

# Functionalization of textile materials with silver nanoparticles

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**Abstract** Nanoparticles gained much scientific attention in the past decade due to their specific surface chemistry and properties which are significantly different from that of the corresponding bulk materials. Silver nanoparticles were the most extensively studied and they can be already found in a wide range of commercially available products. This article reviews the latest developments in finishing of textile materials with differently synthesized silver nanoparticles. Although antimicrobial activity of functionalized textile materials was primarily discussed, the possibilities to apply silver nanoparticles as a colorant or antistatic agent were also evaluated. In addition, the effect of chemical and physico-chemical activation of fibers before loading of silver nanoparticles on their binding efficiency was considered. Taking into account the importance of environmental impact of novel technologies, potential environmental risks emerging from silver release during washing of textile materials have been also discussed.

## Introduction

A rapid global production growth of textile materials for medical, healthcare, hygiene, and sports applications renewed the interest for antimicrobial finishing in the last decade [1]. The microbial growth on textile materials cannot only harm the material, but it may also cause adverse effects on the wear comfort [2]. Various antimicrobial agents (metal salts, quaternary ammonium

compounds, polyhexamethylene biguanides, triclosan, biopolymer chitosan, *N*-halamine, and peroxyacid, etc.) have been used in antimicrobial finishing of textile materials [3]. Although many of them met desired antimicrobial demands, they were not acceptable from economical, environmental, or long-term efficiency standpoint.

For centuries, silver in different forms has been in use for healing of burns and wounds [4, 5]. However, the introduction of penicillin in the 1940s drastically minimized the use of silver. Lately, the resistance of microorganisms to different available antibiotics and development of simple routes for the synthesis of nano-sized silver particles revitalized the interest for this valuable antimicrobial agent. Silver possesses bactericidal activity against more than 650 pathogens (bacteria, fungi, and viruses) [6]. The promising potentials of silver were promptly recognized by textile industry. Silver in both ionic and colloidal form ensures excellent antimicrobial activity. However, ionic silver stains textile materials when exposed to light and the color of the material turns from white to black–brown [7]. This disadvantage can be avoided by the application of silver nanoparticles (Ag NPs). Unlike the conventional finishing methods which often do not provide desired permanent efficiency, it seems that functionalization with Ag NPs not only improves antimicrobial durability but also does not significantly alter the fabric breathability and handle [8]. Small size i.e., high surface to volume ratio of Ag NPs makes them very reactive. In other words, considerable amount of silver atoms on the surface of the NPs is exposed toward surrounding medium, providing an extraordinary bactericidal efficiency. Furthermore, small amount of Ag NPs ensures high antimicrobial efficiency.

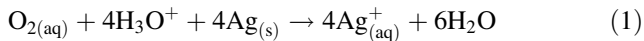
The loading of textile materials with Ag NPs is performed in two different ways: Ag NPs can be embedded into synthetic fibers during the spinning process or they can

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be deposited on textiles in different forms (fibers, yarns, and fabrics) during finishing. Dip-coating method is the most frequently applied where the fabrics are immersed in colloidal solution of Ag NPs. However, the studies on in situ silver ion reduction and formation of Ag NPs on the fibers are also reported.

The mechanism of antimicrobial action of Ag NPs is not well understood yet. One scientific approach relies on the assumption that bactericidal effect originates from Ag ions released from Ag NPs [9–12]. Namely, when exposed to dissolved oxygen in water medium, Ag NPs release small amounts of Ag<sup>+</sup> according to equation [13]:



Another approach is based on the work of Morones et al. [11] who found Ag NPs attached to the cell membrane and inside the bacteria by TEM analysis. As Ag possesses high affinity for sulfur and phosphorous compounds [14], it can be anticipated that Ag NPs will react with sulfur-rich protein in the bacteria cell membrane and interior of the cell or with phosphorous-containing compounds such as DNA [15, 16]. Therefore, detected morphological changes in the cell membrane of bacteria and possible damage of DNA initiated by reaction with Ag NPs have adverse effect on the respiratory chain or cell division processes, causing a cell death [11].

This article gives an overview of latest developments in finishing of textile materials with Ag NPs. The most representative methods for the application of Ag NPs to textile materials are briefly introduced as well as the parameters that influence the Ag NPs deposition. Although antimicrobial activity of functionalized textile materials was primarily discussed, the possible role of Ag NPs as a colorant or antistatic agent was also considered. Several studies indicated that binding of Ag NPs to fiber surface may be a bottleneck in processing of this type of textile composites. Therefore, particular attention in this article has been paid on chemical and physico-chemical activation of fibers before loading of Ag NPs which can enhance their binding efficiency. Keeping in mind the importance of environmental impact of novel technologies, potential environmental risks that appear because of the silver release during washing of textile materials have been also evaluated.

## Cotton

The major research on the functionalization of textile materials with Ag NPs is focused on cotton (Co) fibers. Although the steady replacement of natural fibers with synthetic fibers in medical/healthcare sector, Co fibers are still used to a great extent in manufacturing of

non-implantable medical textile materials (bandages, plasters, gauze dressing, wadding, etc.) and healthcare/hygiene products (surgical gowns and hosiery, gowns, caps, and uniforms) [1].

One of the first studies indicated that Co fabrics padded through 25- and 50-ppm commercial ethanol-based colloid solution of Ag NPs has shown excellent antibacterial efficiency against Gram-positive bacteria *S. aureus* and Gram-negative bacteria *K. pneumoniae* [17]. Maximum bacteria reduction was preserved even after 20 washing cycles, indicating a good laundering durability. However, ICP-MS analysis implied that Ag content decreased seven times already after the fifth washing cycle, while the final content after 20 washing cycles was even 15 times lower. The results indicated that desirable level of antibacterial activity was achieved particularly when loading of Ag NPs was carried out after dyeing (studied dye was not specified) as well as before printing of Co fabrics. Similar behavior was observed on Co woven fabrics that were treated with 20-ppm colloidal solution of Ag NPs (2–3 nm in diameter) [18].

Simultaneous application of commercial powdered Ag NPs and reactive dyes Cibacron deep red S–B and Cibacron navy S–G indicated that color change caused by the presence of Ag NPs depends on the concentration of Ag NPs as well as on the type and concentration of used dyes [2]. Antibacterial activity was tested against several bacteria, but acceptable effects were only achieved with *S. aureus* and *S. faecalis*. Antibacterial efficiency was significantly diminished after 10 washing cycles.

Pohle et al. employed in situ deposition of Ag NPs to orthopedic stockings (85 % Co/15 % PA) from the solution consisting of silver nitrate, sodium borohydride as a reducing agent, and polyvinyl alcohol as a stabilizing agent [10]. Polydisperse spherical Ag NPs with diameters ranging from 10 to 30 nm were detected by TEM. Anodic stripping voltammetry measurements revealed significant release of Ag ions in water within 28 days. High initial release of Ag ions was attributed to weakly bound Ag NPs. It was suggested that release kinetics was mainly governed by diffusion process and not only by a simple wash-out mechanism. Desired level of antibacterial activity was proved against Gram-negative bacteria *E. coli*. The color change caused by Ag NPs loading was determined by visible light diffuse reflection spectroscopy. The coated material showed a broad absorption peak at 405 nm which was assigned to characteristic surface plasmon resonance of Ag NPs. Namely, collective oscillation of conductive electrons of Ag NPs initiated by electromagnetic irradiation is known as localized surface plasmon resonance. The excitation of plasmon by light results in colored colloids containing Ag NPs. The colors can be tuned from yellow to red or blue depending on the size, shape, and dielectric

properties of Ag NPs as well as on dielectric properties of surrounding medium.

