



Cite this: RSC Adv., 2017, 7, 33219

## Multifunctional cellulose-containing fabrics using modified finishing formulations

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Several metal oxide nanoparticles (MO-NPs), namely ZrO-NPs, ZnO-NPs, and TiO<sub>2</sub>-NPs, have been used to modify traditional finishing formulations to develop multifunctional cotton-containing fabrics. The fabrics used were cotton (100%), cotton/polyester blend (65/35) and cotton/polyester blend (50/50), which were treated with each finishing formulation using the pad-dry-cure technique. The imparted functional properties in the absence and presence of the nominated MO-NPs were evaluated. The positive effects of the incorporated MO-NPs in improving and/or imparting new functional properties, like easy-care, UV-protection, antibacterial functionality, water and oil repellency and flame proofing efficiency, were shown to be governed by the type of substrate and its cellulosic/polyester components, type of MO-NPs, finishing formulation components and mode of interaction between the active ingredients and active sites of the treated substrate. Tentative mechanisms were suggested, and the surface modification and composition of the selected fabric samples were analyzed using SEM and EDX. Future studies will further investigate the impact of incorporating the nominated MO-NPs with other active ingredients in the finishing formulation on the durability of fabric against washing, as well as on the change in other performance and physicomechanical properties.

Received 12th May 2017

Accepted 16th June 2017

DOI: 10.1039/c7ra05403c

rsc.li/rsc-advances

## 1. Introduction

Using cotton, a natural cellulosic fiber, alone and in combination with other natural or synthetic fibers is highly desirable for many reasons, such as achieving the properties of biodegradability, hydrophilicity, breathability, comfortability and versatility.<sup>1–3</sup> On the other hand, the demand for multifunctional cotton-containing textiles has remarkably increased to overcome the inherent drawbacks, and to meet the ever-growing demands of textile end-users, such as antibacterial activity, UV-protection functionality, softness, easy-care, flame retardancy, and water and oil repellency,<sup>4–11</sup> as well as to develop innovative textile products that are of high quality, possess desirable functionality and have increased added value.<sup>3,4,12,13</sup>

Accordingly, the main task of the present work was to search for appropriate finishing formulations, using certain organic/nanometal oxide hybrid materials, to impart multifunctional and durable properties to various cotton-containing substrates, namely cotton (100%), cotton/polyester (65/35) and cotton/

polyester (50/50) fabrics, taking into account both applicability and environmental concerns, as well as consumer demands.

## 2. Experimental

### 2.1. Materials

Mill-scoured and bleached plain weave cotton (160 g m<sup>-2</sup>), cotton/polyester (65/35, 140 g m<sup>-2</sup>) and cotton/polyester (50/50, 250 g m<sup>-2</sup>) fabrics were used. Arkofix® NEC EG liq. (low formaldehyde crosslinking agent, based on modified *N*-methylolodihydroxyethylene urea, DMDHEU, Clariant, Switzerland), Ultratex® FMW silicone softener (micro-emulsion based on amino-modified polydimethylsiloxane, Huntsman, USA), UV-SUN® CEL liq. (reactive UV-absorber based on oxanilide, Huntsman, USA), Flovan® CWF (non-durable flame retardant based on an aqueous solution of nitrogen-phosphate and sulfate compounds, Huntsman, USA), Oleophobol® CO (oil/water and stain repellent finish based on a dispersion of fluoropolymers containing extender, Huntsman, USA), and HEIQ® pure TF (antimicrobial freshness cationic agent based on a silver compound, Huntsman, USA) were of commercial grade. Nanometal oxides, namely ZnO-NPs (10–30 nm), TiO<sub>2</sub>-NPs (10–30 nm) and ZrO-NPs (0.3–0.5 nm), in powder form were obtained from SkySpring nanomaterials, Inc., USA. All other chemicals used in this study, such as citric acid (CA), magnesium chloride hexahydrate (MgCl<sub>2</sub>·6H<sub>2</sub>O), Polyethylene glycol

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(PEG-300) and nonionic wetting agent, were of laboratory reagent grade.

## 2.2. Methods

**2.2.1. Nanometal oxide aqueous dispersion.** Aqueous dispersions of ZnO-NPs, TiO<sub>2</sub>-NPs and ZrO-NPs were prepared by adding PEG (2 g L<sup>-1</sup>), under continuous stirring, into the presonicated nanometal oxide dispersion in deionized water according to the reported method.<sup>14</sup>

**2.2.2. Functional coating of cotton-containing fabrics.** The fabric samples were padded twice to achieve a wet-pickup of 80% with an aqueous finishing formulation containing DMDHEU (50 g L<sup>-1</sup>) as a crosslinking agent, and MgCl<sub>2</sub>·6H<sub>2</sub>O/CA (10/2 g L<sup>-1</sup>) as a mixed catalyst, along with one of the nominated finishing agents, namely a silicone softener (30 g L<sup>-1</sup>), UV-absorber (30 g L<sup>-1</sup>), flame retardant (200 g L<sup>-1</sup>), water/oil repellent (50 g L<sup>-1</sup>) and an antibacterial agent (30 g L<sup>-1</sup>), in the absence and presence of the nominated nanometal oxides (25 g L<sup>-1</sup>). The samples were then dried at 100 °C for 3 min, cured at 150 °C/3 min and washed to remove unfixed and excess reactants at 50 °C for 15 min, in the presence of 2 g L<sup>-1</sup> nonionic wetting agent. Finally, the samples were thoroughly rinsed, dried again and conditioned for evaluation.

## 2.3. Characterization

Scanning electron microscope (SEM) images of the selected fabric samples were obtained on a JEOL, JXL 840A electron probe microanalyser, equipped with energy dispersive X-ray (EDX) spectroscopy for surface elemental composition analysis.

## 2.4. Tests

The nitrogen contact (N%) of the finished fabric samples was evaluated according to the Kjeldhal method.<sup>15</sup> The dry wrinkle recovery angle (WRA) was determined according to the AATCC Test Method 66-1995.<sup>16</sup> The roughness of the untreated and softener-loaded fabric samples was assessed using a SE 1700  $\alpha$ , Japan, in accordance with JIS B0601-94 standard.<sup>17</sup> The antibacterial capability of the untreated and functionalized fabric samples was qualitatively evaluated against Gram positive (G+ve, *S. aureus*) and Gram negative (G-ve, *E. coli*) bacteria according to the AATCC Test Method (147-1988), and expressed as the zone of growth inhibition (mm).<sup>18</sup>

UV-protection functionality, expressed as UV-protection factor (UPF), was assessed according to the AS/NZS 4399:1996, and protection was rated as good, very good or excellent, when UPF values were 15–24, 25–39, or above 40, respectively.<sup>19</sup> The water repellency (WRR) rating and oil repellency rating (ORR), were evaluated using the Spray Test Method 22-2005<sup>20</sup> and AATCC Test Method 118-2013, respectively.<sup>21</sup> The flame retardation properties of the untreated and treated fabric samples were analyzed using the flame test procedure US CPSC 16 CFR PART 1610.<sup>22</sup>

## 3. Results and discussion

The present study focused on investigating the positive role of including ZrO-NPs, ZnO-NPs or TiO<sub>2</sub>-NPs into certain conventional finishing formulations, using the pad-dry-cure technique, to develop high performance multifunctional cotton-containing textiles for diverse potential applications, such as apparel fabrics and household textiles, *etc.*

### 3.1. Characterization of the treated cotton fabrics

The SEM images and EDX spectra of the untreated cotton and cotton treated with silicone softener, in the absence and presence of ZnO-NPs, are presented in Fig. 1. The surface morphology of the untreated cotton sample shows a clean surface (Fig. 1a), while the surface of the softener-treated fabric sample shows the distribution of a thin film on the fabric surface (Fig. 1c). A good deposition of Zn-NPs particles was also observed on the softener-finished fabric surface in the presence of ZnO-NPs (Fig. 1e). The EDX spectra of the treated fabric samples confirm the existence of Si and the presence of Si and Zn, for the samples prepared in the absence and presence of the ZnO-NPs, respectively, along with the existence of N in both spectra due to the finishing and softening agents used, compared with the EDX spectrum of the untreated sample.

