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Multifunctional finishing of wool fabrics by chitosan UV-grafting: An approach

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ABSTRACT

The aim of this study was the surface modification of wool fibers to confer a multifunctional finishing to the fabrics, improving the textile value and its applications without damage of comfort properties. The attention was focused on an economical and environmental friendly process to obtain an effective treatment with good durability to washing.

Chitosan in acetic acid solution was applied by padding, and grafted by ultraviolet radiation, through radical reactions promoted by a photoinitiator. 2% chitosan grafted was enough to confer satisfactory antimicrobial activity (67% reduction of *Escherichia coli*) after an oxidative wool pre-treatment and 1 h impregnation at 50 °C. Moreover treated wool fabrics showed a strong dyeability increase toward acid dye. However the evaluation of the treatment durability to laundering showed different behavior depending on the nature of the surfactants. Finally, anti-felting properties with respect to untreated fabrics were revealed, while no effect was shown toward anti-pilling properties.

1. Introduction

Antibacterial activity, anti-felting, anti-shrinking, antistaticity, hydrophobicity or hydrophilicity, fire or stain resistance are just some of many properties that are more and more requested for textile fabrics. A lot of studies were carried out to confer each of these properties individually; however the possibility to confer several properties to textiles by a single product and process is gaining interest both from an economical and technological point of view (Gowri et al., 2010; Gupta & Haile, 2007; Ibrahim, Refaie, & Ahmed, 2010; Ki, Kim, Kwon, & Jeong, 2007; Schindler & Hauser, 2004; Simončič & Tomšič, 2010).

Chitosan, 2-amino-2-deoxy-(1→ 4)-β-D-glucopyranan, derived from the deacetylation of the chitin component of the shells of crustaceans, is undoubtedly one of the more promising multifunctional polymers among the textile finishing agents. It is a biopolymer with unique properties such as biodegradability, non-toxicity, antimicrobial activity. Chitosan shows in fact antibacterial activity against both Gram positive and negative bacteria, thanks to its combined bactericidal and bacteriostatic action (Muzzarelli et al., 1990).

Moreover chitosan shows a great affinity toward a wide range of dyestuffs, hence its grafting to fibers could confer them the same affinity, thanks to the reactive groups added, without affecting the bulk of the fibers (Wong, Szeto, Cheung, & McKay, 2004). The aim of chitosan application was not only the improvement of exhaustion bath reached with conventional dyes for wool, but also the possibility to apply natural dyes, usually not considered for wool fibers (Giri Dev, Venugopal, Sudha, Deepika, & Ramakrishna, 2012; Mongkholrattanasit, Kryštufek, Wiener, & Studničková, 2011).

On the other hand, wool textiles in the wet state are sensitive to felting and tend to shrink when subjected to mechanical stress, as in the case of washing. It is ascribable to the scaled structure of the fiber surface which induces the phenomenon called "differential frictional effect". Anti-felting treatments are aimed to partially remove the scales or to smooth the edges from the overlapping scales in order to reduce the felting tendency and make washable the wool fabrics. However, the antifelting treatments commercially practiced provide for the use of strong oxidants such as chlorine and its derivatives, causing wastewater pollution and changing of the natural soft hand of wool (Dong & Xu, 2008).

The need to use more environmental friendly processes leads to the replacement of conventional chemical treatments with natural based products, such as chitosan. Surrounding wool fibers in form of thin film, chitosan can in fact significantly decrease the friction between the surface scales, reducing both felting and shrinkage (Tonin, Roncolato, Innocenti, & Ferrero, 2007). This effect was justified by hydrophilicity increase of chitosan treated wool due to addition of extra hydrophilic groups, such as amine and hydroxyl, hence the absorbed water could act as plasticizer among the surface scales (Ranjbar-Mohammadi, Hajir Bahrami, & Arami, 2012).

