An eco-friendly facile approach for imparting multifunctional protection properties to cellulose/wool blends

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Abstract

A green facile nano-finishing route was developed to impart high antibacterial efficacy, UV-protection, self-cleaning and anti-wrinkle functions to cotton/wool and viscose/wool blends using TiO2, and/or Ag-NPs, as active ingredients, along with citric acid and/or succinic acid/ SHP as ester-crosslinking/fixing systems. The data so obtained demonstrated that outstanding durable functional properties can be achieved using the following formulation: TiO2/Ag-NPs (20 g/L each), citric acid/ SHP (50 g/L/30 g/L) and the pad- dry microwave fixation at 1300 W for 5 min. SEM and EDX analysis for selected samples as well mode of interactions among the nominated finishing ingredients and the treated substrates were also investigated.

Keywords Multifunctional cellulose · Wool blend · TiO2 NPs · AgNPs · Antibacterial · UV-protective properties

Introduction

Factors affecting multifunctionalization of textile blends include type of blend component, fabric structure, functional finishing formulation constituents, application method, the desired functional properties, environmental concerns and economic aspects [1–4].

Recently, the ever-growing textile consumer demands and expectations for green high value-added, durable, comfortable, and multifunctional protective textile products [5, 6], along with the increasing environmental concerns have received a great
attention and created numerous opportunities for replacement of tradition-hazardous finishing chemicals and non-sustainable finishing methods with environmentally benign chemicals and sustainable emerging technologies, taking into consideration product quality, economy, ecology and social aspects [7–11].

Potential applications of nanotechnology and inorganic nanomaterials like metal and/or metal oxides have been efficiently used along with polycarboxylic acids, as an eco-friendly ester-crosslinking and immobilizing agents, for developing green multifunctional high-added value textile products [4, 8, 12–18]. To the best of our knowledge, few studies have been published on multifunctionalization of cellulose/wool blends using noble metals and/or metal oxides, as multifunctional agents, polycarboxylic acids and sodium hypophosphite, as finishing system, and microwave for fixation step [1].

This study is focused on developing a new, facile and environmentally sound approach to surface modification and multifunctionalization of cotton/wool and viscose/wool substrates using TiO2-NPs and/or Ag-NPs as multifunctional agents, citric acid and/or succinic acid as ester-crosslinking/immobilizing agents, sodium hypophosphite as the catalyst, and microwave fixation instead of using the traditional thermofixation technique. The imparted functional properties, namely antibacterial, UV-shielding capability and anti-wrinkle property were evaluated, and the possible reaction mechanisms were proposed and discussed as well.

**Experimental**

**Materials**

Mill-scoured and bleached cellulose/wool blended fabrics, namely cotton/wool (C/W, 50/50, 230 g/m2, thickness 0.76 mm) and viscose/wool (V/W, 50/50, 190 g/m2, thickness 0.65 mm) were used in this study.

The titanium dioxide nanoparticles TiO2-NPs (powder) was an anatase and supplied by Sigma Aldrich. Polycarboxylic acids, namely citric acids (CA) and succinic acid (SA), sodium hypophosphite monohydrate (SHP, Na H2PO2.H2O) and other chemicals were of reagent grade.

**Methods**

**Preparation of TiO2-NPs aqueous dispersion**

Aqueous dispersion of TiO2-NPs was prepared by the mixing of 7.5 g of TiO2-NPs powder (3 wt%) and appropriate amounts of deionized water in an ultrasonic mixer for 5 h. Then 0.625 g of polyglycol (0.25 wt%, average molecular weight 400 g/mole) was gradually added to the aqueous dispersion for 15 min and then left for 30 min to complete the preparation process [19]. The size of TiO2-NPs
was determined by Transmission Electron Microscopy (TEM) analysis using JEOL model 1200EX electron microscope operated at an accelerating voltage at 120 kV. The image of TiO$_2$NPs showed agglomerates of the nanoparticles and size was ranged from 8 to 15 nm (Fig. 1a).