Fig. 2 shows the surface morphology change and the analysis of the EDX spectrum of the treated cotton fabrics with the organic UV-absorber, UV-Sun®, in the presence of the ZnO-NPs. The SEM image in Fig. 2c shows a heavy deposition of particles related to both UV-Sun® and ZnO-NPs, and some agglomeration of these particles at the upper layer of the finished fabric surface can be obviously seen. The existence of Zn along with other elements, *i.e.*, C, O and N, is presented in the EDX spectrum of the finished fabric sample.

On the other hand, SEM images and EDX spectra of the cotton fabric samples finished using Oleophobol® CO, without and with TiO<sub>2</sub>-NPs, are shown in Fig. 3. A thin layer of the water/oil repellent agent is distributed along the fiber surface, as shown in Fig. 3a. In Fig. 3c, the deposition of MO-NPs particles can be observed clearly on the fabric surface. On the other hand, the EDX spectrum of the fabric finished with Oleophobol® CO in the absence of TiO<sub>2</sub>-NPs shows a fluorine peak (Fig. 3b), while the spectrum of the finished fabric in the presence of TiO<sub>2</sub>-NPs shows a Ti peak related to the TiO<sub>2</sub>-NPs used in the finishing formulation, along with other elements, *i.e.*, F, N, C and O.

Additionally, the differences in the deposition of HEIQ® Pure TF used as an antibacterial agent on the surface of the finished fabric sample in the absence and presence of Zn-NPs can be clearly noticed in the SEM images in Fig. 4a and c. The EDX spectra confirm the existence of Ag related to the antibacterial agent used alone (Fig. 4b), and also confirm the existence of Ag and Zn in the case of using the antibacterial agent in the presence of Zn-NPs.

Finally, Fig. 5 illustrates the SEM images and EDX spectra of the cotton fabric samples treated with Flovan® CWF in the absence and presence of Zn-NPs. Fig. 3a shows the deposition



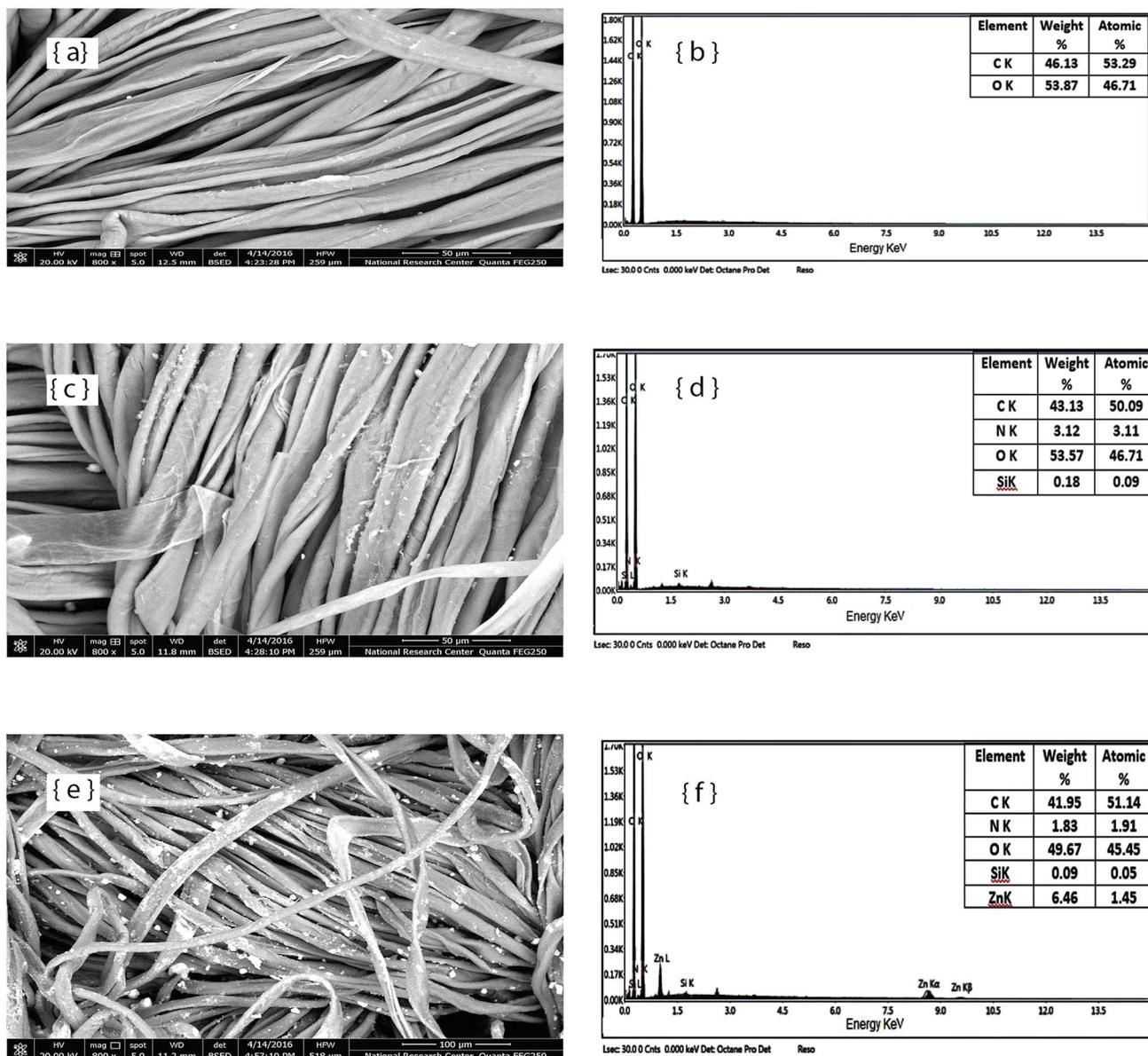


Fig. 1 SEM images and EDX spectra of untreated cotton fabric (a and b); fabric finished with silicon softener (c and d); fabric finished with silicon softener in the presence of ZnO-NPs (e and f).

of the Flovan® CWF particles on the finished fabric surface, and this deposition can be also seen in Fig. 3c, along with the deposition of different types of particles that are attributed to the existence of Zn-NPs on the fabric surface. The EDX spectra of the fabric treated with the flame retardant agent show peaks of phosphorous and sulfur and an increase in the percentage of nitrogen compared with the other finishing formulations. These elements are attributed to the flame retardant used as a finishing agent and are present in the spectral patterns of the finished fabric samples without and with MO-NPs in the finishing formulation, while an additional Zn peak can be clearly observed in the EDX spectrum of the fabric treated with Flovan® CWF in the presence of Zn-NPs (Fig. 5d).