Vigneshwaran et al. [7] proposed interesting method for in situ generation of Ag NPs on Co fabrics. Co fabric immersed in silver nitrate solution was autoclaved at 15  $\psi$ , 121 °C for 15 min. The aldehyde terminal of starch which remained after desizing was utilized for the reduction of Ag ions and in situ formation of Ag NPs on the surface of the Co fabric. The presence of Ag NPs was confirmed by UV–visible absorption spectra as the characteristic peak appeared at 420 nm. In addition, well-dispersed Ag NPs were observed by SEM. FTIR analysis showed that both untreated and modified Co fabrics yielded similar peaks, and it was suggested that no chemical bonding between substrate and silver was established. Co fabrics modified with Ag NPs seem to be selective against different bacteria. Maximum antibacterial efficiency was obtained against *S. aureus* while poor antibacterial properties were found for the *K. pneumoniae*.

Durán et al. [19] reported that Ag ions can be reduced extracellularly using fungus *F. oxysporum*. Elemental spectroscopy imaging maps revealed the presence of Ag, N, and S on generated Ag NPs. It is assumed that fungal proteins stabilize the Ag NPs. The introduction of Ag NPs (size of only 1.6 nm) to Co fabrics resulted in excellent antibacterial efficiency against *S. aureus*.

El-Rafie et al. [20] used biomass filtrate of fungus *F. solani* for the synthesis of very small Ag NPs (3–8 nm). Co fabrics were padded with colloids of Ag NPs at concentrations of 54 and 108 ppm. SEM images revealed uniform distribution of Ag NPs on Co fibers. Antibacterial efficiency of Co fabrics against *S. aureus* was higher in comparison to *E. coli*. The higher the concentration of Ag NPs colloid the better the antibacterial properties. It was shown that antibacterial efficiency decreased after 5, 10, and 20 washing cycles. Incorporation of binder in the finishing formulation led to a significant improvement of laundering durability.

Plant biomaterials such as *Curcuma longa* tuber powder and extract can be efficiently used for the biosynthesis of differently shaped Ag NPs (quasi spherical, triangular, and rod-like) [21]. It is believed that terpenoids are responsible for the bio-reduction of Ag ions. Ag NPs immobilized on Co fabrics using sterile water and polymer polyvinylidene fluoride (PVDF) exhibited excellent antibacterial activity against *E. coli* after five washing cycles.

Ilić et al. [22] applied dip-coating method for the deposition of colloidal Ag NPs which were synthesized by reduction of silver nitrate with sodium borohydride without using any stabilizer. TEM analysis revealed nearly spherical Ag NPs with average diameter of 10 nm. The presence of Ag NPs on Co fibers was observed by SEM. Co fabrics loaded with Ag NPs from 10- and 50-ppm colloid exhibited

excellent antimicrobial activity against fungus *C. albicans*, and bacteria *E. coli* and *S. aureus*. Co fabrics loaded with Ag NPs from 10-ppm colloid showed poor laundering durability. On the contrary, the desirable antimicrobial efficiency of Co fabrics loaded with Ag NPs from 50-ppm colloid was preserved after five washing cycles likely due to larger amount of deposited Ag NPs which was determined by AAS. In addition, the release of silver emerged during washing process. The order of loading of Ag NPs (from 50-ppm colloid) and dyeing with C.I. Direct Red 81 did not affect the antimicrobial efficiency of Co fabrics. However, it was recommended to avoid the loading of Ag NPs after dyeing because of the significant color change of Co fabrics.

The same group of authors compared the effect of colloidal Ag NPs synthesized in just described manner and commercial RUCO-BAC AGP agent with silver chloride as an active component on antibacterial activity of Co fabrics dyed with vat dyes Bezanthren olive T and Bezanthren gray FFB [23]. Co fabrics loaded with colloidal Ag NPs reached the maximum bacteria reduction (*E. coli* and *S. aureus*). Although the dyed Co fabrics modified with RUCO-BAC AGP provided fair antibacterial properties, the maximum bacteria reduction was not always achieved. Better antibacterial properties of Co fabrics modified with Ag NPs were likely due to larger amount of Ag in these samples, which was confirmed by AAS. The treatment with RUCO-BAC AGP did not significantly affect the color of Co fabrics. Oppositely, Co fabrics dyed with Bezanthren olive T underwent considerable color change after treatment with Ag NPs. The results also demonstrated that release of silver from Co fabrics occurred during 24-h long exposure to sweat at pH 5.5 and 8.0. All studied samples released almost the same amount of silver into sweat, independently of dye type and dye concentration as well as of silver form applied. However, about 39 % more silver was released into the alkaline sweat compared with acidic sweat. Color fastness of cotton fabrics exposed to sweat was satisfactory.

Gorjanc et al. [22] slightly modified proposed procedure for the synthesis of Ag NPs by reduction of silver nitrate with sodium borohydride, and they applied the colloidal Ag NPs to bleached and mercerized Co fabric after dyeing with vat dye Bezathren Blau BCE [24]. This modified route for synthesis of colloidal Ag NPs brought about deposition of bigger particles with dimensions between 160 and 210 nm on control Co fabric and 88 and 163 nm on vat dyed Co fabric. The prolongation of loading time resulted in larger amount of deposited Ag NPs but also in more pronounced agglomeration of Ag NPs. It was suggested that dyeing with vat dye positively affected the loading of colloidal Ag NPs due to electrostatic interaction between vat dyed Co fiber and Ag NPs. Large amount of deposited

Ag NPs caused significant color change of Co fabrics. Although these fabrics initially exhibited extraordinary good antibacterial activity against bacteria *S. aureus*, *E. coli*, *S. faecalis*, and *P. aeruginosa*, poor laundering durability after 50 washing cycles has been observed.

Kulthong et al. [25] also followed the release of silver in artificial sweat at different pH (4.3, 5.5, 6.5, and 8.0) from the Co fabrics treated with silver suspension. The agglomerates of Ag NPs were detected by SEM. Antibacterial efficiency of these samples against *S. aureus* was higher compared to *E. coli*. It was suggested that the quantity of released silver into each formulation of artificial sweat was dependent on the initial amount of silver used in the treatment of Co fabrics. The leaching of silver was the lowest in the artificial sweat at pH 5.5 which is similar to the pH of the normal human skin.

In situ coating of Co fabrics with Ag NPs in one bath was proposed by El-Shishtawy et al. [26]. Silver nitrate was reduced with glucose in the presence of cetyl trimethyl ammonium bromide as a stabilizer. The amount of deposited Ag NPs could be controlled by regulation of amount of silver nitrate precursor. These Co fabrics showed excellent antimicrobial activity against *S. aureus*, *E. coli*, *B. subtilis*, and *C. albicans*, which was even improved after repeated washing. Such behavior is attributed to possible disaggregation of Ag NPs during washing.