**Synthesis of Ag-NPs**

AgNPs was prepared by using AgNO$_3$ as a precursor, soluble starch as both reducing and stabilizing agent and water as an appropriate solvent. In this context, 1 g of soluble starch was added to 100 ml of deionized water, heated in microwave oven for complete dissolution, and then 1 ml of 100 mM aq. solution of AgNO$_3$ was added and mixed well. The obtained mixture was kept in an autoclave, at 15 psi/120 ºC for 10 min, to obtain a clear yellow solution of AgNPs [20]. The synthesized AgNPs was spherical in shape observed by TEM. The size of AgNPs was ranged from 3
to 8 nm and the UV–vis spectrum of the synthesized AgNPs showed an absorption peak at about 435 nm (Fig. 1b, c).

**Nano-finishing**

Aqueous functional finishing formulations were prepared by mixing CA and/or SA, SHP-catalyst, with the appropriate amount of TiO$_2$-NPs and/or Ag-NPs, and distilled water in ultrasonic bath at 30 °C for 30 min. Subsequently, the cellulose/wool blended fabrics, i.e. C/W and V/W, were padded twice to reach on average wet pick-up 85% by freshly prepared aqueous finishing formulations. Finally, the incorporation of TiO$_2$-NPs and/or Ag-NPs in finished fabrics was carried out by the pad-dry/cure microwave fixation process at 1300 W for 5 min.

After that, the finished fabric samples were washed and rinsed thoroughly to remove excess and unfixed ingredients and finally dried. Finishing formulation and conditions used were given in the text.

**Testing methods**

- Ti and Ag contents were quantitatively determined using a flame atomic absorption spectrophotometer, GBC-Avanta, Australia.
- Dry wrinkle recovery angles of the treated fabrics (DWRA), were determined according to AATCC standard method 66–1995.
- The antibacterial activity against Gram-positive (G + ve, *S. aureus*) and Gram-negative (G− ve, *E. coli*) pathogenic bacteria, was qualitatively determined according to AATCC test method (147–1988) and expressed as a zone of growth inhibition (ZI, mm).
- UV-protection factor, UPF, was determined according to the Australian/New Zealand standard (AS/NZS 4366–1996). UPF values of 15–24, 25–39, 40–50+ are referred to good, very good and excellent protection, respectively.
- Self-cleaning (SC) property of the untreated and some nanofinished fabric samples were determined by staining with methylene blue (MB-dye) and drying at room temperature. The stained fabric samples were irradiated through exposure to an UV-lamp at wavelength of 400 nm for 12 h and calculated using the following equation [21] according to the following equation:

\[
SC\% = \frac{(K/S)_b - (K/S)_a}{(K/S)_b} \times 100
\]

where \((K/S)_a\) and \((K/S)_b\): color strength after and before exposure at \(\lambda_{\text{max}} = 670\), respectively.
- Durability to wash was determined according to AATCC methods 124.
- The surface morphology of nanofinished fabric samples, SEM was studied using a JEOL, JXA-840A electron probe microanalyzer equipped with disperse X-ray spectrophotometer (EDX) for composition analysis.
- All determinations were done in triplicate and the average was taken as a final result.
Results and discussion

Effect of TiO₂-NPs concentration

Table 1 reports the effect of inclusion of TiO₂-NPs (0–40 g/L) into the ester-crosslinking formulation along with CA (50 g/L), as ester-crosslinking and binding agent and SHP (30 g/L), as an appropriate ester-crosslinking catalyst, on the extent of modification and functionalization of viscose/wool (V/W) and cotton/wool (C/W) substrates. It is clear, regardless of the substrate used and for a given finishing condition, that increasing TiO₂-NPs from zero to 40 g/L brings about an increase in TiO₂-content, an improvement in dry wrinkle recovery angles, DWRA, a noticeable enhancement in anti-bacteria activity against Gram-positive (S. aureus) and Gram-negative (E. coli) pathogenic bacteria, ZI, and a remarkable improvement in UV-shielding ability, UPF, against the harmful UV-radiation.

The increase in TiO₂-content is a direct consequence of the positive role of ester-crosslinking on enhancing the extent of fixation and immobilization of TiO₂-NPs onto/within the fabric structure via free binding and anchoring sites like free –COOH groups, –NH₂, –OH, etc., onto and/or in the cellulose/wool structure [1, 21–23]. On the other hand, the extent of fixation of TiO₂-NPs is governed by the type of substrate, amorphous/crystalline ratio, number, location and availability of active/binding sites as well as the degree of ester-crosslinking and follows the decreasing order V/W > C/W, keeping other parameter constant [1, 4].