### 3.2. Easy-care finish

For a given set of easy-care finishing conditions, the data in Table 1 signify that: (i) combined easy-care and softener treatment of the nominated substrates results in a significant increase in the % N and fabric resiliency (expressed as WRA), as a direct consequence of the ether-crosslinking of cellulose chains and the formation of an elastic network due to the amino functional groups in the silicone softener;<sup>23–29</sup> (ii) the use of easy-care/softener-finishing treatments is accompanied by a decrease in surface roughness, along with a slight improvement in UV-blocking and antibacterial functionality against the nominated pathogens, *i.e.* G+ve (*S. aureus*) and G-ve (*E. coli*) bacteria, compared with the untreated ones; (iii) the enhancements in the softness and protection properties are attributed

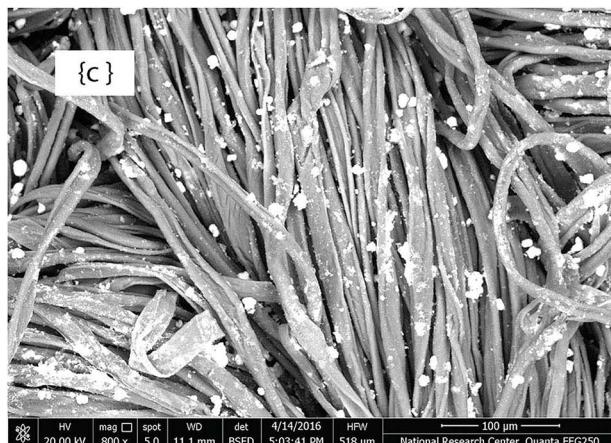
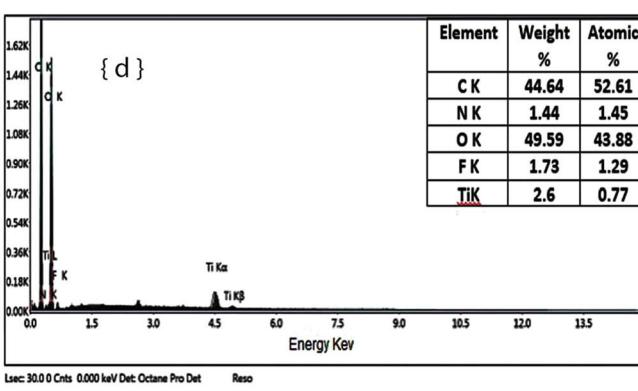
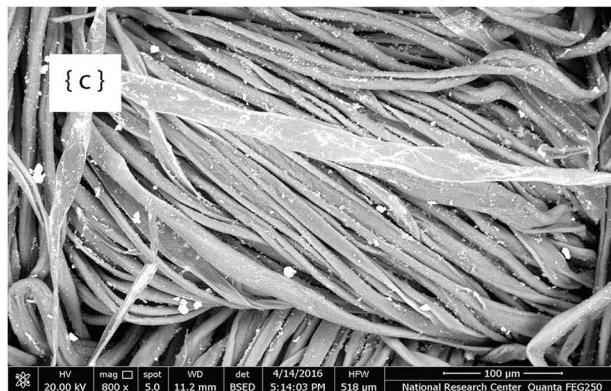
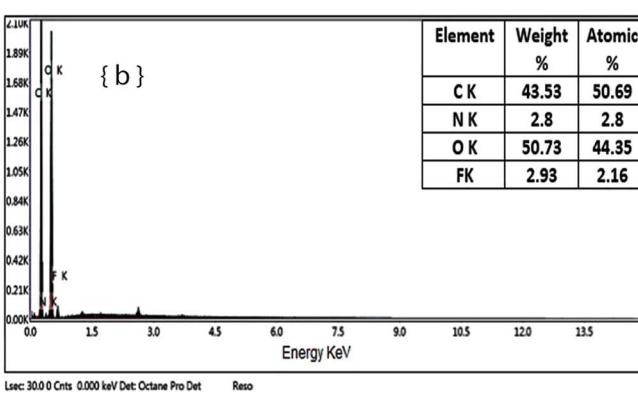
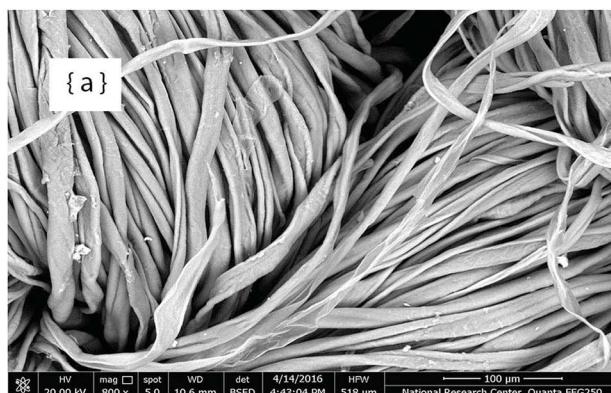
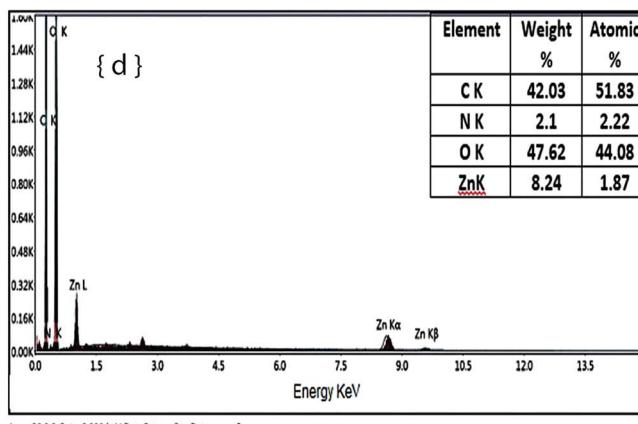


Fig. 2 SEM images and EDX spectra of cotton fabric finished with UV-finishing agent (UV-Sun®) in the presence of ZnO-NPs.

Fig. 3 SEM images and EDX spectra of cotton fabric finished with water/oil agent Oleophobol® CO (a and b); and finished with water/oil agent in the presence of TiO<sub>2</sub>-NPs (c and d).

to the positive effect of the silicone softener on the surface coating, as well as the changes in the surface morphology and properties due to the positive active sites in acidic medium, *i.e.*  $-N^+H_3$ , along with the antibacterial effect of the used reactant resin;<sup>30,31</sup> (iv) the variation in the obtained fabric properties is determined by the type of substrate, *e.g.* fabric weight, cellulose/polyester component, amorphous/crystalline ratio, surface morphology, location, distribution and extent of loading of the

active ingredients, as well as the extent of modification of the treated substrates;<sup>13,23,24</sup> (v) among the finished substrates, cotton/polyester (50/50) blend fabric offers the highest fabric resiliency and softness, along with best UV- and antibacterial-protection properties.

