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ORIGINAL ARTICLE

Treating wool fibers with chitosan-based nano-composites for enhancing the antimicrobial properties

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Abstract

Environmentally friendly finishing methods for imparting antimicrobial properties to various textiles are very desirable. The purpose of the present study is to investigate the synthesis, characterization, and application of various chitosan (Ch) derivatives containing Ag, Cu and Zn nanoparticles (NP_S) on wool yarn. The Ch loaded with various NPs was studied by Scanning Electron Microscopy (SEM), Dynamic light scattering (DLS), Fourier Transform Infra-Red (FTIR) and Differential Scanning Calorimetry (DSC). Wool yarns were treated with Ch-NPs and the treated samples were analyzed by SEM. The weight gain results indicated the successful surface modification of wool fibers with Ch-NPs. The treated samples showed excellent antimicrobial activities (~ 100%) against *Staphylococcus aureus* (*S. aureus*) and *Escherichia coli* (*E. coli*). The treated samples had generally very high antimicrobial activities (> 80%) even after 10 washing cycles. The surface modification of wool fibers with Ch-NPs can be considered as an environmentally friendly method for antimicrobial finishing.

Keywords Chitosan · Nanoparticles · Wool yarn · Antimicrobial finishing · Durable treatment

Introduction

Nanoparticles and nanocomposites have very high surface area-to-volume ratio and therefore they can be used in a large number of industrial applications. Nanoparticles are employed to develop innovative environment-friendly chemical mechanical polishing slurries (Zhang et al. 2018, 2019), which are used in semiconductor and microelectronics industries. In addition, nanoparticles are also used to develop novel machining approaches and diamond wheels (Zhang et al. 2015, 2017, 2018). With the use of nanoparticles, nanoscale precision surfaces are achieved (Zhang et al. 2012a, b, 2013). These studies are a breakthrough and milestone contribution to the environment, effectively eliminate the pollution and contamination induced by traditional machining and manufacturing (Zhang et al. 2019).

The surface properties and functionalities can be enhanced by treating the surface with various NPs. The combination of various NPs may also have some synergistic effect and impart novel characteristics (Giannousi et al. 2015). Some of NPs may be toxic and cause not environmentally acceptable. By fixation of NPs on a biopolymer such as chitosan, it is possible to reduce the consumption of NPs and eliminate the aforementioned problems. Moreover, the inherent properties of biopolymers can also be enhanced and some new functionalities can be generated by the addition of NPs. As an example, the antimicrobial properties can be enhanced by combining metal/metal oxide with biopolymers (Peschel et al. 2011; Petkova et al. 2014).

Chitosan is the second natural polysaccharide after cellulose and is achieved from chitin (Kong et al. 2010). The use of chitosan in the various industry is developing due to its antimicrobial potential, biodegradability, and non-toxicity. However, the solubility, cationic nature, and antimicrobial properties of chitosan decrease by increasing pH above 7. To overcome this problem, chitosan can be chemically modified (Lim and Hudson 2013; Jayakumar et al. 2010; Rinaudo 2006; Zamani and Taherzadeh 2012; Enescu 2008; Sashiwa et al. 2002). Since, the free amino groups of chitosan are very suitable to produce strong complexes with metals/metal oxide, the combination of metal oxide NPs with chitosan

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is another approach to improve its antimicrobial efficiency (Kumar et al. 2012). The metal complexes can improve the stability and antimicrobial activity of chitosan 10–20-fold (Kyzas and Bikiaris 2015). For example, the complex of silver ion on chitosan backbone increased the stability and antibacterial activity of Ag^+ by 20-fold compared to that of chitosan (Nayak et al. 2016), and also ZnO NPs on chitosan were slightly less effective than silver NPs (Li et al. 2010; Vaseeharan et al. 2015; Sanmugam et al. 2017; Kim et al. 2010; Moura et al. 2016; Li et al. 2010; de Godoi et al. 2013).

In this study the antimicrobial activities of treated wool yarns by Ch-NPs are investigated. First, Ch is treated with a series of inorganic salts (e.g., $AgNO_3$, Cu_2O and ZnO) and their combinations. Then, FTIR, SEM, DSC and DLS techniques are utilized for the characterization of Ch-NPs and the treated wool fibers. The objective of this study is to understand the antimicrobial activities and durability of the treated wool samples with Ch-NPs to shed more light on the topic of environmentally friendly wool finishing.

Materials and methods

Chitosan with molecular weight > 600 kD and degree of deacetylation 98% was supplied by Mahtani Chitosan PVT. LTD Chitin India. ZnO, $AgNO_3$, and Cu_2O were purchased from Merck (Germany), and the specification of wool yarn used in this study was 200 Tex/fourfold. Scouring of wool yarns was performed with nonionic detergent (Lotensol, Hansa), and the other materials were of analytical grade.

The functional groups of Ch-NPs were studied by a Nicolet NEXUS FTIR spectrometer (USA) in the area of 400–4000 cm^{-1}. The tests were performed at 20 °C and in a relative humidity of 65%. The surface properties of synthesized Ch-NPs composites and the treated wool samples were studies by scanning electron microscope (SEM) Seron AIS 2300 at an acceleration voltage of 20 kV. The particle size of NPs was determined by the dynamic light scattering (DLS) technique via measuring the intensity of scattered light over time. Differential scanning calorimetry (DSC) was used to study the calorimetry behaviors of the Ch-NPs composites and the treated wool samples under constant nitrogen purge using a TA Instrument in the range of 0–350 °C with the scanning rate of 10 °C/min. Also, the tear strength of all wool samples was measured by the Instron 5566 electromechanical instrument.

Synthesis of Ch-NPs composite

Chitosan (5.0 g) was solubilized in 150 mL acetic acid solution (2% v/v) at 60 °C with continuous stirring. The freshly prepared aqueous solution of $AgNO_3$, Cu_2O, ZnO, or their mixtures (10 mM and 3 mL) was sonicated at 40 °C for 30 min and added to the chitosan solution following the recipe reported in (Aryabadie et al. 2015). The mixing was terminated after 2 h by adding NaOH (1%) and the precipitated Ch-NPs composite was collected by filtration. The particle size of the filtered fine powder was in the range of 0.2–0.4 mm. Figure 1 shows the preparation method of Ch-NPs composite schematically.

Treatment of wool yarns with Ch-NPs

Nonionic surfactant (5% o.w.f) was utilized for scouring of wool yarns at 50 °C for 30 min with the liquor ratio (L.R) of 1:40. Then, the samples were rinsed, and dried at room temperature.

The fine powder of Ch-NPs (1–10% o.w.f.) was dissolved in water (30 mL) containing 4% o.w.f. of citric acid and 4% sodium hypophosphite. Then, the scoured wool yarn (2 g) was immersed in different concentrations of Ch-NPs (1–10% o.w.f.) at 50 °C for 3 h. Afterward, the samples were dried at 80 °C for 5 min, and then cured at 120 °C for 5 min. Finally, the treated wool yarn was rinsed and dried at room temperature. The grafting procedure of prepared Ch-NPs on wool yarns is given in Fig. 2. The amount of Ch-NPs deposited on the samples was determined by the weighing gain analysis of wool yarns before and after treatment.