Improvement in fabric resiliency, DWRA, by increasing TiO₂-NPs concentration reflects the positive role of nano-TiO₂, as a co-catalyst, in accelerating the formation of reactive intermediates, i.e. cyclic anhydrides, which, in turn, positively affects the extent of esterification of the nominated substrates [1, 22]. On the other hand, increasing TiO₂-NPs in amorphous regions of the fabric structure would further enhance the imparted wrinkle recovery by linking the active

Table 1 Effect of TiO₂-NPs concentration on extent of multifunctionalization of cellulose/wool blended fabrics

| TiO₂ NPs (g/L) | TiO₂-content (%) | DWRA (W + F)° | ZI (mm) | C/W | UPF |
|---------------|------------------|----------------|---------|-----|-----|
|               | V/W              | C/W            | V/W     | C/W | G + ve | G − ve | G + ve | G − ve | V/W | C/W |
| 0             | 0.000            | 0.000          | 230     | 210 | 4.0    | 3.0    | 3.0    | 2.0    | 15   | 24   |
| 20            | 3.083            | 2.716          | 246     | 228 | 15.5   | 10.5   | 12.0   | 10.0   | 32   | 55   |
| 40            | 3.320            | 3.104          | 268     | 255 | 20.0   | 18.5   | 17.0   | 16.0   | 65   | 98   |
| Untreated     | 0.000            | 0.000          | 200     | 185 | 0.0    | 0.0    | 0.0    | 0.0    | 10   | 18   |

Finishing formulation: CA (50 g/L), SHP (30 g/L), TiO₂ NPs (0–40 g/L), nonionic wetting agent (2 g/L), wet pick-up (85%), drying/microwave fixation at 1300 W for 5 min

V/W Viscose/wool blend, C/W Cotton/wool blend, DWRA (W + F)°: dry wrinkle recovery angle (warp + weft), ZI Inhibition zone, G + ve Gram-positive bacteria (S. aureus); G − ve Gram-negative bacteria (E. coli); UPF UV protection factor
sites of the fabric components, i.e., cellulose and protein chains and restricting
the molecular movement, i.e., better anti-wrinkle [24, 25].

Additionally, even in the absence of TiO$_2$-NPs, the ester-crosslinked substrate
possesses a certain antibacterial activity against the tested pathogenic bacteria
reflecting the antibacterial action of CA and its ability to interact with the
bacterial components, which in turn, negatively impact its functions and finally
lead to their destruction [26, 27]. The data in Table 1 demonstrate that increasing TiO$_2$-NPs in the ester-crosslinking formulation brings about a remark-
able increase in the imparted antibacterial activity, regardless of the finished
substrate.

This outstanding improvement in antibacterial efficiency could be discussed
in terms of the unique photocatalytic activity of the immobilized TiO$_2$-NPs and
generation of reactive oxygen species like $^\cdot$OH, $^\cdot$O$_2^-$, H$_2$O$_2$, etc. along with the
accumulation of TiO$_2$-NPs in the cell wall and their subsequent negative impacts
on cell membrane, cell viability and cell growth thereby causing bacterial death
[1, 4, 5, 22, 28, 29]. The imparted antibacterial activity against the tested micro-
organisms follows the decreasing order: Gram-positive (S. aureus) > Gram-neg-
ative (E. coli), most probably due to their structural and sensitivity difference
[30–32].

It is also worth noting, Table 1, that increasing the loaded TiO$_2$-NPs con-
centration up to 40 g/L results in a remarkable improvement in UV-protecting
effect irrespective of the treated substrates. The higher the TiO$_2$-NPs concen-
tration and content, the better the UV-shielding capability, expressed as UPF
value. The noticeable increase in UPF value of nanofinished substrates is a
direct consequence of upgrading UV-blocking capability of the immobilized
TiO$_2$-NPs onto the fabric surface via scattering the harmful UV-radiation
along with blocking the open pores of the fabric structure via nanocrosslink-
ing during the microwave fixation step, thereby hindering its transmission
intensity [28, 33, 34]. The imparted anti-UV functionality is governed by the
type of substrate, e.g. fabric structure, weight, thickness, open pores [5, 35,
36], and extent of crosslinking as well as loading of TiO$_2$-NPs onto/within the
fabric structure. The results in Table 1 signify that the outstanding improve-
ment in UV-shielding capability follows the decreasing order: C/W > V/W,
keeping other parameters constant.