It is also clear from Table 1 that the individual inclusion of the nominated nanomaterials into the finishing formulation is accompanied by a marginal increase in % N, an improvement in

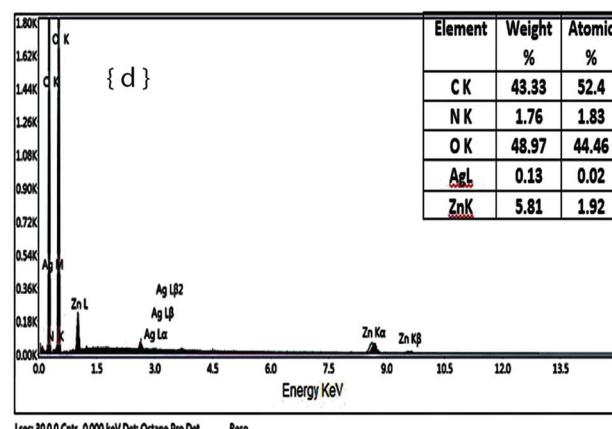
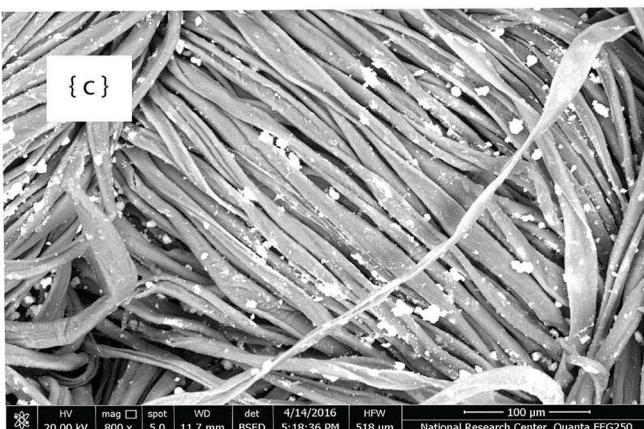
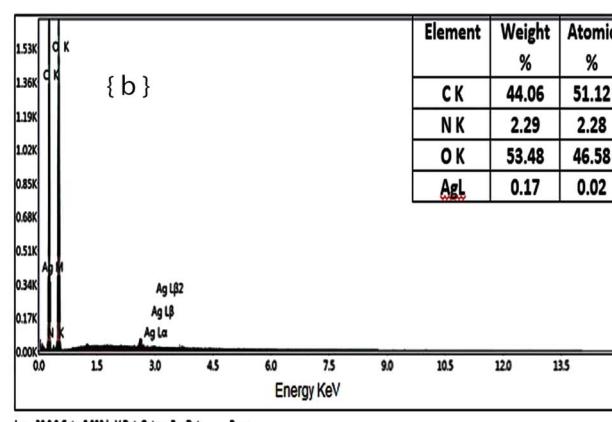
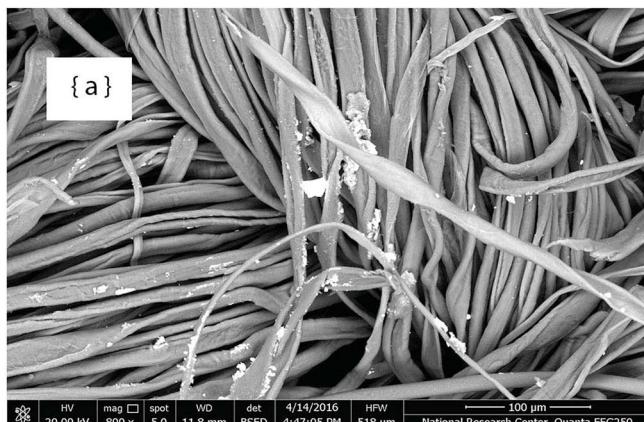


Fig. 4 SEM images and EDX spectra of the cotton fabric finished with the antibacterial agent HEIQ® Pure TF (a and b); and finished with the antibacterial agent in the presence of ZnO-NPs (c and d).

fabric resiliency, a slight variation in surface rigidity and a remarkable improvement in both the anti-UV and antibacterial functionalities, regardless of the substrate used. The marginal increase in % N and the reasonable improvement in the WRA values highlight the positive role of the added nanomaterials in accelerating and enhancing the extent of catalyzation and fixation of the crosslinker and the silicone softener onto/within the fabric structure.<sup>3,25</sup> Moreover, the slight increase in surface rigidity is a direct consequence of the surface immobilization of the used nanometal oxides onto the fabric surface, taking both the particle size and amount into consideration.

Additionally, the remarkable improvement in the UV-protection capability of the nanometal oxide-loaded substrates can be discussed in terms of their ability to block and shield from harmful UV-rays, especially UV-B ( $\lambda$ : 280–315 nm). The extent of the improvement in the UV-protection capability is governed by the type of substrate, fabric morphology, polyester content, extent of crosslinking/coating and loading of the nominated nanometal oxides, as well as the ability of the nanoparticles to be loaded onto the fabric surface, to improve the UV-absorption capacity of the textile materials.<sup>12,32,33</sup> Among the nanometal oxide-loaded substrates, the TiO<sub>2</sub>-NP-loaded

ones demonstrated the highest UPF value to protect human skin.

Moreover, the obvious increase in the antibacterial efficacy of the nanometal oxide-loaded substrates indicate their photocatalytic activity and ability to generate many reactive oxygen species (ROS), including hydroxyl radicals, superoxide anions and singlet oxygen, during photo-oxidation, which in turn can attack and destroy the pathogenic bacteria cells.<sup>26,27</sup> The ZnO-NP-loaded substrates show the best antibacterial functionality, expressed as the ZI value, among the loaded nanometal oxides (Table 1).

The imparted antibacterial functionality against the nominated pathogens follows the decreasing order: G+ve > G-ve, probably due to the differences in their cell wall structure.<sup>28</sup> The variation among the nanometal oxides in the imparted antibacterial functionality can be discussed in terms of differences between their photocatalytic activities, extent and location of loading, and compatibility with other ingredients, which in turn affect their ability to confer antibacterial functionality.

Based on the above mentioned results and discussion, the following simplified tentative mechanism demonstrates the interactions among the cellulose containing substrate (S-Cell'OH), the finishing agent (ROH<sub>2</sub>CN~~F.Agent~~NCH<sub>2</sub>OR), the amino functional silicone softener (AFSi~~NH~~NH<sub>2</sub>) and the nanometal oxide particles (MO-NPs).<sup>2,3,12,24,34</sup>