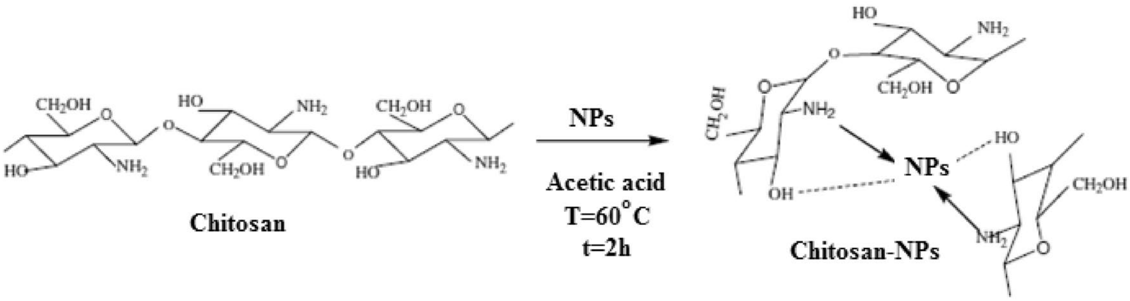


Fig. 1 The synthesis procedure of Ch-NPs composite

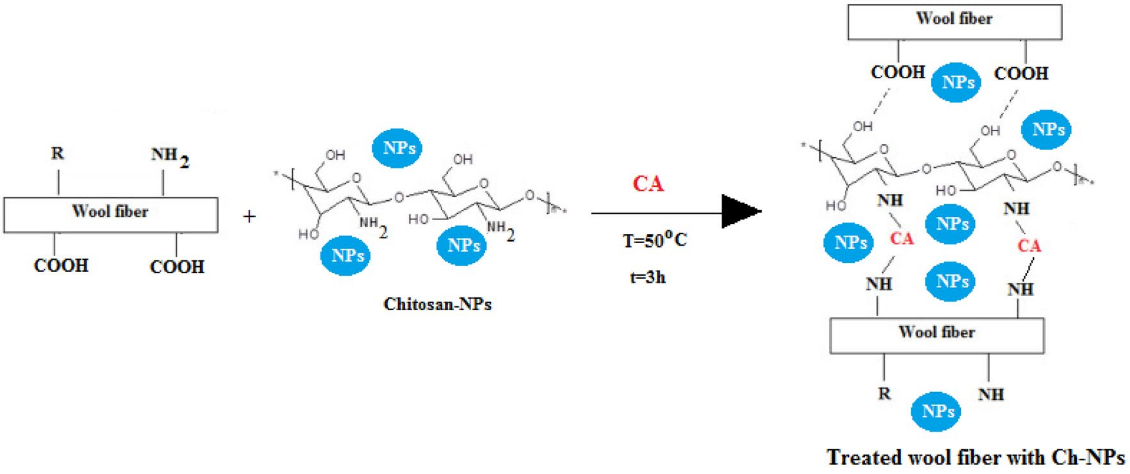


Fig. 2 Grafting procedure of Ch-NPs on wool yarns

Antimicrobial test

A quantitative evaluation of microbial reduction of treated samples with Ch-NPs was completed against Gram-positive *S. aureus* and Gram-negative *E. coli* bacteria according to the AATCC test method 100–2004. In summary, the samples were put into tubes and were autoclaved for 15 min at 121 °C. The suspension of bacteria on culture medium was prepared, and 100 µL of bacteria suspension (10^6 bacteria) was added into tubes, incubation was performed at 37 ± 2 °C for 18 h, and the reduction in the number of colonies on the treated and untreated samples was calculated by Eq. 1:

$$\text{Antimicrobial effect (\%)} = \frac{A - B}{A} \times 100 \tag{1}$$

where A is the number of bacteria recovered from the inoculated wool yarn and B is the number of colonies recovered from the inoculated treated wool yarns after 24 h.

Results and discussion

The interaction mechanism of chitosan with transition metal cations has been reviewed before (Pestov and Bratskaya 2016). There are two possible models of binding metal ions by chitosan: the “bridge” model describing the metal ion coordination with several amino groups belonging to different glucosamine units of the same or different polymeric chains (Fig. 3, structures 2 and 4) and the “pendant” model, in which the metal ion is coordinated with just one amino group (Fig. 3, structures 1 and 3). The most active coordination site for transition metal ions is the nitrogen atom of the chitosan amino group, while many authors investigated the possibility of participation of other chitosan functional fragments in complex formation using quantum chemistry methods-acetamide and hydroxyl groups as well as the oxygen atom of the glycoside bond (Pestov and Bratskaya 2016).

Characterization of Ch-NPs

As illustrated in Fig. 4, the FTIR spectrum of Ch exhibits strong peaks at around 1023 cm^{-1}, 1081 cm^{-1}, and

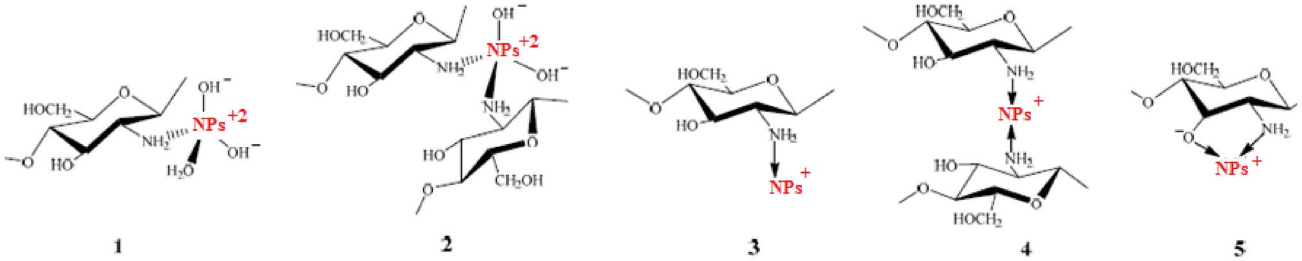


Fig. 3 Possible interactions between metal ions and chitosan (Pestov and Bratskaya 2016)