Co fabrics with durable antimicrobial properties can be obtained using copolymer,  $\beta$ -cyclodextrin grafted with polyacrylic acid, and potassium persulfate as an initiator [27]. Generated copolymer was utilized as a reducing agent and stabilizer in the formation of Ag NPs. Thermal, ultrasonic, and microwave heating have been employed. The prepared Ag NPs and  $\beta$ -cyclodextrin grafted with polyacrylic acid were applied to Co fabric incorporated with epichlorohydrin at different concentrations. Again, it was concluded that antibacterial activity against *S. aureus* and *E. coli* depends on the concentration of applied Ag NPs.

Ag-polyacrylate clusters have been synthesized by reduction of  $\text{AgNO}_3$  with  $\text{NaBH}_4$  or under UV light in the presence of polyacrylates as templating agent [28]. Co fabrics were conventionally dip-coated with synthesized Ag NPs dispersion. SAXS analysis indicated that the size of Ag NPs strongly depend on the applied reduction method ( $\text{NaBH}_4$  or UV exposure) as well as on molecular weight of polyacrylate. Co fabrics functionalized in this manner exhibited excellent antimicrobial properties against *S. aureus*, *S. epidermidis*, *P. aeruginosa*, and *C. albicans*. Equivalent behavior was observed on wool and polyester fabrics.

Zhang et al. [29] proposed one-step procedure for the preparation of colloidal Ag NPs by mixing silver nitrate and amino-terminated hyperbranched polymer (HBP-NH<sub>2</sub>)

and their deposition on Co fabrics. Ag ions were complexed with HBP-NH<sub>2</sub> and then reduced. Large amount of HBP-NH<sub>2</sub> remained on the surface of Ag NPs preventing the agglomeration of Ag NPs. The average diameter of the Ag NPs ranged from 10 to 30 nm. The higher the initial concentration of the colloid the better the antimicrobial properties against *S. aureus* and *E. coli*. This is due to larger amount of deposited Ag NPs. Consequently, the whiteness index decreased. Slight decrease in laundering durability of antimicrobial effects occurred after 20 washing cycles. Ag NPs were quite stable on the surface of the Co fibers likely due to HBP-NH<sub>2</sub> which also acted as a binder.

Thomas et al. [30] showed that amino and hydroxyl groups of biopolymer chitosan attached to Co fabric can be exploited for the binding of Ag ions. The oxidation of Co fabric with periodic acid brought about the formation of cellulose dialdehyde enabling the coupling of amino groups of chitosan to aldehyde groups of cellulose. Ag ions were efficiently bound to amino groups of attached chitosan, and they were reduced by sodium citrate. The presence of Ag NPs on modified Co fabric was proved by TEM, SPR, and EDX. These Co fabrics exhibited fair antibacterial activity against *E. coli*.

Plasma treatment can be applied for the activation of the Co fibers surface prior to deposition of Ag NPs [31, 32]. Gorjanc et al. [31] reported that treatment of bleached and mercerized Co fabrics with water vapor radio-frequency (RF) plasma led to a decrease of C–C bonds and increase of C–O, O–C–O, C=O, and O=C–O bonds on the fabric surface. The increase in oxygen containing groups caused the improvement of Co fiber hydrophilicity. The subsequent deposition of commercial Ag NPs (30 and 80 nm) by exhaust method indicated that smaller Ag NPs were better attached to Co fabric surface. The best antibacterial properties against *E. coli* and *P. aeruginosa* were achieved by treating the Co fabric with Ag NPs (30 nm) from 50-ppm solution, but even then, these results cannot be considered as good. Such behavior is suggested to be due to insufficient initial concentration of Ag NPs and consequently, low amount of deposited Ag NPs. The same group of authors conducted CF<sub>4</sub> RF plasma treatment of Co fabrics prior to loading of Ag NPs [32]. Plasma treatment induced increase of fiber surface roughness, facilitating the deposition of Ag NPs.

Mejía et al. [33] utilized magnetron sputtering with Ag target for the deposition of Ag NPs with sizes of approximately 4.7 nm. It was concluded that the size of Ag NPs was independent on sputtering time. However, the amount of deposited Ag NPs increased with prolongation of sputtering time. The amount of deposited Ag NPs also controlled the antibacterial activity of Co fabrics.

Interesting approach based on the application of supercritical CO<sub>2</sub> which is not expensive and is amenable to

scale-up for industrial manufacturing is proposed by Gittard et al. [34]. It was shown that Ag precursors dissolved in supercritical CO<sub>2</sub> are able to diffuse into the Co fabric and react with Co. This process results in deposition of thin Ag films and Ag NPs. It was assumed that the formation of Ag NPs may be due to either surface diffusion of Ag atoms and small clusters or oxidation/reduction of the precursors at deposited silver sites, which facilitated generation of clusters and nanoparticles. XRD spectra confirmed the presence of Ag on Co fabrics. Impregnated Co fabrics exhibited antifungal activity against *C. albicans*.

Klemenčič et al. [35] modified Co fabric with silver in different forms with an aim to protect the fabric from biodegradation. The biodegradability was measured by soil burial test. It was assumed that form and particle size of silver influence the degree of biodegradability of Co. The agglomeration of Ag NPs diminished antimicrobial activity of Co fabrics because of the only slight release of Ag<sup>+</sup> ions from the surface of the agglomerated particles in the presence of water and oxygen. AgCl was considerably more efficient in the inhibition of biodegradation.

## Wool

Compared to Co fibers, the modification of wool fibers with Ag NPs has been significantly less explored. Hadad et al. [36] reported that sonochemical deposition of small Ag NPs on wool fibers can be performed with great success. The deposition of Ag NPs on wool fibers was carried out by ultrasound irradiation in aqueous solution of silver nitrate, ammonia, and ethylene glycol, which acts as a reducing agent. The system was purged with argon and argon/hydrogen for different times before sonication to remove dissolved oxygen/air. It was shown that the most efficient deposition was obtained when the sonication was conducted after 24 h of purging with argon. The specific surface area of fibers increased from 1 to 4.6 m<sup>2</sup>/g due to introduction of Ag NPs to wool fiber surface. TEM, HRTEM, and HRSEM analyses clearly demonstrated that wool fibers were uniformly covered with nearly spherical Ag NPs with average dimensions of 5–10 nm. In addition to single Ag NPs, some aggregates of Ag NPs (50 nm) were found mainly on the cross-points of fibers. XPS analysis indicated the possible interaction between Ag NPs and sulfur atoms, which likely appeared as a result of the cleavage of S–S bond in the wool fiber. However, the real nature of obtained bonding was not established. This nanocomposite system demonstrated excellent stability even after several washing cycles without any alteration of Ag content.

TEM and EDX analyses of the cross sections of wool fibers that were treated with commercial colloid containing

the Ag NPs revealed interesting observation that NPs of 5–10 nm in size were distributed throughout the cell membrane complex [37]. In other words, Ag NPs diffused toward interior of the fiber through non-keratinous cell membrane complex region.