**Mechanism of modification and functionalization cellulose/wool structure**

The tentative mechanism of possible modification and functionalization reac-
tions among cellulose/wool (Cell.OH/W-XH) blended fabrics, CA, as an eco-
friendly trifunctional ester-crosslinking agent, SHP, as ester-crosslinking cata-
lyst, along with TiO$_2$-NPs, as a photocatalyst, is shown in Scheme 1.

Consequently, a remarkable improvement in desirable functional properties
such as wrinkle recovery, antibacterial efficacy and in UV-shielding capability
i- Formation of cyclic anhydride intermediates and ester-crosslinking [1,37]

\[
\begin{align*}
\text{HO-C-COOH} + &\text{SHP catalyst + TiO}_2\text{-NPs (co-catalyst)} \xrightarrow{\Delta, -H_2O} \text{HO-C-CO-O} \\
\text{CH}_2\text{-COOH} + &\text{CA} \xrightarrow{\Delta, -H_2O} \text{HO-C-CO-O} \\
\text{CH}_2\text{-COOH} \quad (1) \\
\text{CA} \\
\end{align*}
\]

\[
\begin{align*}
\text{HO-C/C/W-XH + catalyst/co catalyst} \xrightarrow{\Delta, -H_2O} \text{HO-C-COO-C/W} \\
\text{CH}_2\text{-COOH} + \text{Blend} \\
\text{CH}_2\text{-COOH} \quad (II) \\
\end{align*}
\]

\[
\begin{align*}
\text{HO-C/C/W-XH + catalyst/co catalyst} \xrightarrow{\Delta, -H_2O} \text{HO-C-COO-C/W} \\
\text{CH}_2\text{-COOH} + \text{Blend} \\
\text{Ester-crosslinked fabric substrate} \quad (III) \\
\end{align*}
\]

ii- Ionic crosslinking [1,38]

\[
\begin{align*}
\text{HO-C/C/W-N}^+ &\text{H}_2 + \text{OOC-ester-crosslinked substrate} \xrightarrow{H^+} \text{HO-C/C/W-N}^+-\text{OOC-ester/ionic} \\
\text{H} &\quad \text{Crosslinked substrate} \quad (4) \\
\end{align*}
\]

iii- Immobilization of TiO$_2$-NPs [1,39,24]

\[
\begin{align*}
\text{Crosslinked C/W structure-COOH} + \text{TiO}_2\text{-NPs} \xrightarrow{\text{Chelation & Electrostatic interactions}} \text{TiO}_2\text{-NPs-loaded substrate} \quad (5) \\
\text{NH}_2 \\
\end{align*}
\]

iv- Generation of reactive oxygen species ROS, e.g. $'OH$, $'O_2^-$, H$_2$O$_2$, Single oxygen, etc. [1,25,24]

\[
\begin{align*}
\text{TiO}_2\text{NPs} + h^+ &\xrightarrow{H_2O} \text{TiO}_2(h^+) + \text{TiO}_2(e^-) \\
\text{where } h^+ \text{ and } e^- \text{ are a positive hole and an electron, respectively} \quad (6) \\

h^+ + H_2O &\rightarrow 'OH + H^+ \quad (7) \\
e^- + O_2 &\rightarrow 'O_2^- \quad (8) \\
'O_2^- + H^+ &\rightarrow HO_2 \quad (9) \\
2HO_2 &\rightarrow H_2O_2 + 2[0] \quad (10) \\
\end{align*}
\]

Scheme 1 The possible ester/ionic-crosslinking and immobilization of TiO$_2$-NPs onto crosslinked cellulose/wool fabric, and the subsequent generation of ROS
of the nominated substrates, C/W and V/W, can be achieved using the developed green-finishing formulation constituents and nanofinishing conditions.