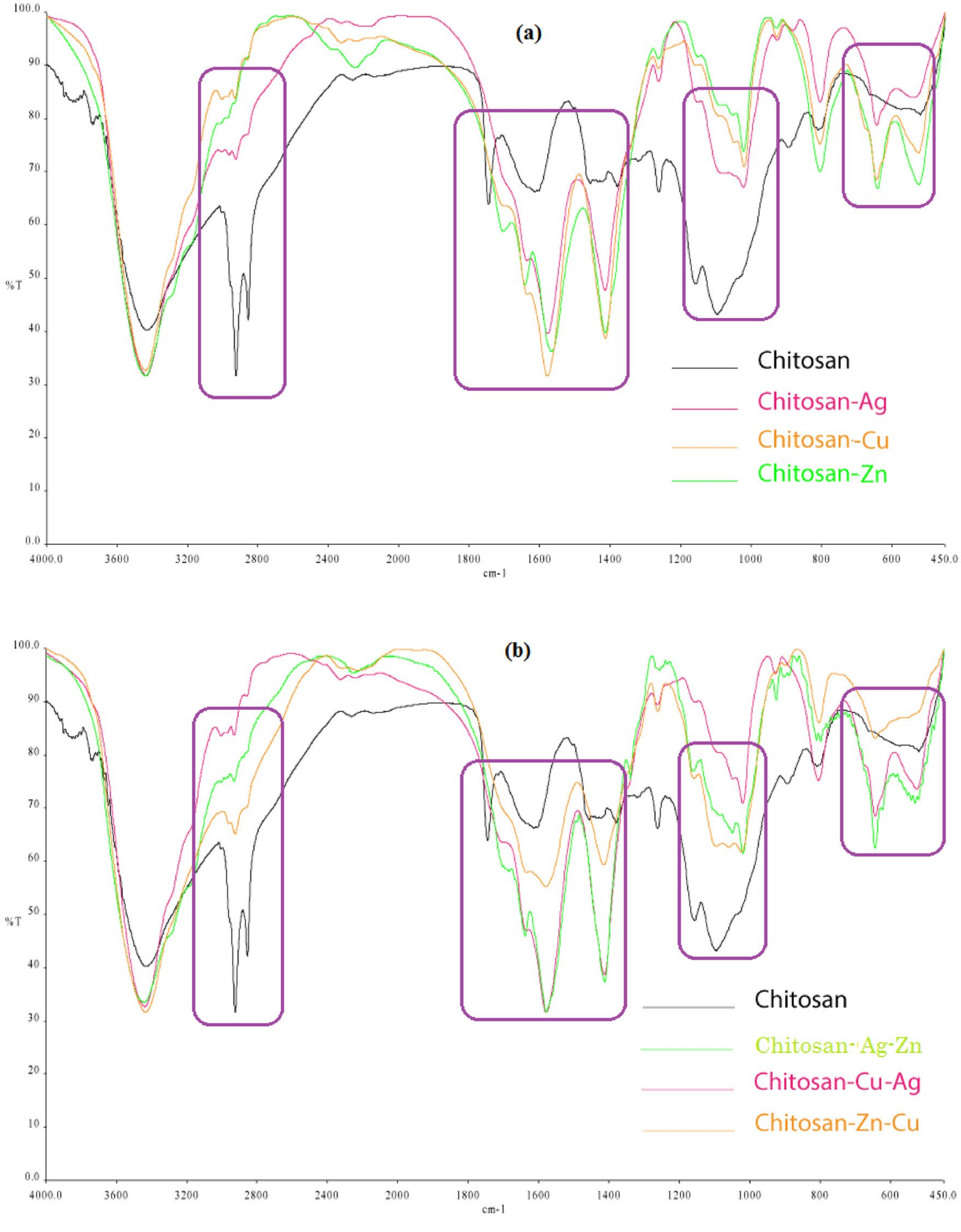


Fig. 4 FTIR spectra of synthesized Ch-NPS composite: **a** chitosan-independent NPs, **b** chitosan-mixture of NPs

1375 cm^{-1}, which are characteristic of a polysaccharide molecule (Sadeghi-Kiakhani et al. 2018; Giri Dev et al. 2009). Additionally the broadband of O–H stretching, and N–H stretching vibrations were observed in the region of 3200–3450 cm^{-1}, and carbonyl groups (C=O) were apparent at 1650 cm^{-1} (Vaseeharan et al. 2015; Sanmugam et al. 2017). The adsorption and complex formation of NPs on chitosan surface follows the three-step model: (1) adsorption of NP$_S$ onto the external surface of chitosan, (2) surface adsorption via electrostatic interactions, van der Waals forces, and hydrogen bondings, (3) coordination and chelation between NP$_S$ and chitosan (Sanmugam et al. 2017;

Sadeghi-Kiakhani et al. 2018). Decreasing the intensity of peaks at the frequencies 2925 and 2854 cm^{-1} corresponding to C–H groups, and disappearance of the peak in 1744 cm^{-1}, and appearance of a new peak at 1485 cm^{-1} indicates NPs ions are involved in complexation with $–NH_2$, –CONH, and –OH groups of Ch (Fig. 3). Also, the representative peak for NP_S at 855 cm^{-1} becomes more visible, and differences are apparent in the range of low frequencies from 750 to 550 cm^{-1}. These variations can exhibit the presence of NPs and their coordination with chitosan (Vaseeharan et al. 2015; Sanmugam et al. 2017).

The distribution of NP_S in the chitosan was investigated by SEM (Fig. 5). SEM micrographs clearly showed that the surface characteristic of chitosan modified by NP_S and the cavities on the surface of chitosan is occupied by NP_S (Govindan et al. 2012; Klaykruayat et al. 2010). Since chitosan molecules act as a reducing agent, even after drying the chitosan molecules do not allow NP_S to get merge with each other.

The glass transition (Tg) and thermal behavior of fibers were studied by DSC. Figure 6 shows the DSC thermograms of Ch and Ch-NPs. Due to the rigid crystalline nature and formation of strong inter/intra-molecular hydrogen bonding of Ch, Tg was not found. It has been reported that Tg of Ch could occur at the higher temperatures than its degradation (Aryabadie et al. 2015; Wazed et al. 2011). Ch thermogram exhibited a broad peak at 279 °C, which can be ascribed to the breakdown of amine groups of Ch (Aryabadie et al. 2015; Wazed et al. 2011). The treated samples indicated the shifting of the peak to the higher temperature (327–335 °C). This phenomenon presented the slow decomposition of new linkages between Ch and NPs with respect to control.

Wool surface characterization

DLS study

Horiba SZ-100 particle size analyzer was used to measure the size of Ch-NPs. The average size obtained by the DLS distribution plot was around 8–15 nm (Fig. 7). The average particle sizes of the Ch-NPs are significantly diverse and the type of metal salts affects its size. Ch–Ag/Cu particles had the smallest average size distribution among other NPs. Generally, to reduce metal ions and form NPs,