Ki et al. [38] treated wool fibers with commercial sulfur nanosilver ethanol-based colloid by conventional pad-dry-cure method. Antibacterial properties of the fibers were tested against *S. aureus* and *K. pneumoniae*. In the case of *S. aureus*, modified wool fibers provided maximum bacteria reduction (99.9 %) independently of applied colloid concentrations (5–30 ppm). Wool fibers loaded with Ag NPs from 5- to 10-ppm colloids exhibited slightly lower reduction of bacteria *K. pneumoniae* (99.70 %) whereas higher concentrated colloids (20 and 30 ppm) ensured maximum bacteria reduction. In addition, wool woven fabric treated with 20-ppm colloid completely inhibited the growth of both bacteria. It was also shown that static electricity of wool fabrics loaded with higher concentrated colloids decreased.

The studies on wool indicated that Ag NPs could act not only as an antimicrobial agent but also as a colorant due to specific optical properties (surface plasmon resonance) of deposited Ag NPs [39, 40]. Deposited Ag NPs on wool fibers give rise to variety of intense brilliant hues. Kelly and Johnston [39] demonstrated that Ag NPs can be generated by in situ reduction of silver ions with trisodium citrate (TSC) as a reducing agent and stabilizer directly on the fiber surface. The change in the concentration of TSC lead to a formation of Ag NPs of varying sizes and hence, differently colored wool. Increase in the amount of applied TSC resulted in the color change of wool from yellow/orange to red/brown to brown/black, and this was quantitatively assessed by CIE L\*a\*b\* measurements. Observed color changes were attributed to increase in the size of Ag NPs. SEM and TEM analyses proved that larger amounts of TSC brought about the appearance of bigger single NPs and aggregates of small NPs. TEM images also revealed much wider particle size distribution on the wool surface in the case of application of higher concentrated TSC solutions. XPS spectra of O1s, N1s, S2p, and Ag3d photoelectron peaks indicated the presence of chemical interactions between Ag NPs and TSC and the sulfur and nitrogen of the amino acids in the wool. This study pointed out that at first, TSC acts as a reducing agent, and then it takes a role of the linker to chemically bound Ag NPs to wool fiber. The presence of chemical bonding ensures washing and rubbing durability of textile nanocomposite systems. The colorfastness of the samples to washing gave a result of five which is the maximum value. Similarly, colorfastness of the same samples to rubbing gave a value of four or five that is above pass level. In addition to coloration changes, Ag NPs formed in this way imparted antibacterial and antistatic properties to wool fibers.

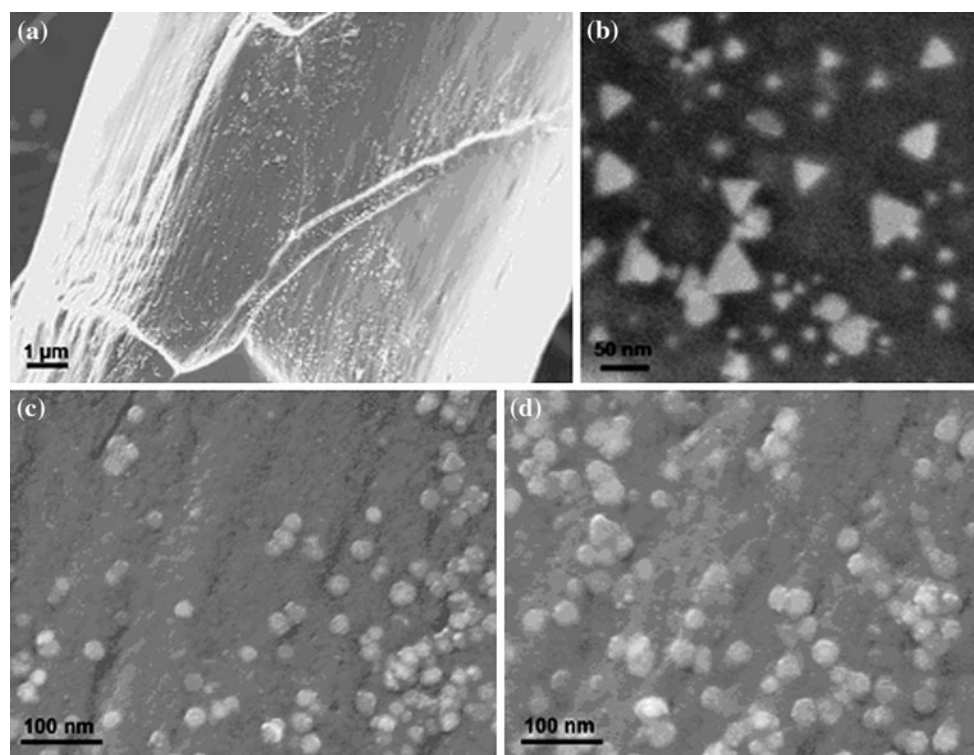
Another group of scientists studied the effect of Ag NPs shape on the color of wool fabrics [40]. The wool fabrics exposed to solution of Ag nanoprisms and two types of differently synthesized Ag nanodisks became blue, red, and yellow colored. The brilliant color of the fabrics derived from the local surface plasmon resonance of deposited Ag NPs. It was noticed that the color of fabrics slightly differs from the color of initial solution. This was suggested to be due to environment changes around Ag NPs: from water to interface of air and wool fiber. SEM images of wool fibers loaded with Ag NPs (Fig. 1) clearly shows that Ag NPs preserved their shape even after deposition on the wool fabric. In this study, citrate was also used as a stabilizer and consequently, Ag NPs carried the negative charge which was confirmed by zeta potential measurements. Hence, it was assumed that electrostatic interaction between carboxylate groups of Ag NPs and amino groups in wool fibers has been established. This assumption is in a good correlation with observations of Kelly and Johnston [39]. Investigated fabrics exhibited satisfactory antibacterial properties against *E. coli*, but maximum bacteria reduction was not obtained.

### Polyester and polyamide

The major research on the application of Ag NPs to polyester (PES) and polyamide (PA) fibers is oriented

toward activation of fiber surface by appropriate chemical or physico-chemical treatment that leads to an improvement of the binding efficiency of Ag NPs. Interesting approach to deposition of Ag NPs to PA fibers based on the layer-by-layer method was proposed by Dubas et al. [41]. Thin film with antibacterial properties can be formed on the PA fibers by sequential dipping of fibers in solutions of poly(diallyldimethylammonium chloride)-PDADMAC and Ag NPs capped with poly(methacrylic acid)-PMA. Layer-by-layer deposition was obtained as a result of electrostatic interaction between anionic Ag NPs capped with PMA and cationic PDADMAC. The color of fibers turned from white to red due to the presence of immobilized Ag NPs. The effect of number of deposition cycles on antibacterial activity against *S. aureus* has been studied. It was shown that fibers covered with 10 and 20 polyelectrolyte layers provided only 0 and 50 % of bacteria reduction. The authors suggested that pretreatment of fibers might considerably change the surface chemistry and thus, improve deposition process.