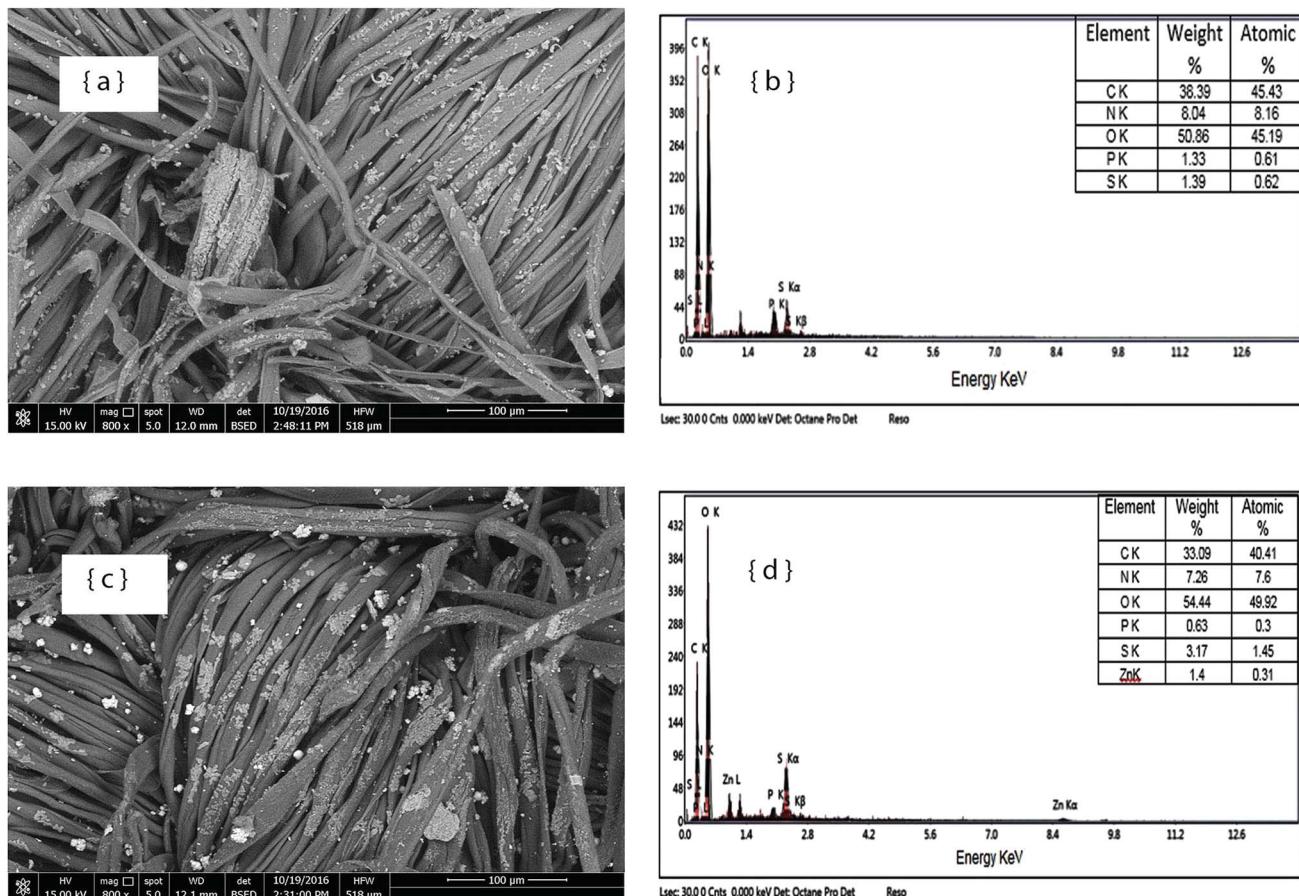


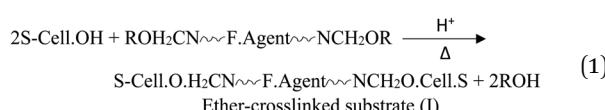
Fig. 5 SEM images and EDX spectra of cotton fabric finished with flame proofing agent (Flavon® CWF) (a and b); and finished with flame proofing agent in the presence of ZnO-NPs (c and d).

Table 1 Effect of individual inclusion of the nanometal oxides into the easy-care finishing formulation<sup>a</sup>

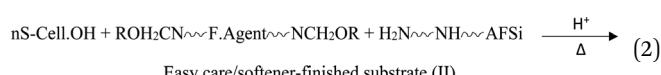
Nanometal oxide (25 g L <sup>-1</sup> )	Cotton				Cotton/polyester (65/35)				Cotton/polyester (50/50)									
	N <sup>b</sup> (%)	WRA <sup>c</sup> (W + F) <sup>°</sup>	SR <sup>d</sup> (μm)	ZIf (mm)	N <sup>b</sup> (%)	WRA <sup>c</sup> (W + F) <sup>°</sup>	SR <sup>d</sup> (μm)	ZIf (mm)	N <sup>b</sup> (%)	WRA <sup>c</sup> (W + F) <sup>°</sup>	SR <sup>d</sup> (μm)	ZIf (mm)						
None	0.456	200	16.83	16	2.0	1.5	0.435	235	16.12	25	3.0	2.0	0.379	250	14.32	33	3.5	2.5
ZrO <sub>2</sub>	0.458	208	16.89	35	11.5	9.0	0.436	240	16.24	45	13.0	11.0	0.380	258	14.40	67	14.5	12.5
ZnO	0.463	214	17.04	48	16.0	14.0	0.453	250	16.38	65	18.0	16.0	0.388	264	14.78	98	19.5	18.0
TiO <sub>2</sub>	0.476	220	16.96	72	13.0	11.5	0.468	262	16.30	87	14.5	13.0	0.395	276	14.58	126	16.0	15.0
Untreated	—	125	20.32	9	—	—	—	160	17.99	15	—	—	—	195	16.84	20	—	—

<sup>a</sup> Finishing bath constituents: Arkofix® NEC (50 g L<sup>-1</sup>); MgCl<sub>2</sub>·6H<sub>2</sub>O/citric acid (10/2 g L<sup>-1</sup>); silicone softener (30 g L<sup>-1</sup>); nanometal oxide (25 g L<sup>-1</sup>); nonionic wetting agent (2 g L<sup>-1</sup>); wet-pickup (80%); drying at 100 °C/3 min; curing at 150 °C/3 min. <sup>b</sup> Nitrogen content. <sup>c</sup> Wrinkle recovery angle (warp + weft). <sup>d</sup> Surface roughness. <sup>e</sup> Ultraviolet protection factor. <sup>f</sup> Zone of inhibition; G+ve: Gram-positive bacteria (*S. aureus*); G-ve: Gram negative bacteria (*E. coli*).

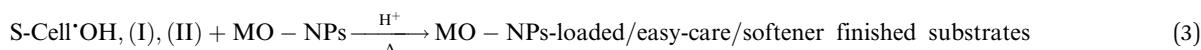
(a) Easy-care finish:



(b) Easy care-finish:



(c) Loading of MO-NPs onto the substrate:



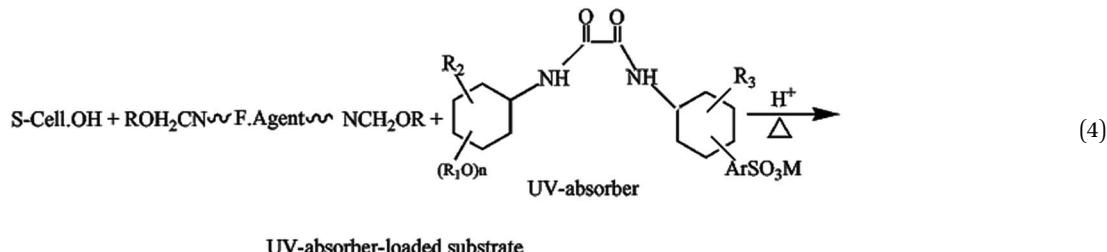
The extent of loading of the nominated MO-NPs onto and/or within the finish/fabric matrix *via* physical adhesion and physical entrapment, as well as *via* chemical interaction with potential reactive sites such as  $-\text{OH}$  and  $-\text{COOH}$  terminal groups of the substrate,  $\sim\text{NH}$  and  $\sim\text{NH}_2$  groups of the reactive silicone softener within the finish/fabric matrix at acidic pH and at high temperature during the fixation step, significantly affects the imparted multifunctional properties.