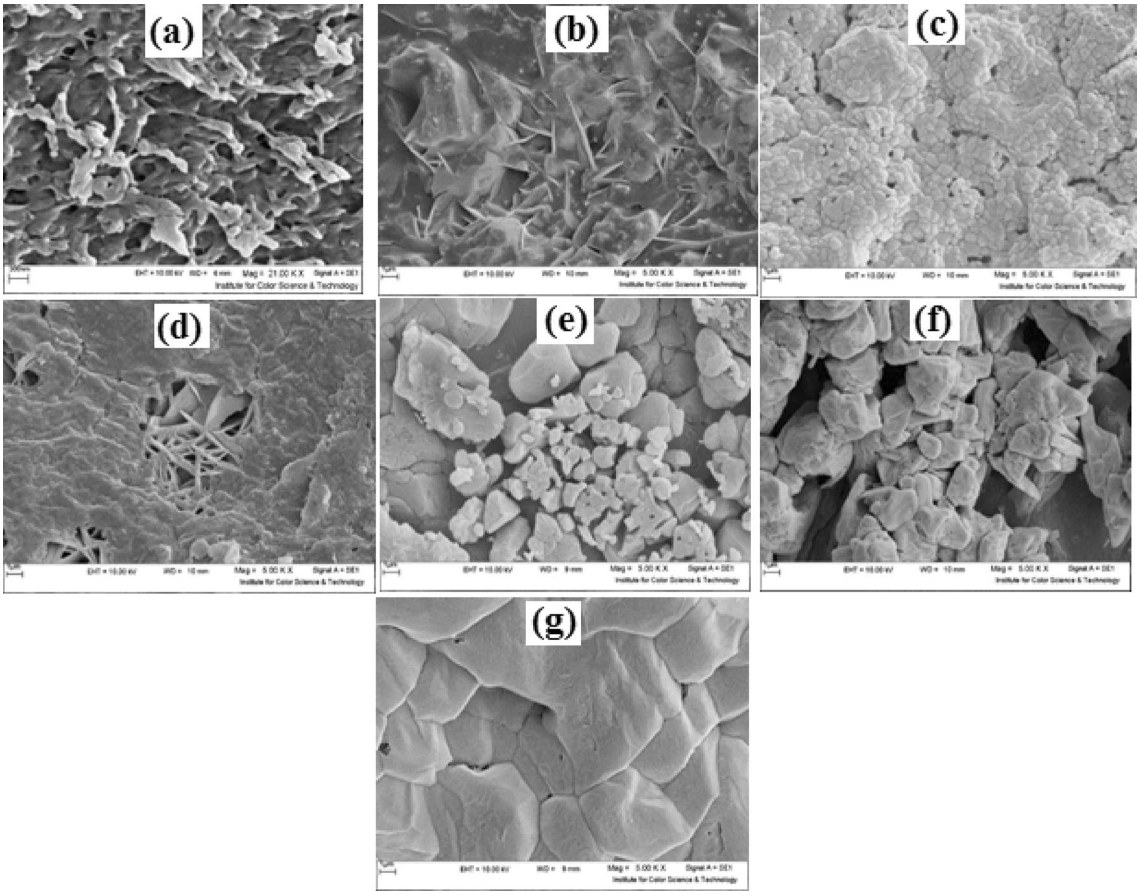
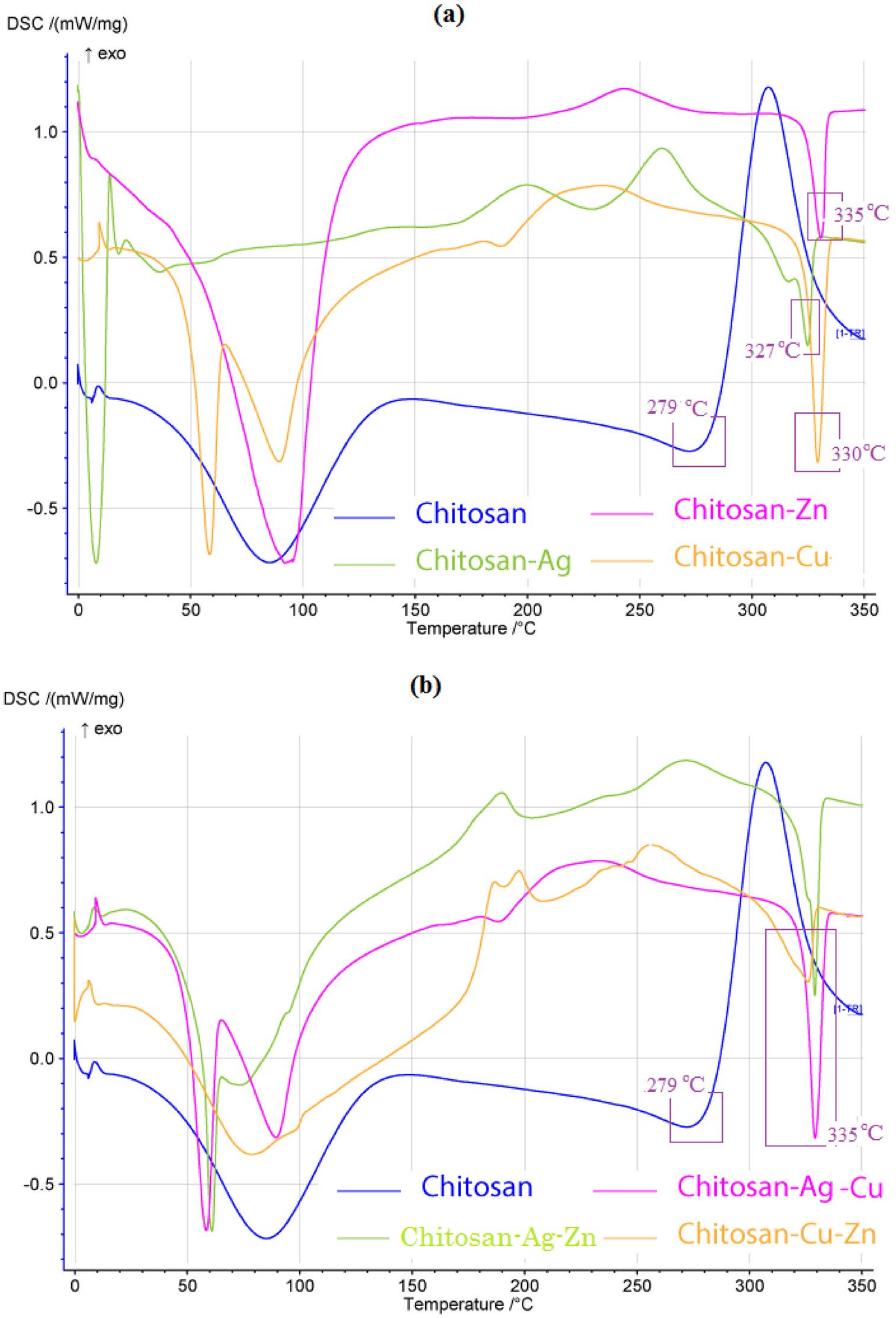


Fig. 5 SEM images of synthesized Ch-NP_S composite: **a** Ch, **b** Ch-Ag, **c** Ch-Cu, **d** Ch-Zn, **e** Ch-Ag/Zn, **f** Ch-Ag/Cu, **g** Ch-Cu/Zn

Fig. 6 DSC spectra of **a** chitosan-independent NPs, **b** chitosan-mixture NPs



a reducing agent is used to produce free electrons. In this study, thiol groups of wool fiber are formed through the degradation of cysteine bonds of wool fibers under moisture and heat (Al-Karawi et al. 2011; An et al. 2011). So, it was concluded that the reduction of metal ions into metal nanoparticles is occurred via available groups in the protein chains of wool fibers and chitosan as a biopolymer without further reducing agents. Here, Ag^+ and NO_3^- and ionic interactions are formed between metal positive ions and thiol groups with a negative charge. Thus, Ch-metal ions can be reformed to Ch-metal NPs with the available thiol groups in wool fibers and functional groups of chitosan.