In order to obtain permanent antibacterial activity Dastjerdi et al. [42] treated PES fabrics simultaneously or separately with polysiloxane emulsion and commercial colloidal Ag NPs at different concentrations. Proposed method relies on embedding of Ag NPs in crosslinkable polysiloxane layer. The application of low concentration of Ag NPs was sufficient to reach satisfactory bacteriostatic



**Fig. 1** SEM images of wool fibers modified with Ag NPs: **a** and **b** nanoprisms, **c** and **d** different nanodisks [38]

activity against *S. aureus* whereas higher concentrations of Ag NPs were required for the equivalent effect in the case of the *K. Pneumoniae*. Crosslinked polysiloxane provides controlled release of silver and thus, long-term antimicrobial activity can be expected. It was also found that simultaneous treatment of PES with polysiloxane and Ag NPs resulted in higher antibacterial efficiency compared with separate finishing.

Sonochemical irradiation procedure as already described in the previous section can be efficiently utilized for the deposition of Ag NPs onto PES and PA fabrics [9]. Actually, this paper compares Ag NPs deposition effect on three different substrates: Co, PES, and PA fabrics. The results of volumetric titration with KCNS according to the Folgard method demonstrated that the amount of deposited Ag NPs on all three analyzed substrates is almost the same (1.1–1.4 wt %). This observation implies that the extent of Ag NPs deposition is independent on the nature of the fibers. It is also very unlikely that deposition of Ag NPs by sonochemical irradiation involves any formation of new bonds between silver and certain functional groups on the fiber surface. Hence, it is suggested that physical adsorption of Ag NPs induced by sonication occurred i.e., ultrasound waves promoted fast migration of the newly formed Ag NPs to the fabric surface. Therefore, strong adhesion of Ag NPs to different fibers is attributed to possible melting of substrate due to the high rate and temperature of Ag NPs thrown to the solid surface by sonochemical micro-jets.

Many studies deal with plasma activation of PES and PA fibers before deposition of Ag NPs. Plasma treatment leads to an introduction of certain functional groups that could be potential sites for binding of Ag NPs as well as to a desired increase in fiber hydrophilicity. Yuranova et al. [43] investigated the effect of RF oxygen plasma and vacuum-UV irradiation on subsequent chemical deposition of Ag NPs on the PES/PA fabric. Plasma-treated or vacuum-UV-irradiated samples were immersed in the silver nitrate solutions of different concentrations and afterward exposed to mild reducing agent (not specified). The presence of Ag NPs on the surface of the PES/PA fibers was confirmed by XPS and TEM analyses. Although Ag<sub>2</sub>O and AgO were found as components of the Ag NPs clusters on the fiber surface, the main component was Ag. However, the accurate determination of the Ag NPs cluster state on the surface of the fibers was very difficult because of the wide NPs size distribution and electrostatic charging of the supported particles. It was also shown that the amount of deposited Ag NPs increased with an increase of the concentration of applied silver nitrate solution. On the other hand, higher concentrations of used solutions caused significant particle growth on the fiber surface as observed by TEM. Deposited Ag NPs imparted antibacterial properties to PES/PA fabric. The minimum silver loading on the

fabrics that is required for the complete inhibition of bacteria *E. coli* growth was also detected. It was shown that this content was dictated by pretreatment.

In order to attain better susceptibility of hydrophobic PES fibers to hydrophilic colloidal Ag NPs, Ilić et al. [44] modified PES fabrics by RF air plasma at low pressure (0.27 mbar) before the deposition of Ag NPs. As already mentioned, Ag NPs were synthesized in aqueous solution of silver nitrate with sodium borohydride as a reducing agent without using any stabilizer [22]. PES fabrics were loaded once or twice with Ag NPs from 50-ppm colloidal solution. Untreated and plasma-treated fabrics loaded with Ag NPs obtained maximum bacteria reduction (*E. coli* and *S. aureus*). Plasma-treated PES fabrics preserved excellent antibacterial efficiency after five washing cycles even when they were loaded with Ag NPs only once. Unlike them, untreated fabrics had to be double loaded with Ag NPs to reach equivalent antibacterial activity after washing. Greater antibacterial activity of plasma-treated samples was due to larger amount of deposited Ag NPs. The total amount of initially deposited Ag NPs on plasma-treated PES fabrics was almost two times larger compared with equivalent untreated PES fabrics. AAS measurements clearly indicated that leaching of silver took place during the washing process. After initial rapid leaching, release of silver slowed down already in the second washing cycle for all samples. This study also revealed that larger amount of Ag NPs retained on the double-loaded samples after washing compared with single-loaded samples. In addition, almost four times larger amount of Ag NPs was left on plasma-pretreated PES fabrics compared to equivalent untreated fabrics.

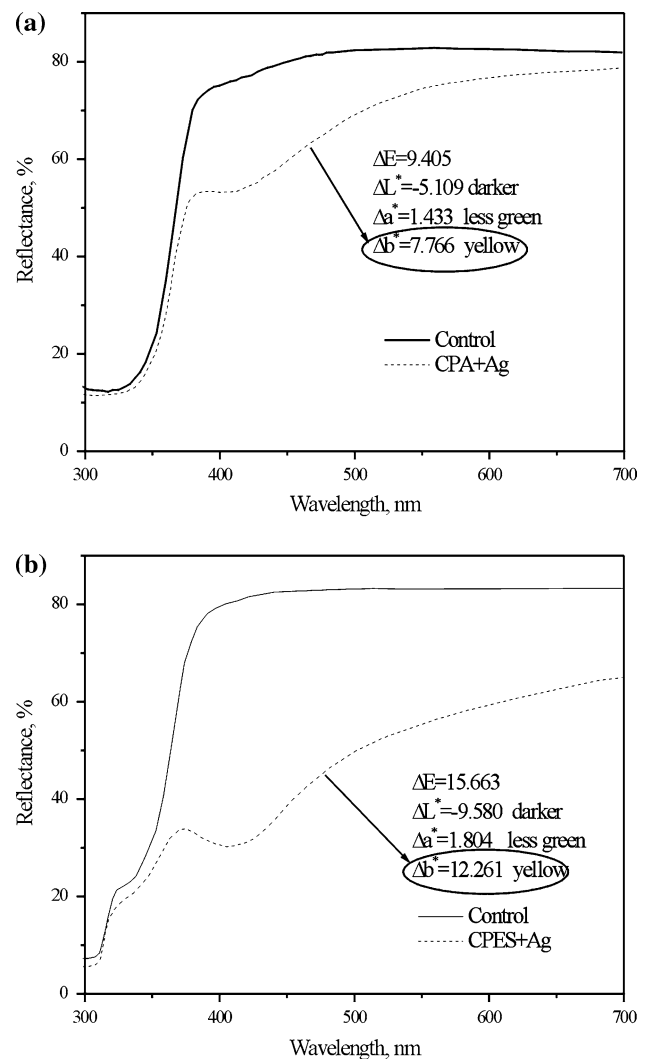
Although low-pressure devices, in particular RF-powered sources, allow easier control of properties and provide a greater stability and uniformity, these systems require more complex handling of textile materials and expensive vacuum pumps [45, 46], which can be avoided using corona and dielectric barrier discharge at atmospheric pressure. Hence, activation of PES and PA fabrics with plasmas at atmospheric pressure before deposition of Ag NPs recently gained much scientific attention [47–54]. Gorenšek et al. [47] compared the effect of corona treatment of raw, washed and washed-thermostabilized PES fabrics on Ag NPs loading. The simultaneous exhaustion of commercial Ag NPs (20 mg/L) and auxiliaries was carried out according to dyeing regime which was performed for dyeing of these samples with disperse dye C.I. Disperse Red 73. The effects of corona treatment were significantly affected by the preparation of the fabrics. Unlike corona-treated raw PES fabric which exhibited the decrease in O/C ratio i.e., increase in the content of C–C/C–H groups and decrease of C–O groups, opposite effect was observed on the surface of washed and washed-thermostabilized PES

samples exposed to corona treatment under the same operating conditions. Corona treatment resulted in an increase of capillary uptake and improved dyeability of PES fabrics. Higher adsorption of Ag NPs (80 nm) on corona-treated raw samples is suggested to be due to increased porosity and surface area. The extent of loaded Ag NPs was higher on corona-treated raw samples compared with cleaned samples. Consequently, corona-treated raw PES fabrics demonstrated better antibacterial activity against *S. aureus*, *E. coli*, *S. faecalis*, and *P. aeruginosa*.