### 3.3. UV-protection finish

The results in Table 2 clearly show that: (i) finishing of the untreated substrates with the reactant resin along with the organic UV-absorber, UV-Sun®, results in a remarkable increase in % N, WRA and UPF values, along with an improvement in the antibacterial functionality of the treated substrates; (ii) the enhancement in the imparted properties is governed by the type of substrate, as well as the extent of the loading of the UV-absorber onto the finish/fabric matrix as follows:

the slight improvement in the antibacterial activity are attributed to the phenolic nature of the UV-absorber, as an oxalic acid dianilide derivative, and its ability to dissipate the UV-energy without radiation;<sup>5,35</sup> (iv) the extent of the improvement in the fabric resiliency and functionality is governed by the type of substrate, as mentioned before, and follows the decreasing order: cotton/polyester (50/50) > cotton/polyester (65/35) > cotton (100%), keeping other parameters constant.

The results in Table 2 also demonstrate that: (i) the incorporation of any of the nominated nanomaterials,  $\text{ZrO}$ ,  $\text{ZnO}$  or  $\text{TiO}_2$ -NPs, as a UV-blocking agent in the reactant resin/organic UV-absorber finishing formulation brings about a slight decrease in % N, a reasonable improvement in fabric resiliency, excellent UV-protection properties (UPF: 50<sup>+</sup>), and a remarkable improvement in antibacterial functionality against both the G+ve and G-ve pathogens, irrespective of the used substrate; (ii) the remarkable improvement in the UV-protection functionality reflects the outstanding ability of the loaded



*via* chemical interactions among  $\sim\text{Cell.OH}$  groups of the substrate,  $\sim\text{NCH}_2\text{OR}$  groups of the reactant resin and  $\sim\text{NH}$  groups of the UV-absorber under the curing conditions, as well as *via* hydrogen bonding; (iii) the significant increase in the UV-protection functionality of the UV-Sun®-loaded substrates and

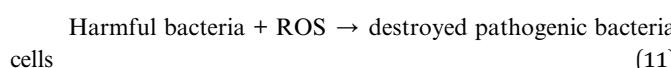
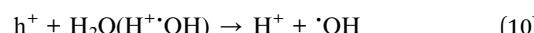
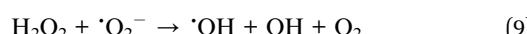
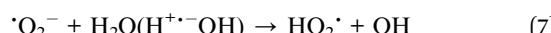
nanomaterials to scatter/refract and shield the harmful UV-B rays, thereby upgrading the protection capacity of the multi-finished substrates; (iii) the significant increase in the imparted antibacterial efficacy of the nanometal oxide-loaded substrates is attributed to their photocatalytic activity and ability to

Table 2 Effect of individual inclusion of the nanometal oxides into the anti-UV finishing formulation<sup>a</sup>

Nanometal oxide (25 g L <sup>-1</sup> )	Cotton				Cotton/polyester (65/35)				Cotton/polyester (50/50)			
	N <sup>b</sup> (%)	WRA <sup>c</sup> (W + F) <sup>o</sup>	UPF <sup>d</sup>	ZI <sup>e</sup> (mm)	N <sup>b</sup> (%)	WRA <sup>c</sup> (W + F) <sup>o</sup>	UPF <sup>d</sup>	ZI <sup>e</sup> (mm)	N <sup>b</sup> (%)	WRA <sup>c</sup> (W + F) <sup>o</sup>	UPF <sup>d</sup>	ZI <sup>e</sup> (mm)
None	0.413	185	44	2.5	2.0	0.392	204	58	3.0	2.5	0.351	232
ZrO	0.386	189	52	13	11	0.383	210	69	15	13	0.338	240
ZnO	0.362	205	68	18	16	0.350	219	89	19	17.5	0.310	254
TiO <sub>2</sub>	0.374	210	96	15	14	0.368	232	114	17	15	0.330	265
Untreated	—	125	9	—	—	—	160	15	—	—	—	195
												20

<sup>a</sup> Finishing bath constituents: Arkofix® NEC (50 g L<sup>-1</sup>);  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ /citric acid (10/2 g L<sup>-1</sup>); UV-Sun® (25 g L<sup>-1</sup>); nanometal oxide (25 g L<sup>-1</sup>); nonionic wetting agent (2 g L<sup>-1</sup>); wet-pickup (80%); drying at 100 °C/3 min; curing at 150 °C/3 min. <sup>b</sup> Nitrogen content. <sup>c</sup> Wrinkle recovery angle (warp + weft). <sup>d</sup> Ultraviolet protection factor. <sup>e</sup> Zone of inhibition; G+ve: Gram-positive bacteria (*S. aureus*); G-ve: Gram negative bacteria (*E. coli*).

generate extremely reactive oxygen species (ROS) in the presence of light and water, which can attack, damage and finally destroy the harmful bacteria cells as follows:<sup>35-37</sup>



where  $h\nu$  represents UV-light,  $\text{e}^-$  is a highly reactive electron,  $\text{h}^+$  represents a hole, cb is the conduction band, vb is the valence band, ROS represents reactive oxygen species ( $\cdot\text{OH}$ ,  $\cdot\text{O}_2^-$ ,  $\text{H}_2\text{O}_2$ ) and MO-NPs are the nanometal oxides.

On the other hand, the extent of the improvement in the imparted functionalities is governed by: (i) the type, particle size, amount, location, photocatalytic activity and shielding capacity of the incorporated MO-NPs; (ii) the synergistic effect of both the organic UV-absorber, UV-Sun®, and the MO-NP UV-blocker; (iii) the extent of the interactions among the nominated active ingredients and the cellulose-containing fabrics under the given thermofixation conditions.

### 3.4. Water/oil repellent finish

Table 3 shows that the incorporation of the dispersed fluoropolymer, Oleophobol® CO, together with the reactant resin and the mixed catalyst under the given thermofixation conditions results in a significant improvement in % N, UPF, WRR and ORR values, along with a reasonable increase in the fabric resiliency and antibacterial activity of the treated substrates, compared with the untreated ones. The enhancement in the aforementioned properties reflects the positive role of the used finishing agents in enhancing the extent of crosslinking and fixation of the fluorocarbon polymer onto the nominated fabric surfaces, thereby changing the surface morphology, decreasing the surface free energy and creating water/oil repellent fabric surfaces.<sup>38,39</sup>

On the other hand, incorporation of any of the nominated nanometal oxides into the conventional water/oil repellent finishing formulation results in a slight decrease in % N, along with a remarkable improvement in easy-care, UV-protection, water/oil repellency and antibacterial functionalities, regardless of the treated substrate and type of MO-NPs. The enhancement in the imparted functional properties of the treated substrates reflects the positive role of the utilized nanometal oxides in: (i) enhancing the extent of fixation, as well as the orientation of the fluorine-containing polymer onto the fabric surfaces, thereby improving the effectiveness and film forming properties; (ii) changing the surface topography and

Table 3 Effect of individual inclusion of the nanometal oxides into the water/oil repellent finishing formulation<sup>a</sup>