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For the reasons above given, chitosan is already used in textile finishing (Lim & Hudson, 2004) and applied by wet thermal curing with energy consumption, costs and possible fabric degradation; moreover the addition of toxic reagents, such as glutaraldehyde, or natural, such as genipin, is sometime required as crosslinking agent (Alonso et al., 2009; El-Tahlawy, El-Bendary, Elhendawy, & Hudson, 2005; Muzzarelli, 2009). In the case of wool fabrics, to obtain a durable finishing, the need of crosslinkers, such as citric acid or succinic anhydride, even coupled with ultrasound to graft chitosan onto wool with irreversible covalent bonds was further confirmed by the recent work by Ranjbar-Mohammadi et al. (2012).

However, UV-grafting of chitosan on cotton and silk fibers to confer antimicrobial activity was already studied obtaining good results (Ferrero & Periolatto, 2012; Periolatto, Ferrero, & Vineis, 2012). In UV curing, radical species are generated by the interaction of UV light with a suitable photoinitiator, which induces grafting reactions of reactive monomers and oligomers at low temperature and quickly, with lower environmental impact and lower process cost than thermal process (Ferrero, Periolatto, Sangermano, & Bianchetto Songia, 2008). The effects of exposure to UV light of chitosan films or blends, forming macroradicals, have been widely studied in the field of UV degradation (Saiki et al., 2010; Sionkowska et al., 2006) and the same radicals can be involved in photopolymerization processes (Alam, Khan, Khan, Ghoshal, & Mondal, 2008).

In the present work, wool knitted fabrics were multifunctionally finished by UV-grafting of chitosan, first of all to confer antimicrobial activity and to enhance the wool affinity toward acid dyes. Then the durability of the treatment to repeated washings was evaluated. Moreover the ability of grafted chitosan to give anti-felting and eventually anti-pilling properties were also investigated.

Pilling is another typical problem of wool fabrics. Pills are cluster or tangle of a number of fibers rounded off into the shape of small tufts, which are created by friction and coiling on the surface of the textile fabric. An anti-pilling finish should be able to cement the fibers within the yarn so that their dragging becomes more difficult, without handle worsening (Rombaldoni et al., 2008). For this reason, one can suppose that a similar effect could also be obtained by chitosan functionalization of fiber surface.

2. Experimental

2.1. Materials

Knitted wool fabrics, 2/48 N m, twist folded yarn 550 turns/m *Z*, twist single yarn 360 turns/m *S*, mass per unit area 292 g/m^2 were used as substrates. To enhance the chemical affinity between chitosan and wool, according to Tonin et al. (2007), the effect of a previous oxidative treatment of the fabric with H_2O_2 (30%, 25 ml/l) at 60 °C, liquor ratio 1:30, for 2 h at pH 9, provided by addition of ammonia laboratory grade, was also investigated.

Low viscosity chitosan, 75–85% deacetylation degree (Fluka) was used as finishing agent. This was dissolved at 2% wt in aqueous solution of 2% (v/v) glacial acetic acid under magnetic stirring at ambient temperature for 24 h. 2-Hydroxy-2-methylphenylpropane-1-one (Darocur 1173, Ciba Specialty Chemicals) was added as photoinitiator at 2% wt with respect to chitosan.

2.2. Fabric finishing

Chitosan and photoinitiator mixture was diluted with the same acetic acid solution and spread on the fabrics. Different impregnation conditions were investigated: contact times of 1 min, 1 h or 24 h at temperature of 25 °C or 50 °C. Samples were then dried for 10 min at 80–100 °C and finally UV-cured. The fabrics were irradiated by a medium-pressure mercury lamp with a light intensity on the fabric of about 20 mW/cm^2, in a small box equipped with a quartz window, under nitrogen atmosphere (oxygen content under 20 ppm). To assure the complete curing on the fabrics, they were radiated for 60 s on both the sides.

The polymer add-on was calculated as:

$$\text{add-on}\ \ (\%) = \frac{w - w_0}{w_0} \times 100 \tag{1}$$

where w is the weight of grafted fabric and w_0 the weight of the original fabric. Chitosan add-on varied between 2% and 12% wt of the fabric.

2.3. Characterization of the treated fabrics

Antimicrobial activity tests were performed according to ASTM E2149-01 method, using *Escherichia coli* ATCC 8739 and *Staphylococcus aureus* ATCC 6538 as microbes, following the procedure detailed in a previous article (Periolatto et al., 2012).