Several studies demonstrated that corona discharge can be efficiently utilized for functionalization of PES and PA fabrics before loading of colloidal Ag NPs. Corona-treated PES and PA fabrics were dip-coated with Ag NPs from 10- to 50-ppm colloidal solution [48]. As expected, corona treatment resulted in enhanced hydrophilicity which was confirmed by water contact angle measurements. In addition, the morphology of PES and PA fiber surfaces was considerably altered, and typical submicrometer-sized ripple-like topography was observed by SEM. SEM analysis also revealed the presence of evenly distributed agglomerates of Ag NPs after their loading on PES and PA fabrics. Double loading of fabrics with Ag NPs from 50-ppm colloidal solution led to an obvious increase in the amount of deposited Ag NPs which completely covered the surface particularly of PES fibers. The corona-treated fabrics loaded with Ag NPs from 10-ppm colloidal solution provided better antibacterial efficiency against *S. aureus* and *E. coli* compared with untreated samples loaded with Ag NPs. However, these samples did not provide desirable level of laundering durability and double loading of Ag NPs from 50-ppm colloidal solution was performed. This treatment ensured maximum bacteria reduction for both untreated and corona-treated samples subsequently loaded with Ag NPs. The positive effect of corona pretreatment became prominent after five washing cycles particularly on the PES samples. Namely, corona-pretreated samples preserved excellent antimicrobial activity. Improved antibacterial properties of corona-pretreated samples were attributed to higher fiber surface roughness and increased hydrophilicity, which made them more accessible to Ag NPs.

The same group of authors also studied the relation between loading of Ag NPs and dyeing of PES and PA fibers. It was shown that the order of loading of Ag NPs and dyeing has strong influence on the color change of PA and PES fabrics [51–53]. The color of PA fabrics dyed with C.I. Acid Green 25 was just slightly affected by Ag NPs deposition independently of the order of operations. On the contrary, the deposition of Ag NPs on fabrics before and particularly after dyeing with C.I. Disperse Blue 3 induced considerable color changes. Color changes became even more obvious on PES fabrics, which were loaded with Ag NPs after dyeing with C.I. Disperse Violet 8. Similar trend

of color changes was observed on corona-pretreated samples. Detected color changes are suggested to be due to the presence of Ag NPs on the fabrics surface as confirmed by SEM, but also indirectly by reflectance curves of untreated and corona-pretreated PES and PA fabrics that were not dyed. Their color turned from white to pale yellow after the loading of Ag NPs [52]. The decrease in reflectance intensity at  $\sim 415$  nm corresponds to plasmon resonance band of Ag NPs (Fig. 2). The shift of plasmon resonance band toward lower energies compared to the position of the plasmon band of non-agglomerated Ag NPs in initial colloidal solution (380 nm) is suggested to be due to higher dielectric constant of the surrounding medium caused by the inter-particle coupling of Ag NPs agglomerated on the fiber surface [55]. Observed color change was more pronounced on corona-pretreated PES fabrics compared with



**Fig. 2** Reflectance spectra of **a** control (untreated fabrics that were not dyed) and corona activated PA and **b** PES fabrics loaded with Ag NPs [52]



corona-pretreated PA fabrics because of the larger amount of deposited Ag NPs.

XPS analysis revealed higher content of Ag on untreated and corona-treated PES fibers surface compared with PA fabrics [53]. It was also shown that corona treatment brought about an increase of C=O and O–C=O on the surface of PES and PA fabrics. The decrease of C–C and C–H groups was expected as it is a characteristic feature of plasma treatment of polymers which occurs as a consequence of polymer chain scission triggered by the action of plasma particles or as a result of a progressive oxidation of the carboxylated groups to release CO<sub>2</sub> [56, 57]. The increased number of carboxylic groups along with existence of benzene rings in polymer structure indicates the possibility for strong interaction between PES fibers and Ag NPs [58, 59]. It has been also postulated that in addition to carboxyl groups, the polar amide groups took part in the interaction between PA fibers and Ag NPs [12]. Antibacterial activity of untreated and corona-treated PES fabrics loaded with Ag NPs against *S. aureus*, and *E. coli* was independent on the order of dyeing and loading of Ag NPs. In order to obtain desired level of antibacterial efficiency of all studied PA fabrics, the loading of Ag NPs after dyeing was recommended [51, 52].

Untreated and corona-treated PES fabrics loaded with Ag NPs also exhibited excellent antifungal activity [53]. Again, the contribution of corona pretreatment on Ag NPs deposition and further, antifungal activity became more evident after washing test. Differently modified PES fabrics exhibited superior antifungal behavior. In addition, the dyeing of PES fabrics with C.I. Disperse Violet 8 did not influence the antifungal activity of PES fabrics independently of the order of dyeing and Ag loading.

Magnetron sputtering can be also used for uniform deposition of Ag nano-structured film on the surface of the PES fabric [60]. FE-SEM images of PES fibers indicate that the thickness of the film as well as Ag NPs size depend on the sputtering time. The prolongation of sputtering time results in an increase of the size of NPs and their aggregation. The presence of silver was confirmed by EDX analysis. The deposition of Ag NPs significantly contributed to increase of UV protection and maximum UPF rating of 50+ was achieved. Wettability of PES fabric surface was evaluated by contact angle measurements. Although PES fibers are hydrophobic by nature, contact angle of studied sample was 0°. Such behavior is due to high porosity of the samples that promotes penetration of water through the untreated fabric. Ag NPs deposition drastically enhanced the fiber surface hydrophobicity, and after 30 min of sputtering, contact angle of 132.2° was observed. As expected, PES fabrics exhibited excellent antibacterial activity against *S. aureus* and *E. coli*.

Interesting idea to impart antistatic and water-repellent properties to PES fabrics with commercial Ag NPs and

fluorine-based agent in the presence of coupling agent was proposed by Shyr et al. [61]. One-bath finishing process relies on the simultaneous application of Ag NPs and water-repellent agent whereas two-bath finishing implied separate finishing, first with Ag NPs and afterward with water-repellent agent and vice versa. One-bath finishing did not provide desired effects, and it was demonstrated that both finishes were unevenly deposited on the fiber surface. The results showed that the order of finishing in the case of two-bath process significantly affect the final effects. The samples that were treated with Ag NPs and afterward with water-repellent agent exhibited superior behavior: desired level of antistatic efficiency and water-repellency was preserved after ten washing cycles.