**Type of polycarboxylic acid**

As far as the charge in TiO$_2$-content and in the imparted wrinkle recovery property, DWRA, antibacterial activity, ZI, and UV-blocking capability to the treated blends, the data in Table 2 signify that the increase in TiO$_2$-content, the improve in DWRA, the enhancement in ZI as well as the ascending in UPF values follow the decreasing order: CA>CA/SA>SA, keeping other parameters constant. This can be discussed in terms of the variation in acid reactivity, number of available functional groups, i.e. $-\text{COOH}$ groups, which in turn, greatly affect the extent of ester-crosslinking and immobilization and fixation of TiO$_2$-NPs onto/into the blend structure [1, 40, 41], considering that SA, as a bifunctional polycarboxylic acid, acts as an esterifying not as a crosslinking agent compared with the used trifunctional counterpart, i.e. CA, as follows:

$$\Delta \text{CH}_2\text{COOH} \xrightarrow{\text{HO-C/W-XH} + \text{CH}_2\text{COOH} + \text{SHP (catalyst)} + \text{TiO}_2\text{-NPs (co-catalyst)}} \text{CH}_2\text{COO-C/W}$$

Blend fabric          SA  Esterified substrate
HO$_2$O

**(11)**

**Types of inorganic nanoparticle**

The development of high-value added multifunctional cellulose/wool blended fabrics using an eco-friendly nanofinishing formulation is the main task of this research work. The effect of using inorganic nanoparticles, namely TiO$_2$-NPs (40 g/L), Ag-NPs (40 g/L) individually and in combination TiO$_2$-NPs/Ag-NPs (20/20 g/L) on

| Table 2 Effect of type and concentration of carboxylic acids on extent of multifunctionalization of cellulose/wool blended fabrics |
|---------------------------------------------------------------|
| Carboxylic acids (g/L) | TiO$_2$-content (%) | DWRA (W+F)$^a$ | ZI (mm) | UPF |
|------------------------|---------------------|----------------|---------|-----|
| CA                     | SA                  | V/W C/W        | V/W C/W | V/W C/W |
| 50                     | 0                   | 3.320 3.104    | 268 255 | 20.0 18.5 |
| 25                     | 25                  | 2.716 2.529    | 250 240 | 15.5 14.0 |
| 0                      | 50                  | 2.495 2.289    | 240 222 | 13.0 12.0 |
| Untreated              | –                   | – 200          | 185 0.0 | 0.0 10  |

Finishing formulation: finishing agent (50 g/L), SHP (30 g/L), TiO$_2$ NPs (40 g/L), nonionic wetting agent (2 g/L), wet pick-up (85%), drying/microwave fixation at 1300 W for 5 min

CA Citric acid, SA succinic acid, V/W Viscose/Wool blend, C/W Cotton/wool blend, DWRA (W+F)$^a$: Dry wrinkle recovery angle (warp + weft), ZI Inhibition zone, G+ve Gram-positive bacteria (S. aureus); G−ve Gram-negative bacteria (E. coli); UPF UV- protection factor
Table 3  Effect of type and concentration of nanomaterial on extent of multifunctionalization of cellulose/wool blended fabrics

| Nanomaterial (g/L) | Nanomaterial -content (%) | DWRA (W + F)° | ZI (mm) | UPF |
|-------------------|---------------------------|---------------|---------|-----|
|                   |                           | V/W           | C/W     |     | V/W | C/W |
| TiO₂NPs           | AgNPs                     |               |         |     |     |     |
| 40                | 0                         | 3.320         | 3.104   | 268 | 255 | 20.0 | 18.5 | 17.0 | 16.0 | 65 | 98 |
| 20                | 20                        | 3.145/0.041   | 2.922/0.033 | 280 | 265 | 22.5 | 20.5 | 21.0 | 19.5 | 90 | 120 |
| 0                 | 40                        | 0.068         | 0.051   | 241 | 225 | 21.0 | 19.0 | 18.5 | 17.0 | 55 | 85 |
| None              | None                      | 0.00          | 0.00    | 230 | 210 | 4.0  | 3.0  | 3.0  | 2.0  | 15 | 24 |

Finishing formulation: CA (50 g/L), SHP (30 g/L), Nanomaterial (40 g/L), nonionic wetting agent (2 g/L), wet pick-up (85%), drying/ microwave fixation at 1300 W for 5 min