Dyeing tests were carried out on untreated fabric and chitosan treated samples prepared with or without pre-oxidation, 2% add-on, with different impregnation methods. Telon Turquoise M5-G 85%, C.I. Acid Blue 185, by Dystar was used as dye; it has a low affinity toward wool, so it is suitable to highlight the treatment effect. Treated and untreated samples, about 1 g wt, were dyed in sealed tubes introduced in a shaken thermostatic bath. Dyeing parameters chosen were: 1% dye on weight fibers, liquor ratio 1:50, pH 4 adjusted by acetic acid addition, 85 °C temperature maintained for 1 h. Dyed samples were then rinsed in cold water and dried in oven at 100 °C.

The final exhaustions of dye bath were evaluated by spectrophotometric measurements, drawing a calibration line on the basis of the absorbance peak at about 615 nm.

Color measurements were carried out on dyed samples by Datacolor Check II instrument, equipped with a pulsed xenon lamp. The measuring geometry was diffuse illumination at 8°. Reflectance measurements every 20 nm wavelength interval and color evaluation according to CIELCH scales were made. Each value was obtained averaging 5 results in different points of the sample. From reflectance, color strength values *K*/*S* were calculated according to the Kubelka–Munk equation:

$$\frac{K}{S} = \frac{(1 - R_\lambda)^2}{2R_\lambda} \tag{2}$$

where R_λ is the reflectance value at wavelength λ.

Durability of grafted chitosan was tested by dyeing samples prepared as above and submitted to 5 washing cycles according to UNI-EN ISO 105 C01 using either standard ECE detergent mixture, provided by EMPA Testmaterials (CH), or Tween 20 non ionic surfactant, by Sigma–Aldrich, at a concentration of 5 g/l.

Anti-felting tests were carried out according to Woolmark Test TM31, while pilling was determined according to ISO 12945-2 modified for Martindale, on samples either untreated or UV-cured with 2% add-on, prepared with impregnation at 50 °C for 1 h. Tested samples were not subjected to preventive oxidation in order to evaluate just the effect of chitosan presence, and not the possible subtractive and smoothing effect on wool scales due to oxidation.

Moreover, thermal resistance (R_{ct}), expressed in m^2 °C/W, and water vapor resistance (R_{et}), expressed in m^2 Pa/W, of fabrics under steady-state conditions, were measured according to ISO 11092 standard. The instrument used was Sweating Guarded Hotplate (SGHP) 10.5 by Measurement Technology Northwest (MTNW), USA. The environmental operating conditions (air temperature T_a and relative humidity *RH*) were set and controlled by a Lunaire TPS, USA, Environmental Chamber CEO932-4; in particular, T_a = 20 °C and *RH* = 65% for R_{ct} measurements, while T_a = 35 °C and *RH* = 40%

for R_{et} measurements. The drift of T_a did not exceed ±0.1 °C; the drift of *RH* did not exceed ±3%. R_{ct} and R_{et} were both calculated as the arithmetic mean of 3 individual measurements. Then the water vapor permeability index (i_{mt}) was calculated too, in accordance with Eq. (3):

$$i_{mt} = S \times \frac{R_{ct}}{R_{et}} \quad (3)$$

where S = 60 Pa/°C.

i_{mt} is dimensionless, and has values between 0 and 1. A value of 0 implies that the material is water-vapor impermeable, that is, it has infinite water vapor resistance, and a material with a value of 1 has both thermal and water vapor resistance of an air layer of the same thickness.

The surface morphology of treated fabrics was examined by SEM with a Leica (Cambridge, UK) Electron Optics 435 VP scanning electron microscope with an acceleration voltage of 15 kV, a current probe of 400 pA, and a working distance of 20 mm. The samples were mounted on aluminum specimen stubs with double-sided adhesive tape and sputter-coated with gold in rarefied argon using an Emitech K550 Sputter Coater with a current of 20 mA for 180 s.

3. Results and discussion

3.1. Antibacterial activity

Results of antibacterial activity tests are reported in Table 1. No antibacterial activity was shown by untreated wool, while, on samples grafted with 2% chitosan add-on, not pre-oxidized before chitosan impregnation, a certain antibacterial activity was revealed, but the values of percentage reduction of *E. coli* were low with chitosan impregnation at 25 °C even for 24 h. It was attributed to low chitosan amount fixed on fibers, not enough to perform a significant antibacterial activity.