Remaratnam et al. [62] used Ag NPs to create ultrahydrophobic PES fabrics (water contact angle above 150°). The idea was to design the surface that will mimic the so-called lotus effect. PES fabrics with different structures were dip-coated with poly(glycidyl methacrylate)/poly(2-vinylpyridine) 70:30, treated with ethanol and Ag NPs suspension, again dip-coated with poly(glycidyl methacrylate) and grafted with polystyrene. Developed textile nanocomposite systems provided an increase in water repellency. However, it was shown that not all the studied fabrics ensured ultrahydrophobicity. It was concluded that it is not sufficient to possess roughness and hydrophobic components, but also adequate fabric roughness. It should be also emphasized that the coverage of the fiber surface with Ag NPs was influenced by their size.

## Polypropylene

Polypropylene fibers (PP) are widely used in the manufacturing of medical and hygienic textile materials where the high level of antimicrobial activity is required (surgical masks, diapers, hygienic bands, etc.). Several studies showed that small amounts of Ag NPs can meet these antimicrobial demands [63–68]. Two approaches to antimicrobial functionalization of PP fibers with Ag NPs are proposed: the first one relies on the mixing of Ag NPs with polymer during the spinning process while the other one implies the deposition of Ag NPs on textile material during the finishing process [63]. First attempt to produce PP/Ag nanocomposite fibers with permanent antibacterial properties has been made by Yeo et al. [64]. The fibers were melt-spun by co-extrusion of PP and PP/Ag master-batches using general conjugate spinning. For this purpose, commercial Ag NPs in the form of powder with average diameter of 15.7 nm have been used. The idea was to produce core-shell fibers with PP/Ag in shell and PP in core section and opposite. DSC measurements indicated that the crystallinity of spun fibers containing Ag NPs

slightly decreased. The presence of Ag NPs in the core part of the fiber did not induce any antibacterial activity against bacteria *S. aureus* and *K. pneumoniae*. In contrast, the fibers having Ag NPs in the shell part exhibited excellent antibacterial activity, but the activity was considerably influenced by the content of incorporated Ag NPs.

The same group of authors padded spun-bond PE/PP non-woven material with different types of commercial nano-sized Ag colloids: Ag NPs dispersed in water, Ag NPs dispersed in ethanol, and nano-sized Ag/S composite particles dispersed in ethanol [65]. All the samples demonstrated excellent antibacterial efficiency against *S. aureus*, but only the sample treated with Ag/S composite nanoparticles provided superior antibacterial activity against both bacteria *S. aureus* and *K. pneumoniae*. The increase in the concentration of Ag NPs colloid caused the improvement of antibacterial activity which is also dependent on the size of deposited NPs.

Tseng et al. [66] successfully grafted 2-methacrylic acid 3-(bis-carboxymethylamino)-2-hydroxy-propyl ester (GMA-IDA) to PP fibers by plasma-induced polymerization before loading of Ag ions. The chelating groups,  $-\text{N}(\text{CH}_2\text{COO}^-)$  on the grafted surface of PP fibers were coordination sites for Ag ions. The growth of Ag NPs was obtained by reduction with UV light and by formaldehyde solution at different pH values. Grafted fibers were immersed in different pH aqueous solutions (pH = 2, 5, 8 and 11) until equilibrium was reached and then the  $\text{Ag}^+$ /polymer system was exposed to reduction process. The results indicated that the amount of GMA-IDA grafted on the surface of PP fibers is dependent on plasma exposure time. Plasma treatment over 3 min should be avoided as the crosslinking on the fiber surface took place due to the presence of significant amount of free radicals, decreasing the extent of grafting. SEM and TEM images demonstrated that the size of Ag NPs decreased with an increase of pH value in the case of reduction by UV light. Oppositely, the size of the Ag NPs after the reduction in formaldehyde solution was the smallest at the lowest pH value. TEM images of the cross sections of the fibers revealed that Ag NPs could be found not only on the fiber surface, but they were also distributed in the interior of the grafted layer. The sizes of Ag NPs on the surface considerably differ from those in the fiber interior. It is suggested that smaller size of inner Ag NPs is due to protective effect of GMA-IDA polymer chains which inhibited aggregation of Ag NPs. Unlike them, Ag NPs on the fiber surface agglomerated easily because of the low thermodynamic stability of nanoclusters and the lack of the polymer protection.

The surface of the spun bonded PP non-woven material can be coated with a film consisting of Ag NPs by RF magnetron sputtering [67]. Argon was used as a sputtering gas. The influence of sputtering time, power, and argon

pressure on antibacterial activity against *S. aureus* and *E. coli* was examined. The maximum reduction of *S. aureus* colonies was obtained independently of operating conditions. Unlike power and argon pressure, sputtering time considerably influenced the antibacterial activity against *E. coli*. The longer the sputtering time, the higher the antibacterial efficiency. This is assumed to be due to larger amount of deposited Ag NPs. SEM and AFM analyses confirmed the presence of Ag NPs clusters on the surface of PP fibers. Their size was also influenced by deposition time.

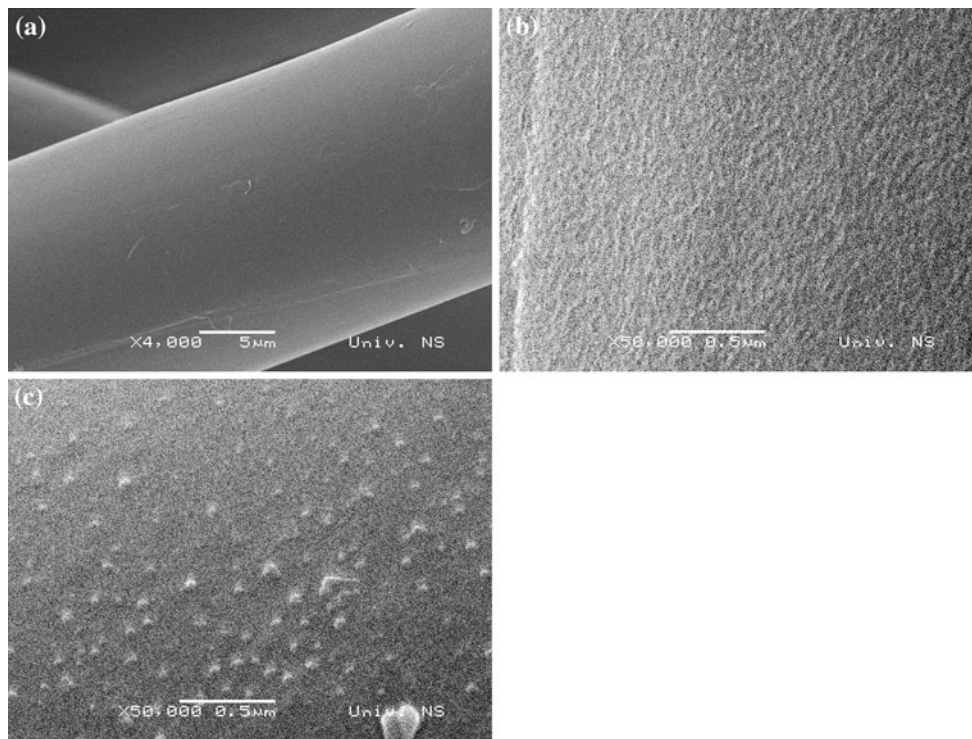
RF plasma treatment can be also efficiently utilized for the activation of the surface of hydrophobic PP fibers before dip-coating of hydrophilic colloidal Ag NPs [68]. Figure 3 illustrates the positive effects of air RF plasma treatment of PP non-woven fabric on the deposition of Ag NPs. SEM images reveal plasma-induced morphological changes i.e., the formation of very uniform nanostructured striations on the PP fiber surface. Obviously, plasma pretreatment facilitated the binding of Ag NPs that were evenly distributed over the surface of the PP fibers.