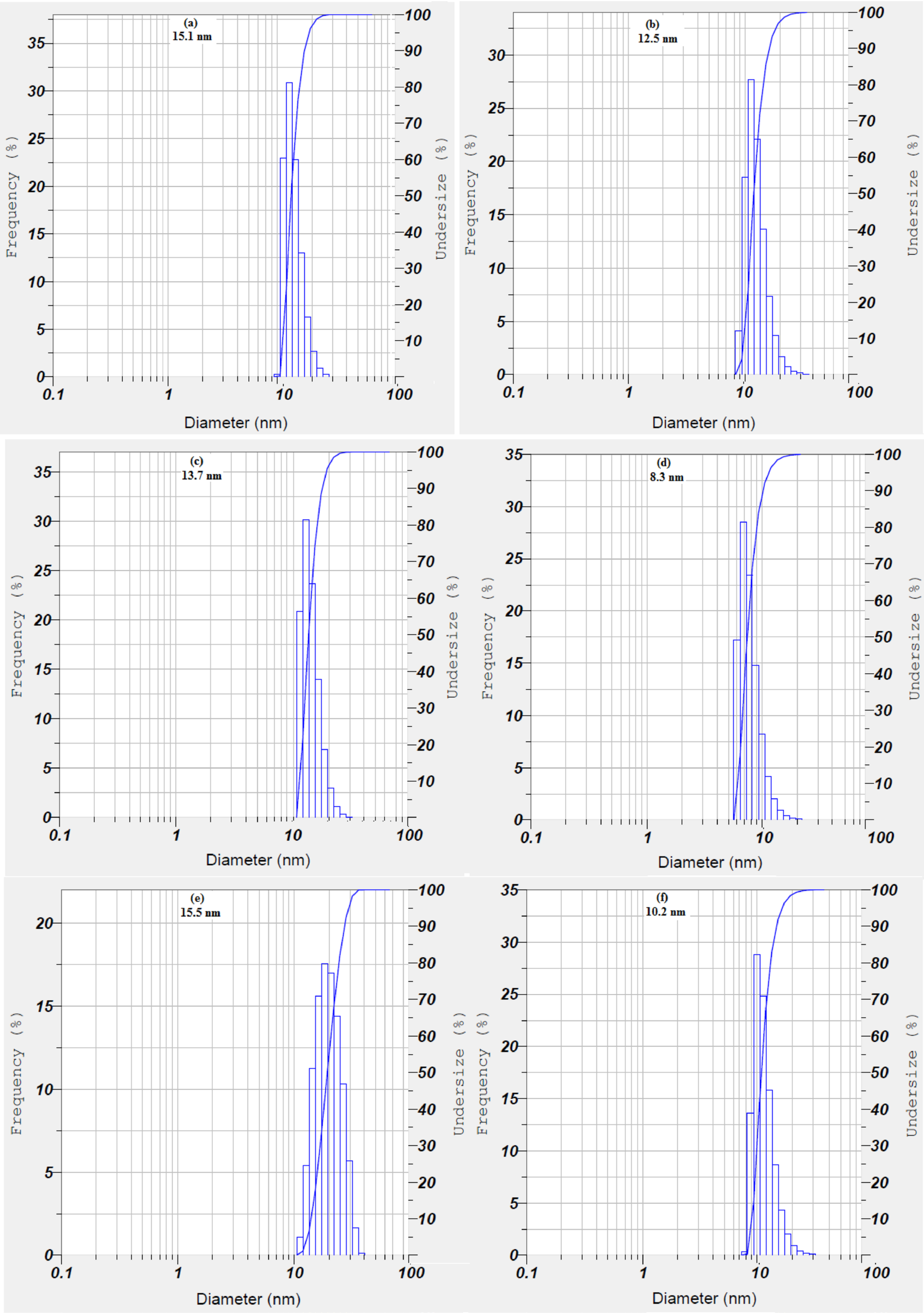


Fig. 7 DLS analyses of Ch-NPs **a** Ag, **b** Cu, **c** Zn, **d** Ag/Cu, **e** Ag/Zn, **f** Cu/Zn (Ch-NPs concentration = 5% o.w.f.)

Weight gain analysis

The weight gain percent of treated samples was measured as a criterion for grafting the Ch-NPs on the wool yarns (Fig. 8). The results showed that the weight gain of the wool fibers treated by Ch-NPs increased somewhat linearly by the initial concentration of Ch-NPs. This can be explained by the fact that the number of adsorbate species increases by their initial concentration and there is a higher chance of adsorption and complexation on wool fibers statistically. While at the more concentrations of Ch-NPs > 5 (%o.w.f.), the active sites available for the interaction of Ch-NPs with wool yarn are inaccessible and relatively limited, so, the concentration of Ch-NPs 5% o.w.f. can be considered as an optimal amount for pretreatment of wool yarns with Ch-NPs.

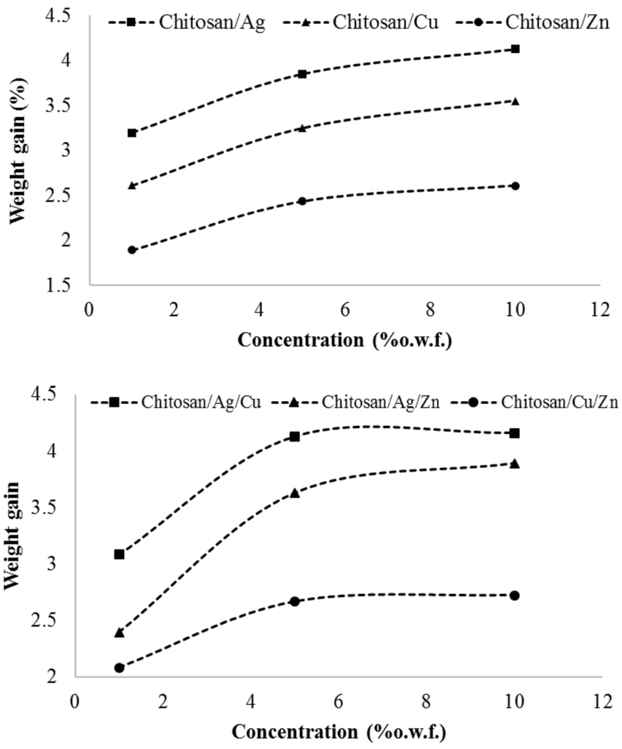


Fig. 8 The effect of Ch-NPs composite concentrations on weight gain of wool (T 50 °C, L.R 30:1, *t* 3 h)

Ch-NPs can attach to polar and ionizable functional groups of wool macromolecules by electrostatic interactions, hydrogen bonding, van der Waals forces, and coordination (Fig. 9). The grafting of Ch-NPs on the textile substrates can be completed via physical adsorption or chemical bonding. Also, the presence of various active sites in the protein chains of the wool fibers can improve the Ch-NPs grafting on the wool, and consequently the formation of Ch-NPs aggregation is diminished. Citric acid can also promote the complex formation between Ch-NPs and wool fibers.

