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Multifunctional finishing of cellulosic/polyester blended fabrics

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ABSTRACT

Innovative/efficient finishing systems for imparting multi-functional properties to cotton/polyester and viscose/polyester blends were developed. Factors affecting the extent of functionalization including type and concentration of the nano-hybrid, i.e. silver nanoparticles/polyvinyl pyrolidone hybrid (Ag-NP's/PVP) or zinc oxide nanoparticles/hyperbranched polyamide–amine hybrid (ZnO-NP's/HBPAA), concentration of Basic Blue 9, or chitosan and sequence of treatment using citric acid as cross-linker were reported. Loading of β-CD, with its hydrophobic cavities, onto the cross-linked substrates and subsequent treatment with Neem-oil, Lavender-oil or 4-hydroxybenzophenone was also studied. The obtained products exhibit a remarkable easy care, antibacterial and/or UV-blocking functional properties. The improvement in the imparted properties and durability to wash is governed by type and amount of loaded active ingredients. Mode of interactions was suggested, and surface modifications together with composition of selected samples were also confirmed by SEM images and EDX spectra.

1. Introduction

It is well known that textile fabrics made of cellulosic fibres such as cotton, flax and viscose provide desirable properties namely: high absorbency, breathability, softness and comfort for wear (Ibrahim, Khalifa, El-Hossamy, & Tawfik, 2010; Ibrahim, Eid, & El-Batal, 2012). Despite the nominated advantages, there are also some undesirable properties such as easy wrinkling, easy soiling, susceptibility to microbial attack, supporting the growth of microorganisms, low UV-Protection as well as low strength (Harifi & Montazer, 2012; Hashem & Ibrahim, 2002; Ibrahim & Hebeish, 1985; Ibrahim, Aboshosha, Elnagdy, & Gaffar, 2002; Ibrahim, Refai, Youssef, & Ahmed, 2005). On the other hand, textile fabrics based on polyester fibres generally are strong, wrinkle resistant, more resistant to microbial attacks by microorganisms and dirt resistant (Gao & Cranston, 2008; Ibrahim, Eid, Youssef, Ameen, & Salah, 2013). However they certainly lack the comfort properties (Eom, 2001). Therefore, blending of cellulosic and polyester fibres along with the used novel finishes and innovative technologies can economically extend the functional and performance properties, and hence values of textile processing and products, to cope with the increasing consumer's demand for innovative multifunctional materials (Gao & Cranston, 2008; Holme, 2007; Ibrahim, Eid, Hashem, Refai, & El-Hossamy, 2010; Sawhney et al., 2008). This high demand, in turn, has stimulated intensive research and development activities in the field of textile finishing to produce high added value textiles that provide consumers with desired textile characteristics and functional performance, such as soft hand, antimicrobial properties, UV-blocking properties, self cleaning properties, durability, easy care and the like (Gao & Cranston, 2008; Gowri et al., 2010; Hebeish & Ibrahim, 2007; Holme, 2007; Ibrahim, Refaie, & Ahmed, 2010; Ibrahim, Amr, Eid, Mohamed, & Fahmy, 2012; Ibrahim, Eid, et al., 2013; Sawhney et al., 2008), Comfort, safety and aesthetics.

This work is dedicated to impart multifunctional properties to the cellulosic/polyester blended fabrics via: (i) immobilization of silver nanoparticles/polyvinyl pyrolidone hybrid (Ag-NP's/PVP) or zinc oxide nanoparticles/hyperbranched polyamide–amine hybrid (ZnO-NP's/HBPAA) onto the finished fabrics through the use of citric acid as a cross-linking agent, (ii) combined basic dyeing and ester-crosslinking, (iii) post-treatment of the obtained basic dyeings with the nominated nano-hybrids, (iv) fixation of chitosan onto the nominated substrates via citric acid as a cross-linker, and (v) Inclusion of Neem seed oil, Lavender oil or 4-hydroxybenzophenone into the grafted βCD cavities loaded onto the cross-linked fabrics surface.

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2. Experimental

2.1. Materials

Mill-Scoured and bleached plain weave cotton/polyester (C/PET, 35/65, 120 g/m^2) and viscose/polyester (V/PET, 30/70, 96 g/m^2) blended fabrics were used throughout the study.

Cavasol® W7MCT (Monochlorotriazinyl β-cyclodextrine,MCT-βCD, average molecular weight 1560, degree of substitution 0.3–0.6 peranhydroglucose unit, Waker, Germany), chitosan (degree of deacetylation of >85%, Sigma), 4-hydroxybenzophenone,(Aldrich), citric acid (Aldrich), sodium hypophosphite (Aldrich), methylene Blue (C.I Basic Blue 9, Merck) and polyvinylpyrolidone PVP-40,000 Dalton, Merck) were used as received.

Neem seed oil (Ozone Biotech Division, Shivanshu Sintered Product Pvt., Ltd., India), Lavander essential oil, as well as Hostapal® CV-ET (nonionic wetting agent based on alkyl aryl polyglycol ether, Clariant) were of commercial grade.

All other chemicals used during this study such as silver nitrate ($AgNO_3$-Sigma), Zinc acetate (Zn-$(CH_3COO)_2{\cdot}2H_2O$, Aldrich), ethyl alcohol, and sodium carbonate were reagent grade.