Better results, that is 30% microorganisms reduction, were obtained for the samples prepared with impregnation at 50 °C for 1 h, thanks to the swelling of the wool fibers enabling to a better penetration of chitosan inside the fibers. Moreover heat can partially remove the hydrorepellent fatty acid layer on the wool surface; in fact it reduces the fibers wetting, acting as a real barrier to the contact between chitosan solution and wool.

In order to investigate the influence of chitosan add-on, some samples were prepared without preoxidation but with about 4%, 8% and 12% add-ons, choosing 1 h at 50 °C as impregnation method. The increase of *E. coli* reduction is evident if compared with results related to 2% weighted sample: from 30% to 87% with 4% chitosan add-on. The slight decrease measured on 12% weighted sample suggests a border weighting value that can be ascribable to the structure of wool fibers. From obtained results, 4% add-on could be indicated as the optimal percentage to obtain a satisfactory antibacterial activity against *E. coli* without any wool pretreatment. However in the same conditions the antibacterial effect on *S. aureus* is limited to 44%.

The results of 2% chitosan grafted wool were significantly improved by the previous oxidation of fabrics, with an enhancement of the antibacterial activity against *E. coli* to more than double percentages in comparison with not pre-oxidized samples prepared with all the impregnation methods. Even in this case the highest microorganisms reduction was obtained with impregnation for 1 h at 50 °C, confirming the positive effect of the maintenance at high temperature. The effect of the oxidative pretreatment can be ascribed to the increase of hydroxyl groups on wool surface; it improves substrate hydrophilicity, promoting its impregnation by chitosan solution, and offers more reactive groups that can be involved in UV-grafting reactions. In the same operating conditions even the antibacterial activity toward *S. aureus* was remarkable, although little lower than that obtained against *E. coli*.

The antibacterial activity can probably be further increased coupling higher add-on to pre-oxidation. Nevertheless, it should take into account that chitosan amount fixed to the fibers higher than 2% can induce loss of soft hand and evident yellowing of the substrate.

3.2. Dyeability improvement and durability evaluation

The images of dyed samples of wool fabric are compared in Fig. 1. It is evident that 2% chitosan finishing on the fabric surface without oxidative pretreatment (Fig. 1b) causes a deeper coloration, although uneven, with respect to untreated wool (Fig. 1a), while on the sample chitosan finished after oxidation pretreatment the coloration is still more intense and even (Fig. 1d). The result cannot be ascribable to the modifications of fiber surface induced by oxidation alone since in this case the dyeing effect is poor (Fig. 1c).

The color strength values obtained from reflectance measurements on the above samples are plotted in Fig. 2. A strong increase of K/S in the wavelength range from 550 to 700 nm is observed mainly for sample grafted with chitosan after oxidation pretreatment.

The averaged numerical results of color measurements are reported in Table 2 with the standard deviation values calculated for each parameter from repeated measurements on 5 different points of the same sample. The lowest values of standard deviation are obtained on the sample chitosan grafted after oxidation pretreatment confirming a better color uniformity in comparison with chitosan finishing without pretreatment. In both cases the lightness (L) decrease is consistent with the increase of color intensity in comparison with the respective reference, higher on pre-oxidized wool. Moreover, chroma (C) and hue (H) are increased in the same manner by chitosan grafting.

Indeed the final bath exhaustion obtained after dyeing of untreated wool fabrics reached just 61% while, in presence of 2% chitosan finishing without oxidative pretreatment, it increased till 84%, as shown in Fig. 3. This improvement could be related to the higher affinity toward anionic dyes conferred by grafted chitosan. The positive effect of the finishing, in this case, is not dependent on the impregnation parameters used during sample preparation, although an exhaustion percentage slightly lower was found in correspondence of 1 min impregnation time at 25 °C.

Table 1
Microorganism reduction of chitosan treated wool fabrics: influence of impregnation, chitosan add-on and oxidative pretreatment.

