Advanced Functional Solid-State Materials, 152*(1–3), 22–27.

Purwar, R., & Joshi, M. (2004). Recent developments in antimicrobial finishing of textiles—A review. *AATCC Review, 4*(3), 22–26.

Rai, M., Yadav, A., & Gade, A. (2009). Silver nanoparticles as a new generation of antimicrobials. *Biotechnology Advances, 27*(1), 76–83.

Salerno-Kochan, R., & Szostak-Kotowa, J. (2001). Biodegradation of cellulose textiles. *Fibres & Textiles in Eastern Europe, 69*(July/September), 72.

Schindler, W. D., & Hauser, P. J. (2004). *Chemical finishing of textiles*. Cambridge: Woodhead Publishing Ltd.. pp. 165–174.

Sharma, V. K., Yngard, R. A., & Lin, Y. (2009). Silver nanoparticles: Green synthesis and their antimicrobial activities. *Advances in Colloid and Interface Science, 145*(1–2), 83–96.

Socrates, G. (2001). *Infrared and Raman characteristic group frequencies*. New York: John Wiley & Sons, Ltd. pp. 347.

Sondi, I., & Salopek-Sondi, B. (2004). Silver nanoparticles as antimicrobial agent: A case study on *E. coli* as a model for Gram-negative bacteria. *Journal of Colloid and Interface Science, 275*(1), 177–182.

Szostak-Kotowa, J. (2004). Biodeterioration of textiles. *International Biodeterioration & Biodegradation, 53*(3), 165–170.

Tankhiwale, R., & Bajpai, S. K. (2009). Graft copolymerizationonto cellulose-based filter paper and its further development as silver nanoparticles loaded antibacterial food-packaging material. *Colloids and Surfaces B: Biointerfaces, 69*(2), 164–168.

Tien, D.-C., Tseng, K.-H., Liao, C.-Y., & Tsung, T.-T. (2009). Identification and quantification of ionic silver from colloidal silver prepared by electric spark discharge system and its antimicrobial potency study. *Journal of Alloys and Compounds, 473*(1–2), 298–302.

Tomšič, B., & Simončič, B. (2009). Antimicrobial properties and biodegradability of cellulose modified by a cationic siloxane. *Proceedings of the 9th Autex conference* (pp. 175–180) Izmir, Turkey: Autex Conference.

Tomšič, B., & Simončič, B. (2005). Antimicrobial activity of 3-(trimethoxysilyl)-propyldimethylalkilamonium chloride. *Tekstilec, 48*(4/6), 79–87.

Tomšič, B., Simončič, B., Cvijin, D., Orel, B., Zorko, M., & Simončič, A. (2008). Elementary nano sized silver as antibacterial agent on cotton fabric. *Tekstilec, 51*(7/9), 199–215.

Tomšič, B., Simončič, B., Orel, B., Černe, L., Forte Tavčer, P., Zorko, M., et al. (2008). Sol–gel coating of cellulose fibres with antimicrobial and repellent properties. *Journal of Sol–Gel Science and Technology, 47*(1), 44–57.

Tomšič, B., Simončič, B., Orel, B., Vilčnik, A., & Spreizer, H. (2007). Biodegradability of cellulose fabric modified by imidazolidinone. *Carbohydrate Polymers, 69*(3), 478–488.

Tomšič, B., Simončič, B., Orel, B., Žerjav, M., Schroers, H. J., Simončič, A., et al. (2009). Antimicrobial activity of AgCl embedded in a silica matrix on cotton fabric. *Carbohydrate Polymers, 75*(4), 618–626.

Vilčnik, A., Jerman, I., Šurca Vuk, A., Koželj, M., Orel, B., Tomšič, B., et al. (2009). Structural properties and antibacterial effects of hydrophobic and oleophobic sol–gel coatings for cotton fabrics. *Langmuir, 25*(10), 5869–5880.

Vince, J., Orel, B., Vilčnik, A., Fir, M., Šurca Vuk, A., Jovanovski, V., et al. (2006). Structural and water-repellent properties of a urea/poly(dimethylsilixane) sol–gel hybrid and its bonding to cotton fabric. *Langmuir, 22*(15), 6489–6497.

Wasif, A. I., & Laga, S. K. (2009). Use of nano silver as an antimicrobial agent for cotton. *Autex Research Journal, 9*(1), 5–13.

Yeo, S. Y., Lee, H. J., & Jeong, S. H. (2003). Preparation of nanocomposite fibers for permanent antibacterial effect. *Journal of Materials Science, 38*(10), 2143–2147.