Nanometal oxide (25 g L <sup>-1</sup> )	Cotton						Cotton/polyester (65/35)						Cotton/polyester (50/50)						
	ZI <sup>g</sup> (mm)			ZI <sup>g</sup> (mm)			ZI (mm)			ZI (mm)			ZI <sup>g</sup> (mm)			ZI <sup>g</sup> (mm)			
	N <sup>b</sup> (%)	WRA <sup>c</sup> (W + F) <sup>o</sup>	WRA <sup>c</sup> (W + F) <sup>o</sup>	WRR <sup>e</sup>	WRR <sup>e</sup>	WRR <sup>e</sup>	WRR <sup>e</sup>	WRR <sup>e</sup>	WRR <sup>e</sup>	WRR <sup>e</sup>	WRR <sup>e</sup>	WRR <sup>e</sup>	WRR <sup>e</sup>	WRR <sup>e</sup>	WRR <sup>e</sup>	WRR <sup>e</sup>	WRR <sup>e</sup>	WRR <sup>e</sup>	
None	0.401	135	25	70	7	3.0	2.5	0.380	195	33	80	7	3.5	3	0.360	210	48	80	7
ZrO	0.382	146	40	90	8	10	9	0.359	212	50	90	8	13	12	0.332	225	69	90	8
ZnO	0.330	165	52	90	8	17	16	0.320	220	76	90	8	19	17	0.301	238	90	90	8
TiO <sub>2</sub>	0.362	180	69	80	8	14	13	0.342	232	98	90	8	16	15	0.319	245	112	80	8
Untreated	—	125	9	0	0	0	0	—	160	15	0	0	0	—	—	195	20	0	0

<sup>a</sup> Finishing bath constituents: Arkofix® NEC (50 g L<sup>-1</sup>); MgCl<sub>2</sub>·6H<sub>2</sub>O/citric acid (10/2 g L<sup>-1</sup>); Oleophobol® CO (25 g L<sup>-1</sup>); nanometal oxide (25 g L<sup>-1</sup>); nonionic wetting agent (2 g L<sup>-1</sup>); wet-pickup (80%); drying at 100 °C/3 min; curing at 150 °C/3 min. <sup>b</sup> Nitrogen content. <sup>c</sup> Wrinkle recovery angle (warp + weft). <sup>d</sup> Ultraviolet protection factor. <sup>e</sup> Water repellent rate. <sup>f</sup> Oil repellent rate. <sup>g</sup> Zone of inhibition; G+ve: Gram-positive bacteria (*S. aureus*); G-ve: Gram negative bacteria (*E. coli*).

Table 4 Effect of individual inclusion of the nanometal oxides into the antibacterial finishing formulation<sup>a</sup>

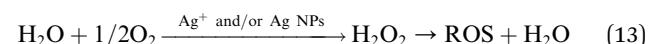
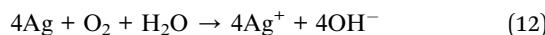
Nanometal oxide (25 g L <sup>-1</sup> )	Cotton				Cotton/polyester (65/35)				Cotton/polyester (50/50)						
	N <sup>b</sup> (%)	WRA <sup>c</sup> (W + F) <sup>o</sup>	UPF <sup>d</sup>	ZI <sup>e</sup> (mm)	N <sup>b</sup> (%)	WRA <sup>c</sup> (W + F) <sup>o</sup>	UPF <sup>d</sup>	ZI <sup>e</sup> (mm)	N <sup>b</sup> (%)	WRA <sup>c</sup> (W + F) <sup>o</sup>	UPF <sup>d</sup>	ZI <sup>e</sup> (mm)			
None	0.416	136	25	15.0	13.0	0.401	185	40	17.0	16.0	0.385	205	52	18.5	17.0
ZrO	0.394	145	39	17.0	16.0	0.371	203	50	19.5	18.0	0.358	220	69	22.0	21.0
ZnO	0.346	158	53	21.0	19.0	0.330	215	70	23.0	22.0	0.313	230	97	24.5	23.0
TiO <sub>2</sub>	0.365	170	69	18.5	17.0	0.348	226	85	21.0	19.5	0.336	238	112	23.0	22.0
Untreated	—	125	9	0.0	0.0	—	160	15	0.0	0.0	—	192	20	0.0	0.0

<sup>a</sup> Finishing bath constituents: Arkofix® NEC (50 g L<sup>-1</sup>); MgCl<sub>2</sub>·6H<sub>2</sub>O/citric acid (10/2 g L<sup>-1</sup>); HEIQ® Pure TF (30 g L<sup>-1</sup>); nanometal oxide (25 g L<sup>-1</sup>); nonionic wetting agent (2 g L<sup>-1</sup>). Wet-pickup (80%); drying at 100 °C/3 min; curing at 150 °C/3 min. <sup>b</sup> Nitrogen content. <sup>c</sup> Wrinkle recovery angle (warp + weft). <sup>d</sup> Ultraviolet protection factor. <sup>e</sup> Zone of inhibition; G+ve: Gram-positive bacteria (*S. aureus*); G-ve: Gram negative bacteria (*E. coli*).

increasing the surface roughness, thereby leading to better hydrophobic effects than when the hydrophobic agent is applied alone, keeping other additives fixed. Furthermore, the presence of the MO-NPs fixed into the finish/fabric matrix, with their UV-shielding and photocatalytic properties, confers additional and better multifunctional properties to the treated cellulose-containing fabrics than those treated in the absence of MO-NPs.<sup>40,41</sup> Additionally, the extent of the improvement in the multifunctional properties of the treated substrates is governed by fabric type, type of MO-NPs, extent of interaction and the fixation of active ingredients on the fabric surface, as well as the change in the surface morphology and surface tension of the nominated substrate in the absence and presence of the nanometal oxides.

### 3.5. Antibacterial finish

The results in Table 4 reveal that treating the nominated substrates with HEIQ® Pure TF, a cationic antimicrobial agent containing silver, along with the crosslinking agent and mixed catalyst, results in an improvement in % N, WRA and UPF values, along with a remarkable increase in the antibacterial activity of the treated substrates. The variation in the imparted functionality is determined by the type of substrate. The fixation of the antimicrobial agent onto/within the finish/fabric matrix changes the surface and chemical properties of the treated substrates, thereby enhancing the nitrogen content, fabric resiliency and UV-shielding ability. On the other hand, the remarkable improvement in the antibacterial functionality is attributed to the interaction of the positively charged cationic sites of the antimicrobial agent with the negatively charged cell walls of the pathogens, which in turn causes the interruption of cell membrane functions and protein activity, as well as the inability to multiply.<sup>25,42</sup> Further, Ag in the finish/fabric matrix can participate in: (i) hindering or deactivating the physiological functions of the bacteria; (ii) interacting with thiol groups and/or binding of Ag<sup>+</sup> to the DNA; (iii) accelerating the formation of reactive oxygen species, highly toxic to cells, and consequently destroying the bacterial cells, as follows:<sup>2,43,44</sup>



The results in Table 4 demonstrate also that inclusion of any of the nominated MO-NPs into the finishing formulation, along with other active ingredients, leads to much better functional properties, *i.e.* easy-care, UV-protection and antibacterial functionality, along with lower % N values, than those of the samples finished in the absence of the nanometal oxides, *i.e.* the control samples.

The noticeable improvement in the imparted functionalities of the treated substrates is a direct consequence of binding/embedding MO-NPs onto/into the finish/fabric matrix, which in turn enhances: (i) the catalytic effect of the used mixed catalyst; (ii) the extent of the interactions among the treated substrate active sites and the crosslinking and antimicrobial finishing agents used; (iii) the UV-blocking capability and antibacterial functionality, as discussed earlier. Additionally, the improvement in the evaluated functional properties reflects the synergistic effect of adding the nominated nanomaterials to the conventional finishing agents in one bath.