2.2. Methods

2.2.1. Synthesis of hyperbranched polyamide-amine zinc oxide nanoparticles (HBPAA/ZnO-NP's)

Synthesis of (HBPAA/ZnO-NP's) hybrid was similar to that reported in the literature (Ibrahim, Abou Elmaaty, Eid, & Abd El-Aziz, 2013).

2.2.2. Synthesis of the silver nanoparticles/polyvinyl pyrolidone hybrid (Ag-NP's/PVP)

Ag-NP's/PVP hybrid was synthesized using Ibrahim, Eid, Abou Elmaaty, & Abd El-Aziz (2013) method.

2.2.3. Multi-functional finishing using nano-hybrids or chitosan

The blended fabric samples were padded twice to a wet-pick-up of 80% with an aqueous finishing formulation containing citric acid (20 g/l), as a crosslinking agent, Na-hypophosphite (10 g/l), as a catalyst, Hostapal® CV-ET (2 g/l) in the absence and presence of Ag-NP's/PVP, ZnO-NP's/HBPAA (0–40 g/l) or chitosan (0–5 g/l), followed by drying at 100 °C/3 min and curing at 170 °C/2 min in circulating air-oven. The cured fabric samples were then washed at 50 °C/15 min in presence of 2 g/l wetting agent and 2 g/l Na-carbonate to remove excess and unfixed reactant, thoroughly rinsed, dried at 100 °C/3 min and conditioned for evaluation.

2.2.4. Multi-functional finished and basic dyeing in one step

To acquire easy care property, UV-and antibacterial functionality together with dyeability with basic dye in one step, the blended fabric samples were padded twice in a dyeing/multifunctional formulation containing: citric acid (20 g/l), Na-hypophosphite (10 g/l), nonionic wetting agent (2 g/l) along with Methylene blue basic dye (0–20 g/l), to give a wet pick up of 80%, followed by drying at 100 °C/3 min and curing at 170 °C/2 min. The dyed/finished fabric samples were rinsed thoroughly in tap water, followed by washing at 50 °C/15 min in the presence of 2 g/l nonionic wetting agent and 1 g/l Na-carbonate to remove excess and unfixed dye/reactants, and finally thoroughly rinsed and dried a gain at 100° C/3 min.

2.2.5. Post-treatment of simultaneously dyed and finished fabrics with the nano-composites

Portions of the simultaneously basic dyed/finished fabric samples were padded twice with an aqueous solution of the prepared nano-composites (20 g/l), i.e. Ag-NP's/PVP and ZnO-NP's/HBPAA, at room temperature to a wet pickup of 80%, followed by thermofixation at 120 °C/3 min, thoroughly rinsed, and finally dried again. Typical formulations used in this study are given in the text.

2.2.6. Post treatment of easy-care finished cellulosic/polyester blends loaded with βCD moieties

Blended fabric samples were padded twice in a finishing bath contains citric acid (20 g/l), Na-hypophosphite (10 g/l), nonionic wetting agent and MCT-βCD (10 g/l), to 80% wet pickup. After drying at 100°/3 min and curing at 170 °C/2 min, the finished fabric samples were rinsed at 50 °C for 15 min in the presence of 1 g/l Na-carbonate and 2 g/l nonionic wetting agent to remove excess and unfixed reactants and finally dried a gain at 100 °C/3 min.

Portions of the above mentioned substrates were immersed in an alcoholic solution of Neem seed oil, Lavender essential oil or 4-hydroxybenzophenone (5% owf), material-to-liquor ratio (1/20), at room temperature for 30 min, followed by padding to 80% wet pick up and air drying.

2.2.7. Measurements

The nitrogen content (*N*%) was determined according to Kjeldhal method.

Dry wrinkle recovery angle (WRA) was determined according to ASTM method D-1296-98.

Colour strength of simultaneously dyed and functionally finished fabric samples (K/S) was calculated from reflectance data using Kubelka–Munk equation (Judd & Wyszeck, 1975).

$$\frac{K}{S} = \frac{(1-R)^2}{2R}$$

where *K*/*S* is the ratio of absorption and scattering coefficient, and R is the reflectance at the wavelength of maximum absorbance of the used basic dye.

Ultraviolet-protection factor (UPF) values calculated according to the Australian/New Zealand Standards (AS/NZS 4366-1996). According to this standard, fabric can be rated as providing good protection, very good protection and excellent protection if their UPF values range from 15 to 24, 25–39 and above 40, respectively.

Antibacterial activity against G+ve (*S. aureus*) and G−ve (*E. coli*) bacteria was assessed using agar diffusion test according to AATCC test method 147-1988.

Durability to washing was evaluated according to ASTM Standard Test Method (D 737-96).

The morphology and particle size of Ag-NP's/PVP and ZnO-NP's/HBPAA composites were obtained by transmission electron microscope (TEM) using a JEOL-JEM 2100 F electron microscope at 200 kV.

The surface morphology (SEM) of some untreated and treated fabric samples was observed with a JEOL, JXL 840A electron probe micro analyzer, equipped with energy disperses X-ray spectroscopy (EDX) for the composition analysis.