Impregnation time and temperature	Chitosan add-on (%)	Without oxidative pretreatment		With oxidative pretreatment	
		E. coli (%)	*S. aureus* (%)	*E. coli* (%)	*S. aureus* (%)
1 min, 25 °C	2	21	–	62	–
24 h, 25 °C	2	25	–	56	–
1 h, 50 °C	2	30	–	67	50
1 h, 50 °C	4	87	44	–	–
1 h, 50 °C	8	88	–	–	–
1 h, 50 °C	12	77	–	–	–

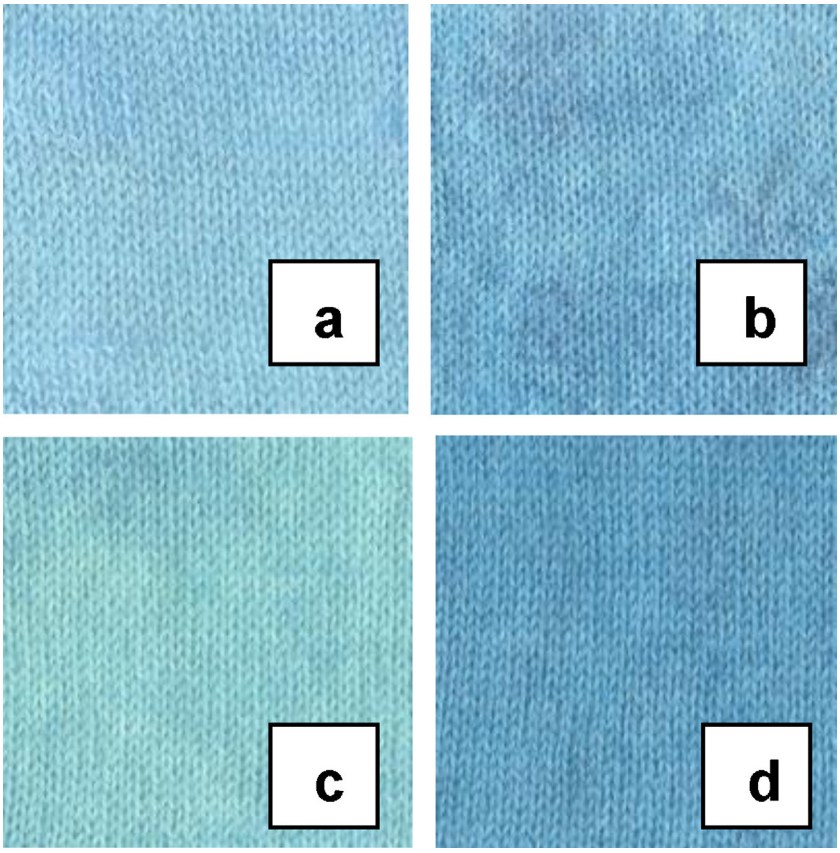

Fig. 1. Dyeing tests with Telon Turquoise on wool: (a) untreated; (b) with 2% chitosan add-on without oxidative pretreatment; (c) after oxidative pretreatment alone; (d) with 2% chitosan add-on after oxidative pretreatment.

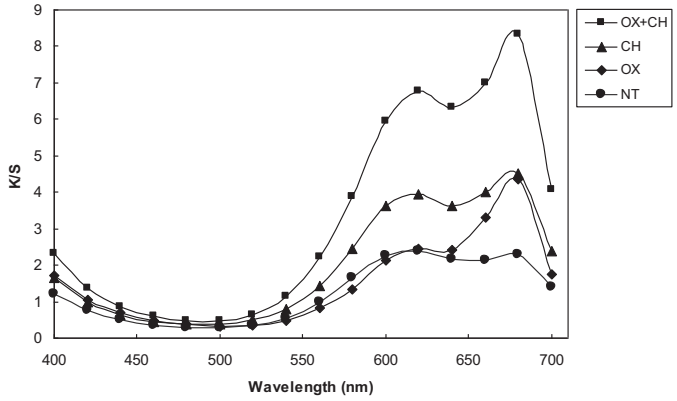

Fig. 2. Color strength of wool samples dyed with Telon Turquoise: untreated (NT), after oxidative pretreatment alone (OX), with 2% chitosan add-on without oxidative pretreatment (CHI), with 2% chitosan add-on after oxidative pretreatment (OX + CH).