SEM analysis

SEM images of all samples were studied to detect the produced variations in surface properties of wool yarns (Fig. 10). The scales are very obviously realized in the surface of wool fibers. Results clearly exhibited that a smooth coating on the surface of wool yarn is provided by Ch-NPs. As a result, the surface samples became softer and smoother due to the presence of a uniform layer on the surface of wool yarn, so that the surface roughness of wool yarn was

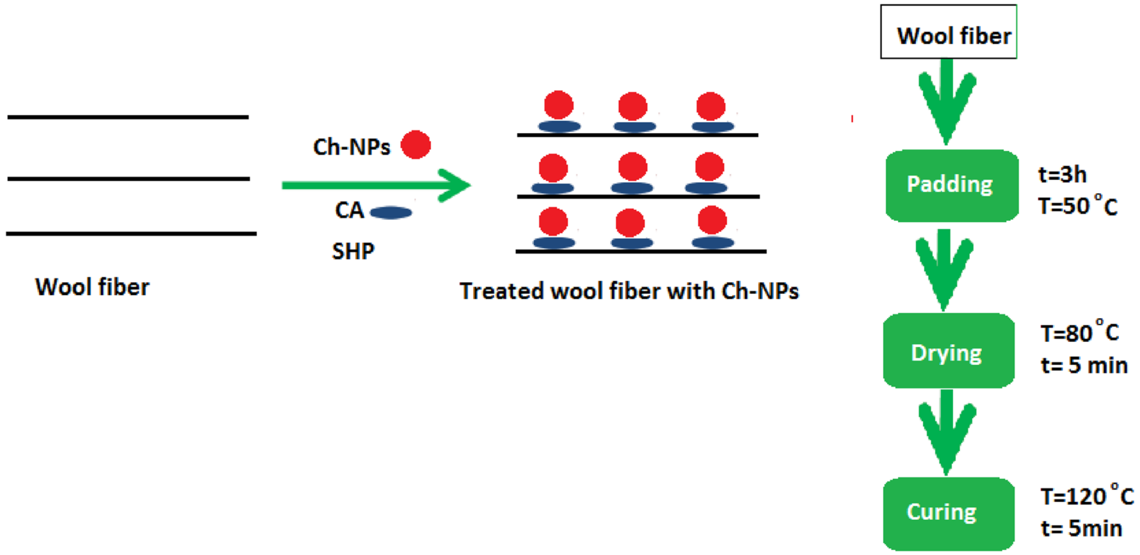


Fig. 9 Treatment of Ch-NPs on wool yarns in the presence of CA (citric acid: cross-linking agent) and SHP (Sodium hypophosphite: catalyst)

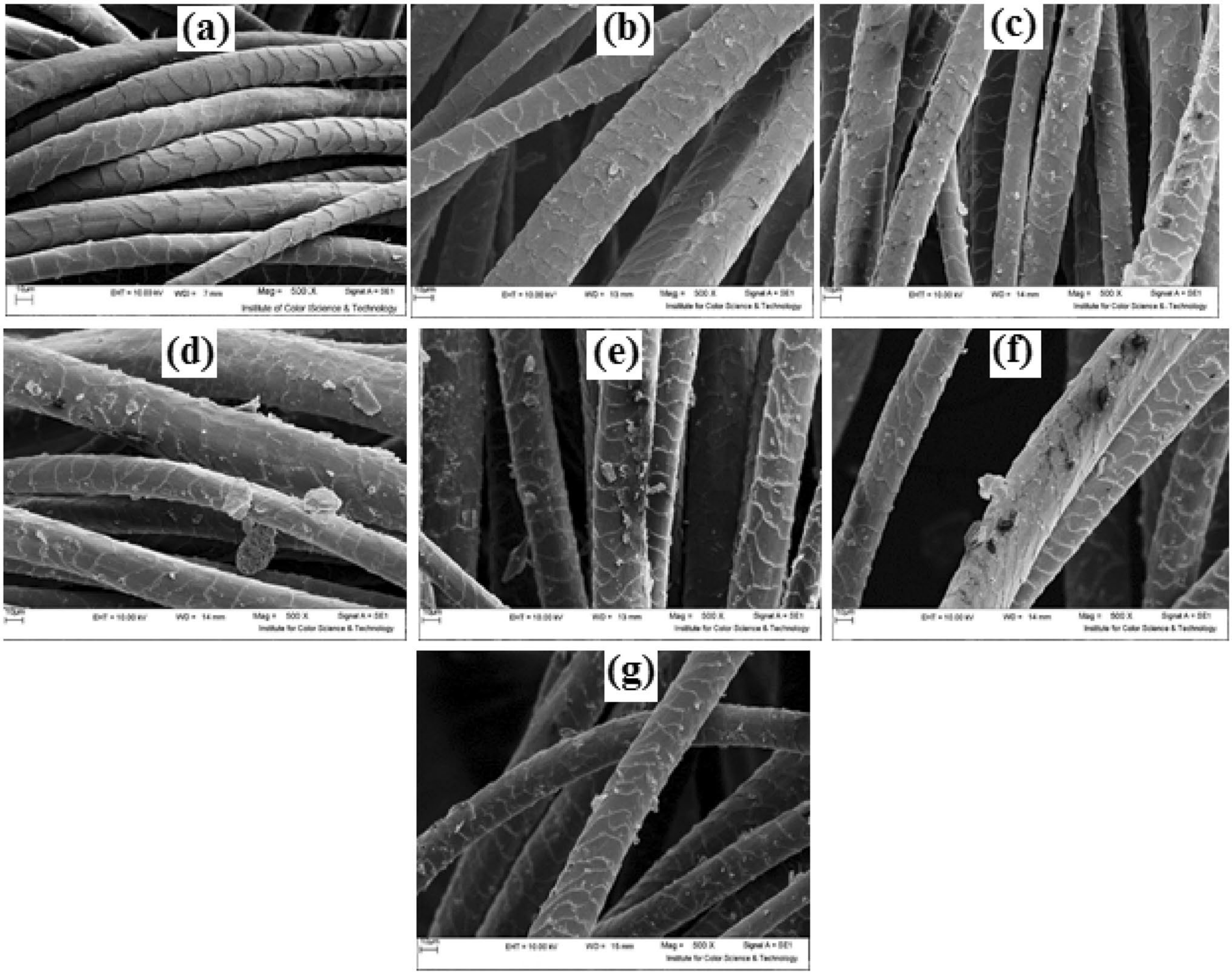


Fig. 10 SEM images: **a** wool, **b** wool-Ch-Ag, **c** wool-Ch-Cu, **d** wool-Ch-Zn, **e** wool-Ch-Ag–Zn, **f** wool-Ch-Ag–Cu, **g** wool-Ch-Cu–Zn (Ch-NPs concentration = 5% o.w.f.)

covered with this modification (Safapour et al. 2019; Sadeghi-Kiakhani et al. 2019a, b).