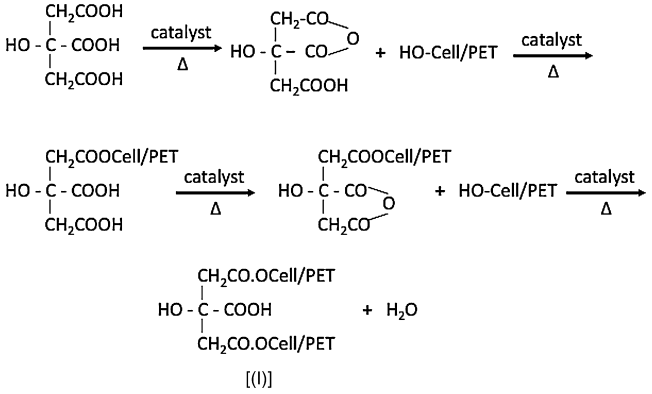
3. Result and discussion

The work is dedicated to the investigation of the technical feasibility of multifunctional finishing of cotton/polyester and viscose/polyester blended fabrics. Factors affecting the imparted functional properties, i.e. easy care, antibacterial and/or anti-UV, such as type and concentration of additive, treatment sequence as well as type of active ingredient used in the post-treatment step has been investigated. Results obtained along with their appropriate discussion follow.

3.1. Tentative mechanism

Presence of citric acid, as a cross-linking agent, Na-hypophosphite, as a catalyst, along with Ag-NP's/PVP, ZnO-NP's/HBPAA, Basic Blue 9 or MCT-βCD, as a reactive additive, followed by padding, to give a wet pickup of 80%, drying at 100 °C/3 min and thermofixing at 170 °C/2 min would be expected to promote several chemical reactions, the most dominant of which are:

i) Ester crosslinking of the cellulosic/polyester blend (Harifi & Montazer, 2012; Ibrahim et al., 2002)



(1)

ii) Loading of Ag-NP's/PVP onto the cellulosic/polyester blend (Fahmy & Abdel-Hlim, 2010; Fahmy, Abo-Shosha, & Ibrahim, 2009)

$$CA + \text{Ag-NP's/PVP} + HO \cdot \text{Cell/PET} \xrightarrow[\Delta]{\text{catalyst}} \text{Crosslinked/Ag} - \text{NP's} - \text{loaded substrate} \quad (2)$$

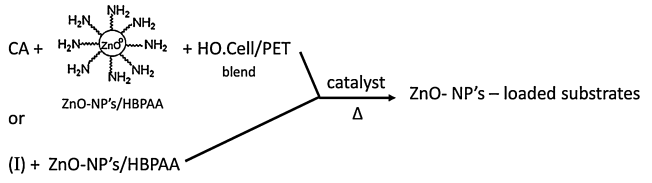
or

$$\text{Ag-NP's/PVP} + (I) \xrightarrow[\Delta]{\text{catalyst}} \text{Ionic crosslinked substrate} \quad (3)$$

$$n\text{Ag-NP's/PVP} \xrightarrow{\Delta} \text{Crosslinked/entangled PVP sheath} - \text{loaded with Ag-NP's} \quad (4)$$

$$n\text{Ag-NP's/PVP} + CA \xrightarrow[\Delta]{\text{catalyst}} \text{Crosslinked polymeric deposits bearing Ag-NP's} \quad (5)$$

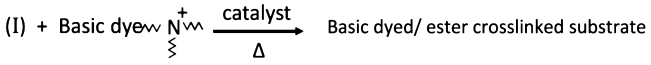
iii) Loading of ZnO-NP's/HBPAA onto the ester-crosslinked substrate (Ibrahim, Abdel-Rehiem, & El-Batal, 2010; Ibrahim, Fahmy, Abdel Rehim, Saraf, & Abo-Shosha, 2010; Ibrahim, Eid, et al., 2012; Ibrahim, Amr, et al., 2012; Ibrahim, Abou Elmaaty, et al., 2013)



(6)

$$CA + \text{ZnO} - \text{NP's/HBPAA} \xrightarrow[\Delta]{\text{catalyst}} \text{Crosslinked-entangled polymeric deposits bearing ZnO-NP's onto PET component} \quad (7)$$

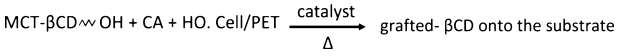
iv) Basic dyeing and ester-crosslinking (Ibrahim, Eid, et al., 2013; Martel, Weltroski, Ruffin, & Morcellet, 2002)



(8)

$$\text{PET component} + \text{Basic dye} \xrightarrow{\Delta} \text{Basic dyed PET component} \quad (9)$$

v) Fixation of βCD moieties onto the crosslinked substrate



(10)

$$\text{MCT} - \beta\text{CD} + CA \xrightarrow[\Delta]{\text{catalyst}} \beta\text{CD-loaded onto the PET component} \quad (11)$$