V/W Viscose/wool blend, C/W Cotton/wool blend, DWRA (W + F)°: dry wrinkle recovery angle (warp+weft), ZI Inhibition zone, G+ve Gram-positive bacteria (S. aureus); G-ve Gram-negative bacteria (E. coli); UPF UV- protection factor
upgrading and imparting new functional properties to the used substrates is shown in Table 3. As evident from Table 3, the nanofinished fabric samples displayed a remarkable improvement in DWRA, ZI, UPF values of the multifunctionalized substrates. The extent of improvement in the above-mentioned properties is governed by the type of inorganic nanomaterial and follows the decreasing orders:

Regarding to:
- DWRA: TiO$_2$-NPs > TiO$_2$-NPs/Ag-NPs > Ag-NPs > None,
- ZI: TiO$_2$-NPs/Ag-NPs > Ag-NPs > TiO$_2$-NPs ≥ None (Fig. 2), and.
- UPF: TiO$_2$-NPs/Ag-NPs > TiO$_2$-NPs > Ag-NPs ≥ None, keeping other parameters constant.

On the other hand, the variation in nanomaterial content is determined by the extent of fixation and immobilization of used inorganic nanomaterials via chelation and electrostatic interactions, e.g. $-COO^-$ … $Ag^+$ and/or $-COO^-$ … TiO$_4^{4+}$ [1,39,41].

The remarkable improvement in antibacterial efficacy of Ag-NPs-loaded substrates could be discussed in terms of their ability to: bind to the bacterial outer membrane, interact with the thiol groups of bacterial proteins and to generate reactive oxygen species in the presence of dissolved oxygen as follows [33,42]:

\[4Ag^0 + O_2(aq) + H_2O \rightarrow 4Ag^+ + 4OH^-\]  \hspace{1cm} (12)

\[H_2O + \frac{1}{2}O_2 \xrightarrow{Ag^+ \text{ and/or } Ag^0} H_2O_2 \rightarrow [O] \rightarrow H_2O\] \hspace{1cm} (13)

Thereby leading to subsequent inactivation and oxidation of the bacterial molecular structure [26,42].

Moreover, the incorporation of Ag-NPs along with TiO$_2$-NPs in the finishing formulation plays a synergistic effect in imparting unique antibacterial and UV-blocking functional properties, regardless of used substrate. The high antibacterial activity of TiO$_2$NPs/AgNPs substrates could be discussed in terms of the synergistic

Fig. 2 Inhibition zone of viscose/wool blended fabric samples treated with TiO$_2$-NPs 1, TiO$_2$-NPs/Ag-NPs 2, Ag-NPs 3 against S. aureus and E. coli
activity of the generated reactive oxygen species, ROS, along with the loaded Ag\(^+\) from Ag-NPs against the tested pathogenic bacteria [33, 42–44].

Additionally, the enhanced photocatalytic activity of TiO\(_2\)-NPs/Ag-NPs reflects the positive role of Ag-NPs is acting as electron trappers, thereby minimizing and/ or inhibiting the rate recombination of the generated electron–hole pairs [Eq. 5] by light on TiO\(_2\)-loaded substrates [44–46], which, in turn, positively affects the UV-protection capability.

**Durability of the imparted functional properties**

From the previous experimental results, Table 4 that incorporation AgNPs/TiO\(_2\)NPs (20/20 g/L) into the finishing formulation along with CA (50 g/L) and SHP (30 g/L) brings about remarkable improvement in the imparted functional properties regardless of the used substrate. So, these optimum nanofinishing conditions are used to evaluate the durability of the imparted functional properties namely wrinkle recovery, UV-protection properties, self-cleaning efficiency and antibacterial capability to wash. The data listed in Table 4 demonstrate that increasing the number of washing cycles from 1 to 10 is accompanied by a reasonable decrease in the imparted functional properties, which reflects the high extent of modification and immobilization of the used nanoparticles onto/within the nanofinished substrates, as discussed earlier. The remarkable improvement in the self-cleaning property (SC\%) of the nanofinished cellulose/wool blended fabrics is attributed to the photocatalytic action of loaded nanomaterials, thereby increasing the extent of discoloration of MB-stains. On the other, hand, the extent of variation in the durability of the imparted functional properties is governed by the type of blended substrate, as discussed before [21, 35, 47, 48].