Antimicrobial activity of wool yarn

The antimicrobial activity of all the wool samples treated with various Ch-NPs was tested against *E. coli*, and *S. aureus* bacteria (Table 1). It was found that both chitosan and Ch-NPs significantly inhibited completely bacterial growth after 24 h incubation. Antimicrobial activity of chitosan against microorganisms is due to the formation of electrostatic interactions of anionic groups of microbial cell membranes with the positively charge of amine groups. So, the growth of the cells stops by disrupting nutrient intake to them (Sadeghi-Kiakhani et al. 2019a, b; Matyjas-Zgondek et al. 2008; Rezaie et al. 2017; Tang et al. 2014). Moreover, the results indicated that metal inorganic could increase the antimicrobial activity of chitosan, which can be attributed to synergistic antibacterial activities of both chitosan and NPs. The photocatalytic production of reactive oxygen species (ROS) is formed owing to the disruption of the bacterial cell membranes by NPs ions. Also, the formation of ROS finally results in the damage of bacterial structure and cell death (Sadeghi-Kiakhani et al. 2019a, b; Matyjas-Zgondek et al. 2008; Rezaie et al. 2017; Tang et al. 2014). The treated wool yarns with Ch-Ag had the highest antimicrobial activity among all of the used Ch-NPs. The concentration of Ch-NPs was an essential factor in antimicrobial activates of the tread samples, so that the higher inhibition of growth of bacteria is achieved by increasing the initial concentration of Ch-NPs. It was found that suitable antimicrobial activities were obtained at initial Ch-NPs concentration of 5% o.w.f., which was considered as the optimum concentration for treating the wool samples.

Table 1 Antimicrobial activity of all samples against *E. coli* and *S. aureus*

Sample	% (o.w.f.)	Antimicrobial activity (%)	
		E. coli	*S. aureus*
Wool	–	–	–
Wool-Ch	1	68	62
	5	95	91
	10	> 99.99	> 99.99
Wool-Ch-Ag	1	88	82
	5	100	100
	10	100	100
Wool-Ch-Ag/Zn	1	82	77
	5	100	100
	10	100	100
Wool-Ch-Ag/Cu	1	85	80
	5	100	100
	10	100	100
Wool-Ch-Zn	1	71	67
	5	100	100
	10	100	100
Wool-Ch-Zn/Cu	1	75	72
	5	100	100
	10	100	100
Wool-Ch-Cu	1	79	76
	5	100	100
	10	100	100

The durability of the antimicrobial treatment of the samples was also tested after repeated washing cycles according to ISO 6330-1984 standard test method (Table 2). The strength of bonding between Ch-NPs and wool fibers is a detrimental parameter on the washing durability of the antimicrobial finishing. The results indicated that the samples treated with Ch-Ag exhibited a very good antimicrobial durability (over 92%) after 10 repeated washing cycles. The poorest result was achieved for the samples treated with Ch-Zn and the antimicrobial activity dropped to 43% after 10 repeated washing cycles. It is likely that the grafted Ch-NPs can be separated from the wool surface after repeated washing times which adversely affects the antimicrobial activity. When the samples are treated with the Ch-NPs using citric acid, the antimicrobial activity and their durability were improved. Indeed, without citric acid as a crosslinking agent, satisfactory antimicrobial activities cannot be obtained. That shows that citric acid acts as a crosslinking agent between the wool fibers and Ch-NPs.

Table 2 Antimicrobial activity to washing durability of all samples (Ch-NPs concentration = 5% o.w.f.)

Sample	Repeated washing cycles	Antibacterial activity (%)	
		E. coli	*S. aureus*
Ch-Ag	–	100	100
	5	98.40	97.31
	10	95.60	92.57
Ch-Cu	–	100	100
	5	91.81	88.80
	10	86.36	82.23
Ch-Zn	–	72.62	67.28
	5	56.44	54.01
	10	48.13	42.85
Ch-Ag–Zn	–	100	100
	5	94.21	82.31
	10	89.66	80.93
Ch-Ag–Cu	–	100	100
	5	77.02	74.13
	10	61.87	68.68
Ch-Cu–Zn	–	100	100
	5	91.85	86.00
	10	86.61	82.95

Conclusions

This study deals with an eco-friendly method for improving antimicrobial activities of Ch-NPs grafted on the wool fibers. The obtained results from FTIR, and SEM showed that the grafting of Ch-NPs was successfully performed. The distribution plot of DLS showed that the average size obtained by various Ch-NPs was around 8–15 nm, and Ch-metal ions can be converted to Ch-metal NPs with the accessible functional groups of chitosan and thiol groups in wool fibers. Furthermore, the antimicrobial activities of treated wool samples with Ch-NPs indicated that Ch-Ag among all of the used Ch-NPs could improve significantly the antimicrobial potential of chitosan, which can be attributed to synergistic antibacterial activities of both chitosan and NPs. Also, the results showed that the reduction growth of bacteria on the treated samples with Ch-Ag was above 92% after 10 repeated washing times.

References

Al-Karawi JM, Al-Qaisi ZHJ, Abdullah HI, Al-Mokaram AMA, Al-Heetimi DTA (2011) Synthesis, characterization of acrylamide grafted chitosan and its use in removal of copper (II) ions from water. Carbohydr Polym 83:495–500

An J, Luo Q, Yuan X, Wang D, Li X (2011) Preparation and characterization of silver-chitosan nanocomposite particles with antimicrobial activity. J Appl Polym Sci 120:3180–3189

Aryabadie S, Sadeghi-Kiakhani M, Arami M (2015) Antimicrobial and dyeing studies of treated cotton fabrics by prepared chitosan-PAMAM dendrimer/Ag nano-emulsion. Fibers Polym 16:2529–2537

de Godoi FC, Rodriguez-Castellon E, Guibal E, Beppua MM (2013) An XPS study of chromate and vanadate sorption mechanism by chitosan membrane containing copper nanoparticles. Chem Eng J 234:423–429

Enescu D (2008) Use of chitosan in surface modification of textile materials. Roum Biotechnol Lett 13:4037–4048

Giannousi K, Menelaou M, Arvanitidis J et al (2015) Hetero-nanocomposites of magnetic and antifungal nanoparticle as a platform for magneto-mechanical stress in induction in *Saccharomyces cerevisiae*. J Mater Chem B 3:5341–5351

Giri Dev VR, Venugopal J, Sudha S, Deepika G, Ramakrishna S (2009) Dyeing and antimicrobial characteristics of chitosan treated wool fabrics with henna dye. Carbohydr Polym 75:646–650

Govindan S, Nivethaa EAK, Saravanan R, Narayanan V, Stephen A (2012) Synthesis and characterization of chitosan-silver nanocomposite. Appl Nanosci 2:299–303