3.2. Type and concentration of the nano-composite

As far as the changes in the chemical and functional properties of the treated cellulosic/polyester blended fabrics as a function of type and concentration of the nanocomposite, the data in Table 1 signify that (i) increasing Ag-NP's/PVP nano-hybrid (particle size ≈11 nm) concentration up to 40 g/l brings about an increase in the N%, a slight decrease in the fabric resilience, expressed as WRA, a slight improve in the UPF values, along with an enhancement in the antibacterial activity, expressed as ZI values, regardless of the used substrate, (ii) the enhancement in the N% as well as the antibacterial activity is a direct consequence of enhancing the extent of fixation of the nominated Ag-NP's/PVP composite onto the cross-linked structure [Eqs. (1)–(4)], (iii) the slight decrease in the fabric resiliency is attributed to the decrease in the extent of cross-linking via side interactions between the cross-linker, CA, and the nano-composite [Eq. (5)], (iv) the slight improvement in the UPF values reflects the positive impact of the deposited polymeric material on coating the fabric surface and blocking its porous structure thereby decreasing the extent of UV-transformation and penetration (Ibrahim, Amr, et al., 2012), (v) the enhancement in the antibacterial activity of the Ag-NP's loaded substrates reflect their positive impact on damaging of the bacterial membrane and/or accelerating the generation of reacting oxygen species in the presence of dissolved oxygen as follows (Mahapatra & Karak, 2008; Ibrahim, Eid, et al., 2013; Jones & Hock, 2010)

$$H_2O + 1/2O_2 \xrightarrow{\text{Ag-NP's}} H_2O_2 \rightarrow H_2O + [O] \quad (12)$$

thereby causing oxidation of the molecular structure of bacteria, (vi) the antibacterial activity G+ve (*S. aureus*) and G−ve (*E. coli*) bacteria follows the decreasing order G+ve > G−ve, most probably due to their differences in the cell wall structure as well as amenability to disruption (Jones & Hock, 2010; Orhan, Kut, & Gunesoglu, 2009), and (vii) the extent of improvement in the

Table 1
Multifunctional finishing[a] of cellulosic/polyester blends using nano-hybrids.

Nano -hybrid Conc. (g/l)	Substrate	Ag-NP's/PVP					ZnO-NP's/HBPAA				
		N (%)[b]	WRA (W + F)[c]	UPF[d]	ZI (mm)[e]		*N* (%)[b]	WRA (W + F)[c]	UPF[d]	ZI (mm)[e]	
					G+ve	G−ve				G+ve	G−ve
0	Cotton/PET (35/65)	0.00	286	18	5.2	4.5	0.00	286	18	5.5	4.5
	Viscose/PET (30/70)	0.00	269	12	3.0	2.0	0.00	265	10	3.0	2.0
20	Cotton/PET (35/65)	0.232	275	25	9.0	7.5	0.405	280	42	11.0	10.0
	Viscose/PET (30/70)	0.201	250	20	7.5	6.0	0.353	255	32	9.0	7.0
40	Cotton/PET (35/65)	0.440	264	30 (20)	14.0 (11.0)	12.5 (9.5)	0.520	270	58 (45)	16.0 (13.0)	15.0 (12.0)
	Viscose/PET (30/70)	0.328	240	26 (16)	13.0 (10.0)	11.0 (8.5)	0.419	248	46 (36)	14.5 (11.5)	12.0 (10.0)

[a] Finishing formulation: citric acid (20 g/l); NaH_2PO_2 (10 g/l); nano- hybrid (0–40 g/l); nonionic wetting agent (2 g/l); wet pick up (80%); drying at 100° /3 min; curing at 170° /2 min.
[b] N: nitrogen content.
[c] WRA: wrinkle recovery angle (warp + weft).
[d] UPF: UV-protection factor.
[e] ZI: zone of inhibition; G + ve: *S. aureus*, G−ve: *E. coli* bacteria.
Values between parentheses correspond to the retained UPF and antibacterial after 15 laundering cycles.

aforementioned properties reflects the differences between the substrate in cellulose/polyester content, fabric weight, amorphous to crystalline area ratio, extent of cross-linking as well as extent of loading Ag-NP's onto the fabric surface (Ibrahim, E.L-Zairy, El-Zairy, & Khalil, 2011).

For a given set of finishing conditions, the data in Table 1 also demonstrate that incorporation of ZnO-NP's/HBPAA (particle size ≈34 nm) into the ester-crosslinking formulation up to 40 g/l along with other ingredients namely citric acid (20 g/l) and Na-hypophoshpite (10 g/l) brings about a noticeable increase in the *N*%, UPF values as well as antibacterial efficacy, ZI values, along with a slight decrease in the fabric resiliency, irrespective of the used substrate. The improvement in the above mentioned properties is a direct consequence of enhancing the extent of fixation of the nominated nanocomposites onto/within the fabrics structure as well as loading of the ZnO-NP's [Eqs. (6) and (7)]. The imparted anti-UV and antibacterial functional properties to the finished substrate reflects the positive effect of the loaded ZnO-NP's on enhancing the UV-blocking property due to their increased surface area together with intense absorption in the UV-region (Bringer & Hofer, 2004; Ibrahim, El-Zairy, et al., 2013d), as well as their ability to produce very powerful oxidizing and toxic species, such as superoxide anions, single oxygen and hydroxyl radicals, to organic compounds in the bacteria cell respectively (Ibrahim, Refaie, et al., 2010; Erem, Ozean, & Skrivars, 2011). Moreover, the abrasion effect of ZnO-NP's on the cell of bacteria and its effects on damaging the cell membrane, and facilitating the diffusion into the cell thereby leading to the death of bacteria can't be ruled out (Erem et al., 2011).