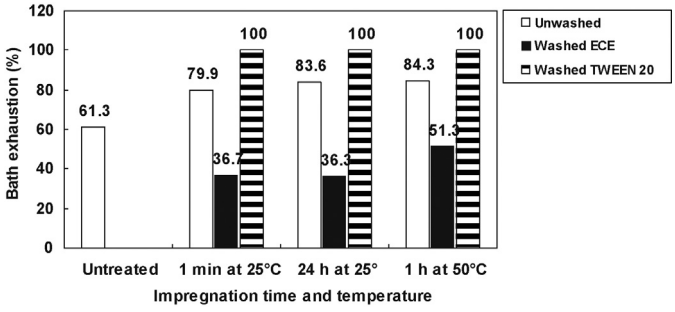

Fig. 3. Bath exhaustion in dyeing tests with Telon Turquoise of chitosan treated wool, 2% add-on without oxidative pretreatment and with different impregnation, after washings with different surfactants.

Table 2
Color measurements on wool dyed with Telon Turquoise.

	Untreated		2% Chitosan not pre-oxidized		Pre-oxidized only		Pre-oxidized + 2% chitosan	
	Value	St. dev.	Value	St. dev.	Value	St. dev.	Value	St. dev.
L	62.69	1.47	57.86	1.68	63.07	1.54	53.14	1.21
C	29.46	1.78	32.65	2.13	29.25	1.00	36.64	0.55
H	205.15	1.01	208.99	0.64	190.48	2.35	208.44	0.53
ΔL	–	–	−4.83[a]	–	–	–	−9.93[b]	–
ΔC	–	–	3.19[a]	–	–	–	7.38[b]	–
ΔH	–	–	3.84[a]	–	–	–	17.96[b]	–

[a] Differences calculated with respect to the untreated sample.
[b] Differences calculated with respect to the pre-oxidized sample.

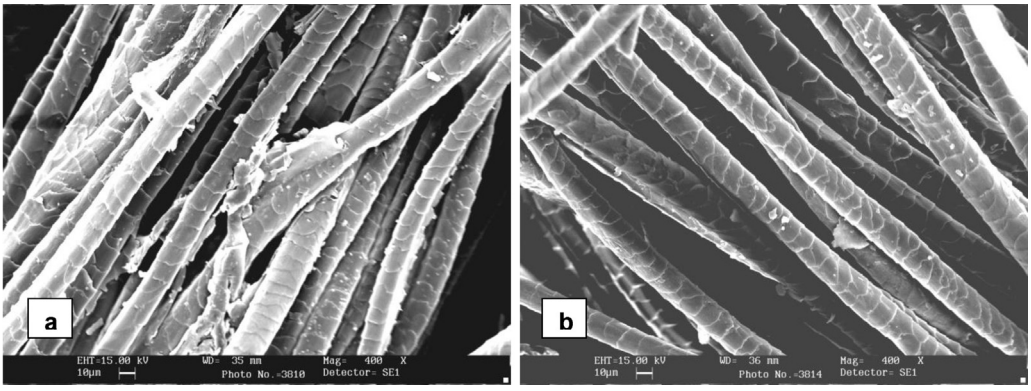

Fig. 4. SEM images of chitosan treated wool, 2% add-on: (a) unwashed and (b) washed with ECE detergent (magnification ratio 400×).

The wool dyeing with Telon Turquoise can be considered a simple and effective method to test chitosan presence, and it was employed also to test the treatment durability to domestic laundering, through dyeing of the treated samples after washings with different surfactants. The results are reported also in Fig. 3, where the influence of the surfactant nature appears relevant.

Dyebath exhaustions obtained with samples washed with ECE detergent, a mixture of anionic and non ionic surfactants, highlight a worsening with respect to the results before washing, but also to untreated wool. On the other hand, on samples washed with Tween 20, the complete dyebath exhaustion was reached, regardless the impregnation method of wool, with a further improvement of chitosan effect. The different behavior after washings is surely ascribable to the different character of the polar head of the surfactants. Cationized chitosan is able to establish strong bonds with anionic surfactants like LAS (Lim & Hudson, 2004), hence in this case it can be partially removed by washing, whereas it cannot be practically removed by repeated washings with a non ionic surfactant such as Tween 20.