**Surface morphology study and EDX analysis**

The surface morphologies of the nanofinished viscose/wool and cotton/wool blended fabrics with TiO\(_2\)-NPs and Ag-NPs individually or in combination are illustrated in Figs. 3, 4, 5, 6a, c, d using a different type of carboxylic acid as a crosslinking agent. All the images showed deposition of the nanoparticles onto the fiber surface. The nanofinished fabric samples with combined TiO\(_2\)-NPs/Ag-NPs showed higher deposition of nanoparticles than the nanofinished fabric samples with TiO\(_2\)-NPs or Ag-NPs, irrespective of the used substrate and ester crosslinking agent.

The EDX spectra and elemental analysis of nanofinished viscose/wool and cotton/ wool fabric samples using CA/SHP as crosslinking are presented in Figs. 3 and 4b, d, f, respectively, while viscose/wool and cotton/wool fabric samples using SA/SHP as crosslinking are presented in Figs. 5 and 6b, d, f, respectively. All the Figures confirm the existence of the Ag, Ti and Ag/Ti elements in case of nanofinishing with AgNPs, and TiO\(_2\)NPs individually and in combination, along other elements, i.e. carbon, nitrogen and oxygen. The extent of loading of the used nanoparticles is higher in case of using CA/SHP as an ester crosslinking system, regardless of the
Table 4 Durability of the imparted functional properties to wash

| Finished substrate | V/W | C/W |
|--------------------|-----|-----|
| Functional property | DWRA (W+F)° | UPF | SC (%) | ZI (mm) | DWRA (W+F)° | UPF | SC (%) | ZI (mm) |
|                     | G+ve | G–ve | G+ve | G–ve | G+ve | G–ve |
| Washing cycles      |      |      |      |      |      |      |
| one                 | 280  | 90   | 75.2 | 22.5 | 20.5 | 265  | 120  | 69.9 | 21.0 |
| 10                  | 270  | 81   | 70   | 20.0 | 17.5 | 250  | 105  | 65.5 | 18.0 |
| Untreated           | 230  | 15   | 10   | 4.0  | 3.0  | 24   | 12.0 | 3.0  | 2.0  |

Finishing formulation: finishing agent (50 g/L), SHP (30 g/L), Ag/NPs/TiO$_2$ NPs (20/20 g/L), nonionic wetting agent (2 g/L), wet pick-up (85%), drying/microwave fixation at 1300 W for 5 min.
used substrates. Moreover, treated viscose/wool Figs. 3 and 5b, d, f samples showed higher loading of NPs than cotton/wool treated samples Figs. 4 and 6b, d, f, regardless of the used carboxylic acid.

**Conclusion**

- In this study, an eco-friendly facile approach for multifunctionalization of cellulose/wool blended substrates using TiO$_2$ and/or AgNPs along with polycarboxylic acids was reported.
Factors affecting the extent of functionalization, namely type and concentration of nanoinorganic materials, kind and concentration of polycarboxylic acid as well as type of blended substrate were investigated.

The obtained results demonstrated that the incorporation of TiO$_2$-Ag binary nanoparticles (20 g/L each) along with CA/SHP (50/30 g/L) in the finishing formulation of V/W and C/W substrates using the pad-dry-microwave fixation

Fig. 4 SEM and EDX for wool/cotton fabric treated with AgNPs (40 g/L) (a, b), TiO$_2$NPs (40 g/L) (c, d), and AgNPs/TiO$_2$NPs (20/20 g/L) (e, f) in presence of citric acid (50 g/L)
technique developed sustainable functional characteristics including antibacterial activity, UV-blocking efficacy, self-cleaning capability as well as antiwrinkle property before and after washing, regardless of the used substrate.

- The change in the fabric morphology and immobilization of nanoparticles onto some selected samples and durability to wash were confirmed.

**Fig. 5** SEM and EDX for wool/viscose fabric treated with AgNPs (40 g/L) (a, b), TiO$_2$NPs (40 g/L) (c, d), and AgNPs/ TiO$_2$NPs (20/20 g/L) (e, f) in presence of succinic acid (50 g/L)
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Declarations

Conflict of interest
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Fig. 6 SEM and EDX for wool/cotton fabric treated with AgNPs (40 g/L) (a, b), TiO$_2$NPs (40 g/L) (c, d), and AgNPs/ TiO$_2$NPs (20/20 g/L) (e, f) in presence of succinic acid (50 g/L)
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