The extent of improvement in the *N*%, UPF as well as the antibacterial activity is governed by type of immobilized nanoparticles, i.e. ZnO-NP's/HBPAA > Ag-NP's/PVP, as well as of cellulosic/polyester blend, i.e. cotton/polyester > viscose/polyester, Keeping other parameters fixed.

Moreover, the given data reveal that the retention of the imparted functional properties, expressed as UPF and ZI values, was still high even after 15 laundering cycles, most probably due to their high extent of fixation and immobilization of the nominated nano-materials onto/within the finished substrates.

On the other hand, the SEM images and EDX spectra of Ag-NP's and ZnO-NP's-loaded substrates Fig. 1(a–d) and Fig. 1(e–h) respectively confirmed the loaded and the existence of both Ag and Zn elements on the obtained finished blends.

3.3. Combined basic dyeing and multifunctional finishing

As far as the changes in *N*%, WRA, *K*/*S*, UPF and ZI values as a function of basic blue 9 concentration, the obtained results in Table 2 disclose that: (i) incorporation of the dye into the finishing formulation up to 20 g/l results in an enhancement in the *N*%, *K*/*S*, UPF as well as the ZI, together with a decrease in the WRA values, irrespective of the used substrate, (ii) the enhancement in the above mentioned properties is a direct consequence of increasing the extent of dye fixation onto/within the crosslinked cotton/polyester and viscose/polyester fabric samples (Eqs. (8) and (9)) (iii) the remarkable improvement in the protection capacity against the harmful UV-B radiation, expressed as UPF, reflects the ability of dark shaded samples to absorb and/or block this kind of radiation (Ibrahim, El-Zairy, & Eid, 2010; Ibrahim, Eid, et al., 2013), (iv) the deep dyed fabric samples show better antibacterial activity, expressed as ZI values, as a direct consequence of enhancing the extent of dye fixation with its quaternary ammonium groups thereby facilitating the extent of attraction interactions between the cationic ammonium groups and the negatively charged cell membrane of the bacteria, which in turn causes the interruption of all essential functions of the cell membrane and thus the interruption of protein activity (Ibrahim, Eid, et al., 2010; Simoncic & Tomsic, 2010; Ma & Sun, 2005), (v)