Jayakumar R, Menon D, Manzoor K, Nair SV, Tamura H (2010) Biomedical applications of chitin and chitosan-based nanomaterials. Carbohydr Polym 82:227–232

Kim YS, Song MY, Park JD, Song KS, Ryu HR, Chung YH, Chang HK, Lee JH, Oh KH, Kelman BJ, Hwang IK, Yu IJ (2010) Subchronic oral toxicity of silver nanoparticles. Part Fibre Toxicol 7:20

Klaykruayat B, Siralertmukul K, Srikulkit K (2010) Chemical modification of chitosan with cationic hyperbranched dendritic polyamidoamine and its antimicrobial activity on cotton fabric. Carbohydr Polym 80:197–207

Kong M, Chen XG, Xing K, Park HJ (2010) Antimicrobial properties of chitosan and mode of action: a state of the art review. Int J Food Microbiol 144:51–63

Kumar PTS, Laskmanan VK, Anilkumar TV, Ramya C, Reshmi P, Unnikrishnan AG, Nair SV, Jayakumar R (2012) Flexible and microporous chitosan hydrogel/nano ZnO composite bandages for wound dressing: in vitro and in vivo evaluation. ACS Appl Mater Interfaces 4:2618–2629

Kyzas GZ, Bikiaris DN (2015) Recent modifications of chitosan for adsorption applications: a critical and systematic review. Mar Drugs 13:312–337

Li LH, Deng JC, Deng HR, Liu Z-L, Xin L (2010) Synthesis and characterization of chitosan/ZnO nanoparticle composite membranes. Carbohydr Res 345:994–998

Lim SH, Hudson SM (2013) Review of chitosan and its derivatives as antimicrobial agents and their uses as textile chemicals. J Macromol Sci C Polym Rev 43:223–269

Matyjas-Zgondek E, Bacciarelli A, Rybicki E, Szynkowska MI, Kołodziejczyk M (2008) Antibacterial properties of silver-finished textiles. Fibres Text East Eur 16:101–107

Moura D, Mano JF, Paiva MC, Alves NM (2016) Chitosan nanocomposites based on distinct inorganic fillers for biomedical applications. Sci Technol Adv Mater 17:626–643

Nayak D, Minz AP, Ashe S, Rauta PR, Kumari M, Chopra P, Nayak B (2016) Synergistic combination of antioxidants, silver nanoparticles and chitosan in a nanoparticle based formulation: characterization and cytotoxic effect on MCF-7 breast cancer cell lines. J Colloid Interface Sci 470:142–152

Peschel D, Zhang K, Fischer S, Groth T (2011) Modulation of osteogenic activity of BMP-2 by cellulose and chitosan derivatives. Acta Biomater 8:183–193

Pestov A, Bratskaya S (2016) Chitosan and its derivatives as highly efficient polymer Ligands. Molecules 21(330):1–35

Petkova P, Francesko A, Fernandes MM, Mendoza E, Perels I, Gedanken A, Tzanov T (2014) Sonochemical coating of textiles with hybrids ZnO/chitosan antimicrobial nanoparticles. ACS Appl Mater Interfaces 6:1164–1172

Rezaie AB, Montazer M, Rad MM (2017) A cleaner route for nanocolouration of wool fabric via green assembling of cupric oxide nanoparticles along with antibacterial and UV protection properties. J Clean Prod 166:221–231

Rinaudo M (2006) Chitin and chitosan: properties and applications. Prog Polym Sci 31:603–632

Sadeghi-Kiakhani M, Tehrani-Bagha AR, Safapour S (2018) Enhanced anti-microbial, anti-creasing and dye absorption properties of cotton fabric treated with Chitosan-Cyanuric Chloride hybrid. Cellulose 25(1):883–893

Sadeghi-Kiakhani M, Safapour S, Ghanbari-Adivi F (2019a) Grafting of chitosan-acrylamide hybrid on the wool: characterization, reactive dyeing, antioxidant and antibacterial studies. Int J Biol Macromol 134:1170–1178

Sadeghi-Kiakhani M, Tehrani-Bagha AR, Gharanjig K, Hashemi E (2019b) Use of Pomegranate peels and Walnut Green husks as the green antimicrobial agents to reduce the consumption of inorganic nanoparticles on wool yarns. J Clean Prod 231:1463–1473

Safapour S, Sadeghi-Kiakhani M, Doustmohammadi S (2019) Chitosan-cyanuric chloride hybrid as an efficient novel bio-mordant for improvement of cochineal natural dye absorption on wool yarns. J Text I 110(1):81–88

Sanmugam A, Vikraman D, Park HJ, Kim HS (2017) One-pot facile methodology to synthesize chitosan-ZnO-graphene oxide hybrid composites for better dye adsorption and antibacterial activity. Nanomaterials 7:363

Sashiwa H, Shigemasa Y, Roy R (2002) Chemical modification of chitosan 11: chitosan-dendrimer hybrid as a tree like molecule. Carbohydr Polym 49:195–205

Tang B, Sun L, Kaur J, Yu Y, Wang X (2014) In-situ synthesis of gold nanoparticles for multi-functionalization of silk fabrics. Dyes Pigments 103:183–190

Vaseeharan B, Sivakamavalli J, Thaya R (2015) Synthesis and characterization of chitosan-ZnO composite and its antibiofilm activity against aquatic bacteria. J Compos Mater 49(2):177–184

Wazed AS, Rajendran S, Joshi M (2011) Synthesis and characterization of chitosan and silver loaded chitosan nanoparticles for bioactive polyester. Carbohydr Polym 83:438–446

Zamani A, Taherzadeh MJ (2012) Production of super absorbents from fungal chitosan. Iran Polym J 21:845–853

Zhang Z, Song Y, Xu C, Guo D (2012a) A novel model for undeformed nanometer chips of soft-brittle HgCdTe films induced by ultrafine diamond grits. Scr Mater 67:197–200

Zhang Z, Huo F, Zhang X, Guo D (2012b) Fabrication and size prediction of crystalline nanoparticles of silicon induced by nanogrinding with ultrafine diamond grits. Scr Mater 67:657–660

Zhang Z, Huo Y, Guo D (2013) A model for nanogrinding based on direct evidence of ground chips of silicon wafers. Sci China Technol. Sci 56:2099–2108

Zhang Z, Wang B, Kang R, Zhang B, Guo D (2015) Changes in surface layer of silicon wafers from diamond scratching. CIRP Ann Manuf Technol 64:349–352

Zhang Z, Cui J, Wang B, Wang Z, Kang R, Guo D (2017) A novel approach of mechanical chemical grinding. J Alloys Compd 726:514–524

Zhang Z, Shi Z, Du Y, Yu Z, Guo L, Guo D (2018) A novel approach of chemical mechanical polishing for a titanium alloy using an environment-friendly slurry. Appl Surf Sci 427:409–415

Zhang Z, Cui J, Zhang J, Liu D, Yu Z, Guo D (2019) Environment friendly chemical mechanical polishing of copper. Appl Surf Sci 467–468:5–11