The partial removal of chitosan is confirmed by the comparison, reported in Fig. 4, of the images obtained by SEM analysis of wool treated with 2% chitosan add-on, unwashed and repeatedly washed with ECE detergent. The unwashed sample presents an uneven distribution of chitosan on the fiber surface, with agglomerates no longer visible after washings. A similar result was not observed after washings with Tween 20.

3.3. Anti-felting and anti-pilling

The untreated wool fabric, after washing, suffered a strong felting and shrinking, as expected. In particular, the dimensional change was more relevant along longitudinal direction; it can be due to the structural characteristics of the fabric, related to the direction of surface scales of wool.

Comparing these values with results obtained on chitosan treated fabric, a strong decrease of both felting and shrinking along the longitudinal direction can be noted, reaching values quite comparable to those measured on untreated fabric along the cross direction (Table 3).

In particular, on treated fabrics the relaxation dimensional change decreased from 13.5% on untreated wool to 1.2% on chitosan treated while the total shrinkage decreased from 16.9% to just 3%. It can be concluded that chitosan conferred dimensional stability to wool fabrics, strongly reducing its felting and making them wet-washable.

No differences between treated and untreated samples were instead revealed by pilling test: on samples treated with 2% chitosan weight on; a maximum pilling grade of 5, as the untreated sample, was in fact measured.

Table 3
Relaxation dimensional change and total shrinkage on untreated and 2% chitosan treated wool fabrics.

	Sample	Relaxation dimensional change (%)	Total shrinkage (%)
Cross direction	Untreated	0	−1.0
	Treated	−1.5	−2.9
Longitudinal direction	Untreated	−13.5	−16.9
	Treated	−1.2	−3.0

Table 4
Comfort properties, evaluated by Skin Model, on untreated and 2% chitosan treated wool fabrics.

	R_{ct} (m^2 °C/W)	R_{et} (m^2 Pa/W)	i_{mt}
Untreated	0.0304 ± 0.0011	3.51 ± 0.08	0.52
Treated	0.0477 ± 0.0051	5.13 ± 0.26	0.56

3.4. Comfort properties

Results of comfort tests carried out on treated and untreated fabrics are reported in Table 4. Both thermal and water vapor resistances are increased on finished fabric and it can be ascribable to the chitosan presence that, despite the low add-on, partially occluded the interstitial holes of wool fibers.

Nevertheless, the effect on R_{ct} and i_{mt} are of low significance. The higher increase was measured on R_{et}. According to the Skin Model of the Hohenstein Institute (Umbach, 1994), 5 breathability levels can be established for textiles, depending on the measured R_{et}: extreme breathability if $R_{et} < 6$, good breathability if $6 < R_{et} < 13$, normal breathability if $14 < R_{et} < 20$, low breathability if $21 < R_{et} < 30$, negligible breathability if $R_{et} > 30$.

The value of R_{et} measured on the treated fabric was still lower than 6, meaning that an extreme breathability was however maintained, so it can be concluded that the chitosan presence does not affect the comfort behavior of the wool fabric.

4. Conclusions

In conclusion, from the obtained results, chitosan UV-grafting can be indicated as a valid eco-friendly method to confer a multifunctional finishing to wool fabrics without affecting the comfort properties.

A good antimicrobial activity (67% reduction of *E. coli* and 50% of *S. aureus*) was achieved even at low chitosan add-on (2%) after an oxidative pretreatment and 1 h impregnation at 50 °C. With the same treatment a strong increase of wool affinity toward acid dye was obtained with a uniform coloration. However the influence of surfactants chosen for washing was found crucial for the treatment durability.

Moreover an evident reduction of felting after washing were obtained by the applied finishing, while no effect was shown toward pilling. Further work should deeply investigate the grafting reactions occurring, while an optimization of the process parameters will be needed for an industrial scale-up.

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