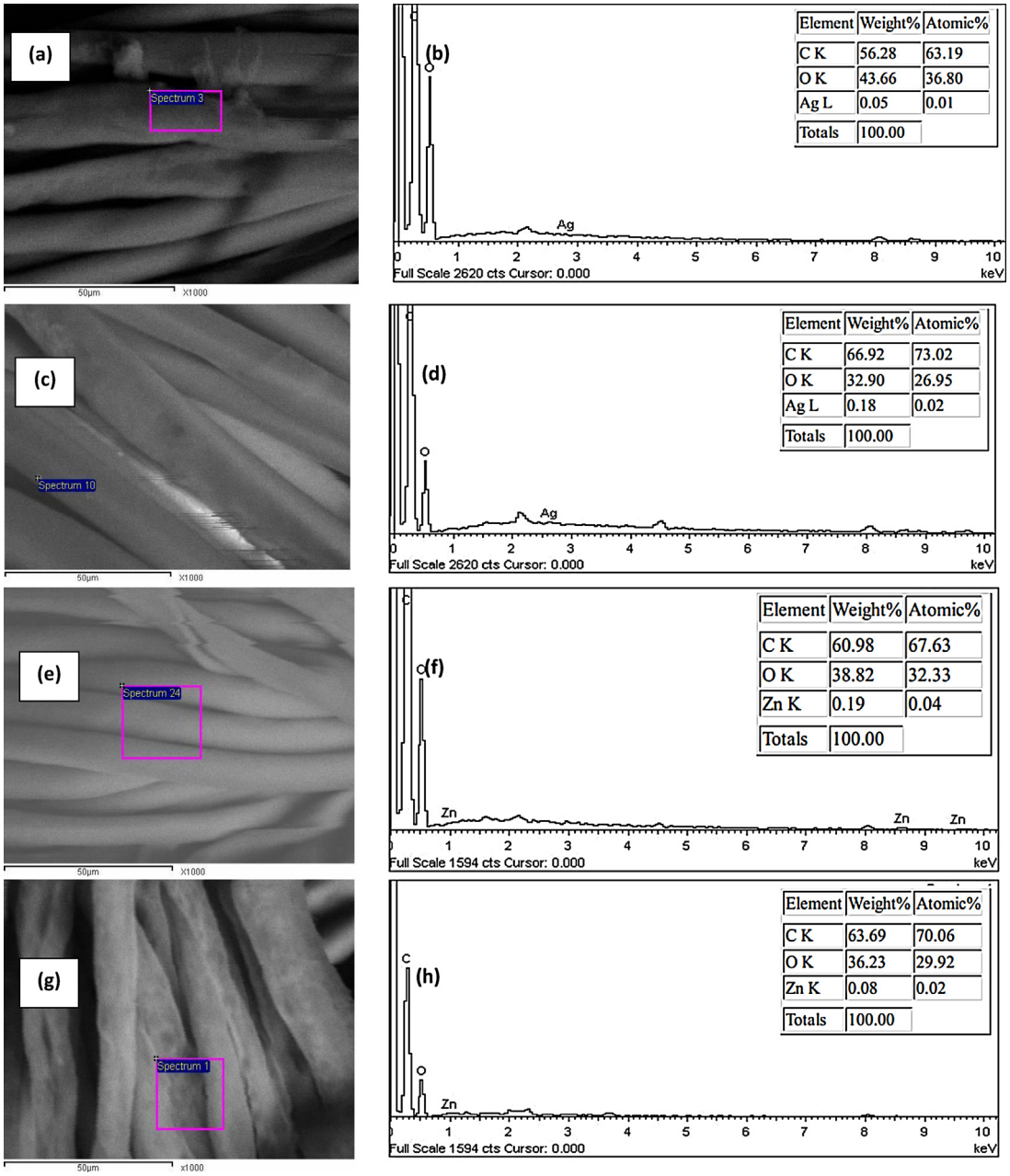


Fig. 1. SEM images and EDX spectra of: cotton/polyester loaded with AgNP's (a and b), viscose/polyester loaded with AgNP's (c and d), cotton/polyester loaded with ZnONP's (e and f), viscose/polyester loaded with ZnONP's (g and h).

the decrease in the WRA of the obtained dyeings reflects the negative impact of increasing the dye concentration up to 20 g/l on the extent of ester-crosslinking, (vi) the variation in the dyeing, easy care and the imparted functional properties is determined by the type of substrate, and (vii) the imparted inactivation efficiency against G+ve bacteria (*S. aureus*) was better than that of G−ve bacteria (*E. coli*).

3.4. Effect of treatment sequence

Table 3 demonstrates the variation in the performance and functional properties of the treated cellulosic/polyester blended fabrics as a function of treatment sequence. For a given set of treatment conditions, it is evident that: (i) post-treatment of the obtained basic dyeings with Ag-NP's/PVP or ZnO-NP's/HBPAA hybrid is accompanied by a slight increase in the *N*%, WRA and *K*/*S* values along with a reasonable improve in the imparted UV-blocking and anti-bacterial function properties, irrespective of the used substrate, (ii) the improvement in the abovementioned properties is a direct consequence of enhancing the extent of fixation of the nominated hybrid materials onto the simultaneously dyed/finished fabric samples as well as immobilization of Ag-NP's or ZnO-NP's thereby enhancing both the UPF and ZI values especially in case of using ZnO-NP's/HBPAA hybrid, (iii) the extent of enhancing both the UV-protection and antibacterial efficacy is governed by the sequence of treatment and follows the decreasing order: combined dyeing/finishing → Post-treatment with ZnO-NP's/HBPAA > combined dyeing/finishing → Post-treatment with Ag-NP's/PVP > combined dyeing/finishing ≫ untreated, which reflects the synergistic effect of post-treatment with the nominated hybrids and the precombined basic dyeing and easy care finishing step, and (iv) the

Table 2
Combined basic dyeing and multifunctional finishing[a] of cellulosic/polyester blends.

Basic Blue-9 dye Conc. (g/l)	Substrate	*N* (%)[b]	WRA (W + F)[c]	*K*/*S*[d]	UPF[e]	ZI (mm)[f]	
						G+ve	G−ve
0	Cotton/PET (35/65)	0.00	286	0.00	18	5.5	4.5
	Viscose/PET (30/70)	0.00	269	0.00	12	3.0	2.0
5	Cotton/PET (35/65)	0.095	279	7.05	49	8.0	6.0
	Viscose/PET (30/70)	0.072	260	6.51	32	7.0	5.5
10	Cotton/PET (35/65)	0.322	268	8.21	62	11.0	9.0
	Viscose/PET (30/70)	0.231	249	7.85	40	9.5	7.0
20	Cotton/PET (35/65)	0.520	255	10.22	79	15.0	13.5
	Viscose/PET (30/70)	0.472	238	9.55	52	13.5	12.0

[a] Finishing formulation: citric acid (20 g/l); NaH_2PO_2 (10 g/l); Methylene Blue dye (0–20 g/l); nonionic wetting agent (2 g/l); wet pick up (80%); drying at 100°/3 min; curing at 170°/2 min.
[b] N: nitrogen content.
[c] WRA: wrinkle recovery angle (warp + weft).
[d] *K*/*S*: colour strength.
[e] UPF: UV-protection factor.
[f] ZI: zone of inhibition; G+ve: *S. aureus*, G−ve: *E. coli* bacteria.

functionalized dyeings showed a better efficiency against G+ve bacteria in comparison with the G−ve one reflecting their difference in thickness of the cell wall.