The obtained results also signify that the enhancement in the functional properties is directly affected by the characteristics of the substrate, such as its chemical nature, surface morphology, adsorption capacity, active groups and available binding sites. This enhancement is also related to the properties of the MO-NPs, such as their chemical structure, particle size, specific surface used, photocatalytic activity, and synergistic effect. Other factors include the mode of interaction, extent of fixation and loading of the active ingredients onto/within the finish/fabric matrix, and the degree of agglomeration of the NPs, which in turn controls the release of MO-NPs from the coated fabric surface.

The enhancement in the imparted functionalities using the nominated MO-NPs can be ranked in descending order as follows:

(i) Regarding easy-care and UV-blocking functions: TiO<sub>2</sub>-NPs > ZnO-NPs > ZrO-NPs > control ≫ untreated.

(ii) Regarding antibacterial function: ZnO-NPs > TiO<sub>2</sub>-NPs > ZrO-NPs > control ≫ untreated, keeping other parameters constant.



Table 5 Effect of individual inclusion of the nanometal oxides into flame proofing formulation<sup>a</sup>

Nanometal oxide (25 g L <sup>-1</sup> )	Cotton			Cotton/polyester (65/35)			Cotton/polyester (50/50)		
	N <sup>b</sup> (%)	WRA <sup>c</sup> (W + F) <sup>o</sup>	ZI <sup>e</sup> (mm)	N <sup>b</sup> (%)	WRA <sup>c</sup> (W + F) <sup>o</sup>	ZI <sup>e</sup> (mm)	N <sup>b</sup> (%)	WRA <sup>c</sup> (W + F) <sup>o</sup>	ZI <sup>e</sup> (mm)
None	2.012	170	20	1.5	1.0	11	1.843	203	36
ZrO	1.841	179	33	13.5	12.0	16	1.780	212	54
ZnO	2.036	196	45	17.5	15.0	22	1.890	225	68
TiO <sub>2</sub>	2.076	212	59	16.0	14.0	18	1.981	236	83
Untreated	—	125	9	0.0	0.0	4	—	160	15

<sup>a</sup> Finishing bath constituents: Arkofix® NEC (50 g L<sup>-1</sup>); MgCl<sub>2</sub>·6H<sub>2</sub>O/citric acid (10/2 g L<sup>-1</sup>); Flavan® CWF (200 g L<sup>-1</sup>); nanometal oxide (25 g L<sup>-1</sup>); nonionic wetting agent (2 g L<sup>-1</sup>); wet-pickup (80%); drying at 100 °C/3 min; curing at 150 °C/3 min. <sup>c</sup> Wrinkle recovery angle (warp + weft). <sup>e</sup> Ultraviolet protection factor. <sup>o</sup> Zone of inhibition; G+ve: Gram-positive bacteria (*S. aureus*); G-ve: Gram negative bacteria (*E. coli*). <sup>f</sup> Flammability: relative ease of ignition and relative ability to sustain combustion (second).

### 3.6. Flame retardant finish

The impacts of the individual inclusion of the nominated nanometal oxides into the conventional flame retardant finish formulation are summarized in Table 5. It is clear that conventional finishing of untreated substrates with Flovan® CWF as a flame retardant agent, along with Arkofix® NEC as a crosslinking agent, under the given conditions results in a significant increase in the nitrogen content, fabric resiliency, UV-shielding ability, flame retardancy functional properties and antibacterial activity of the treated substrates. The remarkable improvement in the burning performance, expressed as burning time in seconds, can be discussed in terms of the ability of the flame retardant components used, nitrogen/phosphate/sulfate compounds, and the crosslinker to change the pyrolytic pathways of thermal decomposition of the nominated substrates, or the ability to form a protective coating or barrier on the surface of the decomposing substrate.<sup>45,46</sup>

Table 5 also shows that the addition of any of the nominated MO-NPs in the conventional flame-retardant finishing formulations is accompanied by a slight variation in % N, a reasonable improvement in WRA, and significant increases in UPF, antibacterial activity and burning time, regardless of the treated substrate. The enhancements in the imparted functionalities, gained through modifying the finishing formulation, reflect the positive impacts of the added MO-NPs on the surface morphology, location and distribution of crosslinks, creation of antibacterial active sites on the finish/fabric matrix and thermal stability and fire-retardant functionality of the treated substrates, thereby improving UV-protection, easy-care, antibacterial activity and increasing the flammability time, respectively.<sup>47</sup> The enhancement in the flame retardant attributes of the treated substrates is governed by the type of immobilized MO-NPs, and their thermal stability, synergetic effects, ability to act as a barrier to heat and mass transfer, capability to change the degradation pathway of the textile polymer and ability to hinder the mobility of textile polymer chains and/or to absorb the generated active species,<sup>48</sup> keeping other parameters fixed. The degree of fixation of both the phosphorous sulfur and nitrogen components to the finish/fabric matrix cannot be rolled out. Moreover, the results in Table 5 demonstrate that the enhancement in flame-retardant functionality as a function of the added MO-NPs can be ranked as: ZnO-NPs > TiO<sub>2</sub>-NPs > ZrO-NPs > control ≫ untreated, keeping the type of substrate fixed. Additionally, the change in the evaluated functional property values upon using the nominated MO-NPs is governed by their type, photocatalytic activity, thermal stability and compatibility with other ingredients in the conventional finishing formulation, as mentioned before.

## 4. Conclusion

A new approach for improving and/or imparting new functional properties to cotton-containing fabrics in one step was investigated by including ZrO-NPs, ZnO-NPs or TiO<sub>2</sub>-NPs into the traditional finishing formulations.

The obtained results demonstrate that the incorporation of the nominated MO-NPs into an easy-care/softener finishing formulation is accompanied by an enhancement in fabric resiliency and surface softness, along with a noticeable improvement in UV-protection and antibacterial functionalities, regardless of the type of MO-NPs or treated substrates. Inclusion of the nominated MO-NPs into UV-protection finish formulation brings about a remarkable improvement in the UV-protection functionality, along with a significant improvement in the antibacterial efficacy and a reasonable increase in fabric resiliency, irrespective of the used MO-NPs and the finished substrate. We have also shown that the addition of the nominated MO-NPs into a water/oil repellent finishing formulation results in significant improvements in UPF, ERR and ORR values, along with a reasonable improvement in fabric resiliency, and the extent of improvement is determined by the type of MO-NPs and the kind of substrate. Coating the substrates with the antibacterial finish in the presence of the nanometal oxides also results in a remarkable improvement in the antibacterial activity according to the following order: ZnO-NPs > TiO<sub>2</sub>-NPs > ZrO-NPs > control >> untreated, along with an enhancement in the UPF values as follows: TiO<sub>2</sub>-NPs > ZnO-NPs > ZrO-NPs > control >> untreated, keeping the other parameters constant. Furthermore, the addition of any of the nominated MO-NPs to the conventional flame retardant finishing formulation results in a significant increase in burning time, UPF and antibacterial activity along with a reasonable increase in fabric resiliency. The enhancement of the flame retardant properties as a function of the type of MO-NPs can be ranked as: ZnO-NPs > TiO<sub>2</sub>-NPs > ZrO-NPs > control >> untreated. Finally, this very simple and easily scaled-up single step process can be applied to achieve multifunctional textile products with outstanding performance and protective properties.

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