### Environmental impact of the Ag NPs

The results presented in previous sections clearly show that Ag NPs can impart extraordinary antimicrobial properties to different textile materials. Although small amount of Ag NPs is sufficient to provide desired effects, it is little known about their fate during exploitation and maintenance of textile goods. The information on the amount and form of Ag NPs release into water is of great importance, as this knowledge would imply their potential environmental risks. Actually, Ag NPs may be discharged into environment during synthesis, manufacturing and incorporation of NPs into goods, exploitation of goods and while recycling or disposal of goods and Ag NPs [69]. Toxicity and exposure data for Ag NPs are currently lacking [67]. Only few studies considered Ag NPs release from textile fibers into water and possibility of their removal from effluent [19, 44, 70, 71].

Durán et al. [19] demonstrated that Ag NPs released during washing of Co fabrics can be efficiently eliminated from effluent by biosorption with *C. violaceum*. SEM analysis revealed that bacteria cells changed their form from rods to spheres in the presence of Ag NPs.

Benn and Westerhoff [70] investigated the release of silver from six types of commercially available socks. The socks contained different quantities of Ag NPs, but the maximum amount found was 1,360  $\mu\text{g/g}$ . The simulation of washing in water without detergents indicated that release of silver took place (1.5–650  $\mu\text{g}$  in 500 mL of water), but that dynamics and the extent of silver release



**Fig. 3** SEM images of **a** untreated PP fiber, **b** PP fiber treated by air RF plasma, and **c** PP fiber treated by air RF plasma and loaded with silver nanoparticles [68]

were basically affected by the manufacturing procedure of investigated socks. Some socks released certain amount of silver during washing while the other released the whole amount of deposited silver. Filtration and ion selective electrode analyses pointed out that silver was released in both colloidal and ionic form. In addition, it was predicted that wastewater plants should have capacities that are sufficient for larger loads of silver from wastewater streams which are reasonable to be expected due to increased number of consumers of goods containing Ag NPs.

Geranio et al. [71] studied different commercially available textile materials functionalized with Ag NPs. They followed the influence of pH, surfactant and bleaching agents on silver release. It was shown that at pH 10, which is relevant to conventional washing, negligible dissolution of Ag NPs was evident. Bleaching agents like hydrogen peroxide or peracetic acid can significantly accelerate the dissolution of Ag NPs. When perborate and TAED in concentration that is equivalent to conventional washing was applied at elevated temperature, a rapid increase in  $\text{Ag}^+$  ions was noticed. This group of scientists confirmed the previous observation that silver release is controlled by the textile type i.e., the manufacturing procedure.

Lazic et al. studied the possibility to utilize recycled wool-based nonwoven material [72, 73] for removal of silver from wastewater, which derived from washing of

PES fabrics treated with RF air plasma and colloidal Ag NPs [44]. Namely, wash baths washing were collected and AAS measurements revealed that the concentration of silver in collected sample was 0.5 mg/L. After 3 h of sorption, 70 % of silver was removed. The removal of silver increased up to 84 % after 24 h of sorption. Recycled wool-based nonwoven material was modified with hydrogen peroxide and particularly with biopolymer alginate enhanced the efficiency of silver removal, and about 90 % of silver was eliminated already after 3 h of sorption.

The analysis of risk to freshwater ecosystems from Ag NPs incorporated into textile materials and plastics was assessed on the basis of estimated silver use in the year 2010 [74]. The analysis was focused on the river Rhine as a case study. It was predicted that up to 15 % of silver emissions into water in Europe will be from plastics and textiles. Keeping in mind the growing market of textile and plastics products with Ag NPs, they assumed that by 2015 these goods will account for substantial share of total silver emissions in European Union. Immediate silver release to environment originates from sewage treatment plants effluents, untreated wastewater, and sewage sludge that are disposed to agricultural fields.

Recently Arvidsson et al. [75] estimated current emissions of Ag NPs by application of particle flow analysis method. The results are uncertain but they imply that textile goods may become a large source of Ag NPs emissions

in the future. The authors suggest that the application of Ag NPs should be limited to wound dressings. The tendency of widespread consumption of textile products with Ag NPs may also induce adverse effect on bacteria which can become resistant to silver.

There is still no evidence that humans are being adversely affected by Ag NPs while using the products with Ag NPs, but it is very likely that Ag NPs will be released into environment where they persist or bioaccumulate [69]. Hence, the concern for environmental and human health risks is growing and consequently, further research that may discover the real role of Ag NPs in environment is needed.

## Conclusion

Silver nanoparticles by far are the most often explored nanomaterials in the field of textiles due to extraordinary antimicrobial activity against numerous microbes. Simple methods for antimicrobial finishing of textile materials with silver nanoparticles are suitable for industrial implementation and hence textile goods comprising silver nanoparticles recently became commercially available. The initial intention was to utilize antimicrobial properties of silver nanoparticles for manufacturing of medical and hygienic textile materials. However, growing popularity of “silver textiles” due to increasing consumer requirements for textiles with antimicrobial and odor reduction properties drastically broaden the list of textile products with silver nanoparticles. Such tendency may impose negative environmental risks because of potential emission of silver nanoparticles during production and exploitation.

This review demonstrated that much work has been done in this field, but there are still plenty of gaps which have to be filled. Major research was focused on antimicrobial effects of modified textile materials but essentially no certain conclusions on binding mechanism between silver nanoparticles and textile fibers have been drawn. Although many different procedures for antimicrobial finishing of textile materials with silver nanoparticles have been developed, none of them guarantee permanent antimicrobial activity and ever present release of silver pose emerging environmental problem. Therefore, it is predictable that further research will be more oriented toward environmental aspect of exploitation of textile products with silver nanoparticles. However, the process of imposing new regulations is much slower than the nanotechnology growth. The main obstacle for complete assessment of ecological risks is the lack of adequate toxicology characterization of silver nanoparticles. It is very likely that nanotoxicology will be considerably different from toxicology of the bulk silver. The development of suitable and

accurate nanotoxicology methods is not easy task since behavior of silver nanoparticles is very much governed by their size and shape. In addition, more research on health risk and possible side effects of silver nanoparticles is necessary.

Despite exquisite potentials of silver nanoparticles as antimicrobial agents, their fate and possible restriction in application to textile materials will be very much influenced by future findings concerning the environmental risks.

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