Table 3 also clearly indicates that the finished substrates exhibited very sufficient functional properties even after 15 washing cycles

On the other hand Fig. 2(a–d) and (e–h) demonstrates the SEM and EDX spectra on the nominated substrates and confirm the deposition of both Ag-NP's and ZnO-NP's onto the basic dyed substrates

3.5. Grafting of fabric with βCD for antibacterial finishing

As far as the change in the *N*%, WRA as well as the antibacterial activity values (Table 4) as a function of grafting MCT-βCD onto the nominated substrates using citric acid as a cross-linking agent followed by subsequent treatment with Neem seed oil, Lavender oil or 4-hydroxybenzophenone, the obtained results demonstrate that: (i) incorporation of the MCT-βCD (10 g/l) along with the citric acid (20 g/l) and Na-hypophosphite as a catalyst (10 g/l), followed by padding, drying and curing results in a significant increase in the *N*% as well as a slight decrease in the WRA values of the treated substrates, (ii) this enhancement in *N*% is a direct consequence of grafting of MCT-βCD onto cellulosic/polyester blends [Eq. (10)], (iii) the slight decrease in the WRA values reflects the side interaction between the citric acid and the MCT-βCD [Eq. (11)] and/or the formation of intra crosslinks among the —OH groups of cellulose, the citric acid and the —OH groups of MCT-βCD thereby decreasing the extent of inter crosslinking, i.e. lower WRA values (Ibrahim, El-Zairy, EL-Zairy, & Khalil, et al., 2010; Popescu, Muresan, & Grigorin, 2011; Voncina & Marechal, 2005), (iv) the negative impact of the formation of citric acid/MCT-βCD deposits on the resiliency of the grafted substrates cannot be ruled out; (v) the antibacterial effect of the grafted fabric samples reflects the biocidal effect of the triazinyl group in MCT-βCD (Amrit, Agrawal, & Warmoeskerken, 2011) and/or of the citric acid due to its lower pH thereby hindering the bacteria survive as well as its preserving property (Orhan et al., 2009), (vi) post-treatment of the βCD-loaded substrates with the nominated active ingredients, i.e. Neem oil, Lavender oil and 4-hydroxybenzophenone, results in a remarkable increase in the imparted antibacterial activity against both G+ve and G−ve as a direct consequence of the formation of an inclusion complex with guest active ingredients (Ibrahim, EL-Zairy, et al., 2013; Szejtli, 2003; Ibrahim and El-Zairy, 2009) as follows:

$$\underset{\text{substrate}}{\text{Substrate} - \beta\text{CD}} + \underset{\text{guest}}{\text{Active ingredient}} \rightleftharpoons \text{Substrate} - \beta\text{CD} - \text{Active ingredient} \quad (13)$$

Table 3
Effect of treatment sequence [a] on the performance and functional properties of cellulosic/polyester blends.

Substrate	Treatment sequence	*N* (%)[b]	WRA (W + F)[c]	*K*/*S*[d]	UPF[e]	ZI (mm)[f]	
						G+ve	G−ve
Cotton/PET (35/65)	Untreated	0.000	286	0.00	10	0.0	0.0
	Combined dyed/Finished substrate	0.520	255	10.22	79 (65)	15.0 (11.5)	13.5 (10.0)
	Post- treated with Ag-NP's/PVP	0.540	256	10.38	84 (68)	17.0 (13.5)	16.0 (12.5)
	Post- treated with ZnO-NP's/HBPAA	0.552	268	10.50	99 (80)	20.0 (16)	18.5 (14.5)
Viscose/PET (30/70)	untreated	0.000	269	0.00	8	0.0	0.0
	Combined dyed/Finished substrate	0.472	238	9.55	52 (43)	13.5 (10.5)	12.0 (9.5)
	Post-treated with Ag-NP's/PVP	0.495	248	9.72	60 (48)	15.5 (12.0)	14.0 (10.5)
	Post- treated with ZnO-NP's/HBPAA	0.515	259	10.03	80 (68)	17.5 (14.5)	16.0 (13.0)

[a] Treatment sequence: – Basic dyeing/ easy care finishing: citric acid (20 g/l); NaH_2PO_2 (10 g/l); Basic Blue-9 dye (20 g/l); nonionic wetting agent (2 g/l); wet pick up (80%); drying at 100°/3 min; curing at 170°/2 min. – Post-treatment: the dyed/finished fabric samples were post treated with nano-hybrid (20 g/l); wet pick up (80%); followed by thermofixation at 120°/3 min.
[b] N: nitrogen content.
[c] WRA: wrinkle recovery angle (warp + weft).
[d] K/S: colour strength.
[e] UPF: UV-protection factor.
[f] ZI: zone of inhibition; G + ve: *S. aureus*, G−ve: *E. coli* bacteria. Values between parentheses correspond to the retained UPF and antibacterial after 15 laundering cycles.

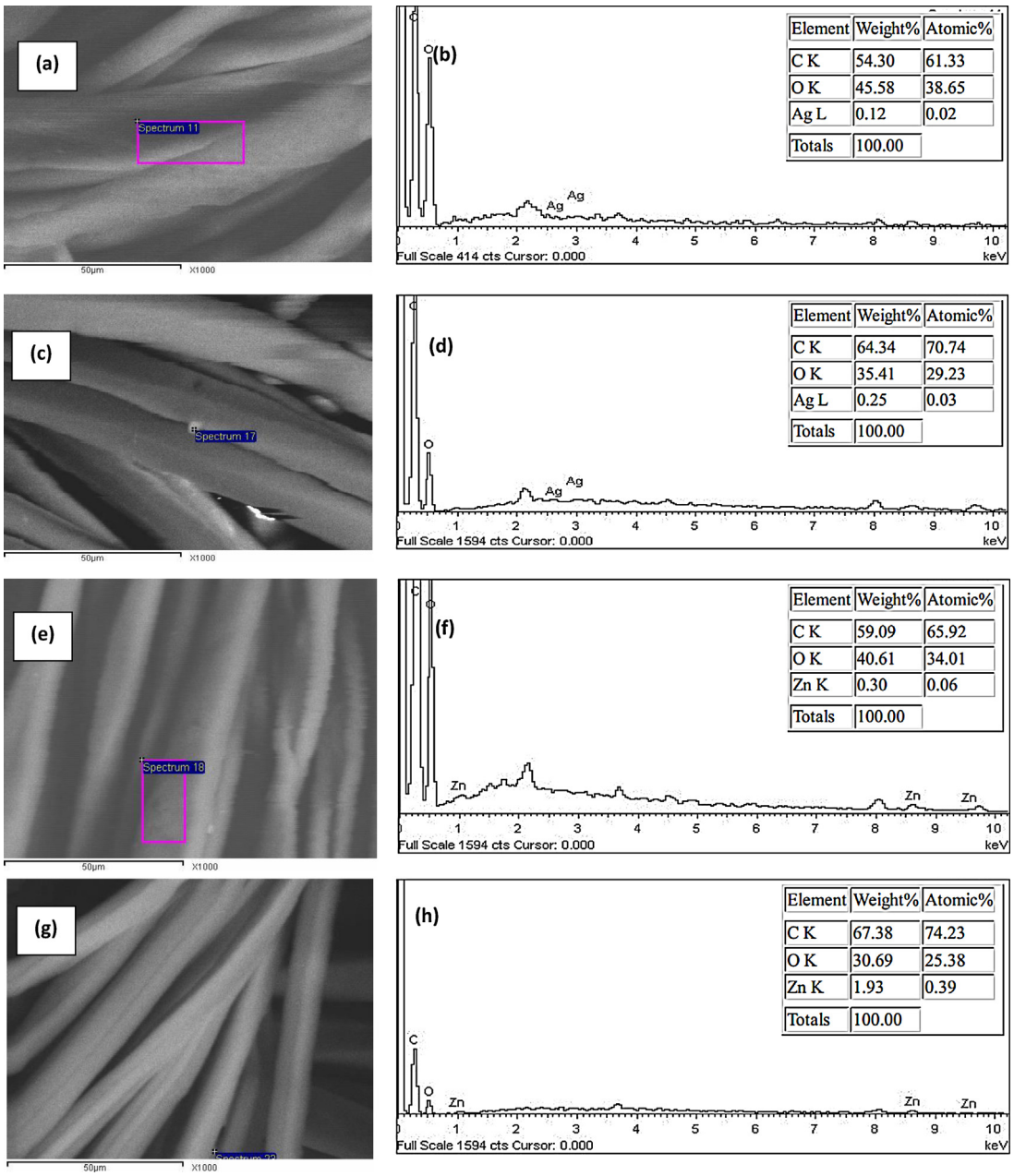


Fig. 2. SEM images and EDX spectra of: basic dyed cotton/polyester loaded with AgNP's (a and b), basic dyed viscose/polyester loaded with AgNP's (c and d), basic dyed cotton/polyester loaded with ZnONP's (e and f), basic dyed viscose/polyester loaded with ZnONP's (g and h).

Table 4
Effect of post-treatment[a] of crosslinked[b] cellulosic/polyester blends containing βCD moieties on their antibacterial properties.

Substrate	*N* (%)[c]	WRA (W + F)[d]	Antibacterial activity (ZI[e], mm)							
			Without post-treatment		Post-treatment with Neem oil		Post-treatment with Lavander		Post-treatment with Benzophenone	
			G+ve	G−ve	G+ve	G−ve	G+ve	G−ve	G+ve	G−ve
Cotton/PET (35/65)	0.522	278	7.0 (4.5)	6.0 (3.5)	18.0 (14.5)	16.5 (13.0)	21.0 (17.5)	18.5 (15.5)	23.0 (20.5)	21.0 (20.5)
Viscose/PET (30/70)	0.479	260	5.0 (3.0)	4.0 (2.5)	17.0 (13.5)	15.0 (12.0)	19.0 (16.0)	17.0 (14.0)	21.5 (19.5)	20.0 (16.5)

[a] Post-treatment: bio-active material (5% owf) in alcoholic solution; LR (20/1); at 30 °C/for 30 min followed by air drying.
[b] Crosslinking formulation: citric acid (20 g/l); NaH_2PO_2 (10 g/l); MCT- βCD (10 g/l); nonionic wetting agent (2 g/l); wet pick up (80%); drying at 100°/3 min; curing at 170°/2 min.
[c] N: nitrogen content.
[d] WRA: wrinkle recovery angle (W: warp, F: weft).
[e] ZI: zone of inhibition; G+ve: *S. aureus*, G−ve: *E. coli* bacteria.
Values between parentheses correspond to the retained UPF and antibacterial after 15 laundering cycles.
Properties of untreated cotton/PET are: %*N* = 0.00, WRA = 286, antibacterial activity against G+ve & G−ve bacteria = Zero.
Properties of untreated viscose/PET are: %*N* = 0.00, WRA = 269, antibacterial activity against G+ve & G−ve bacteria = Zero.

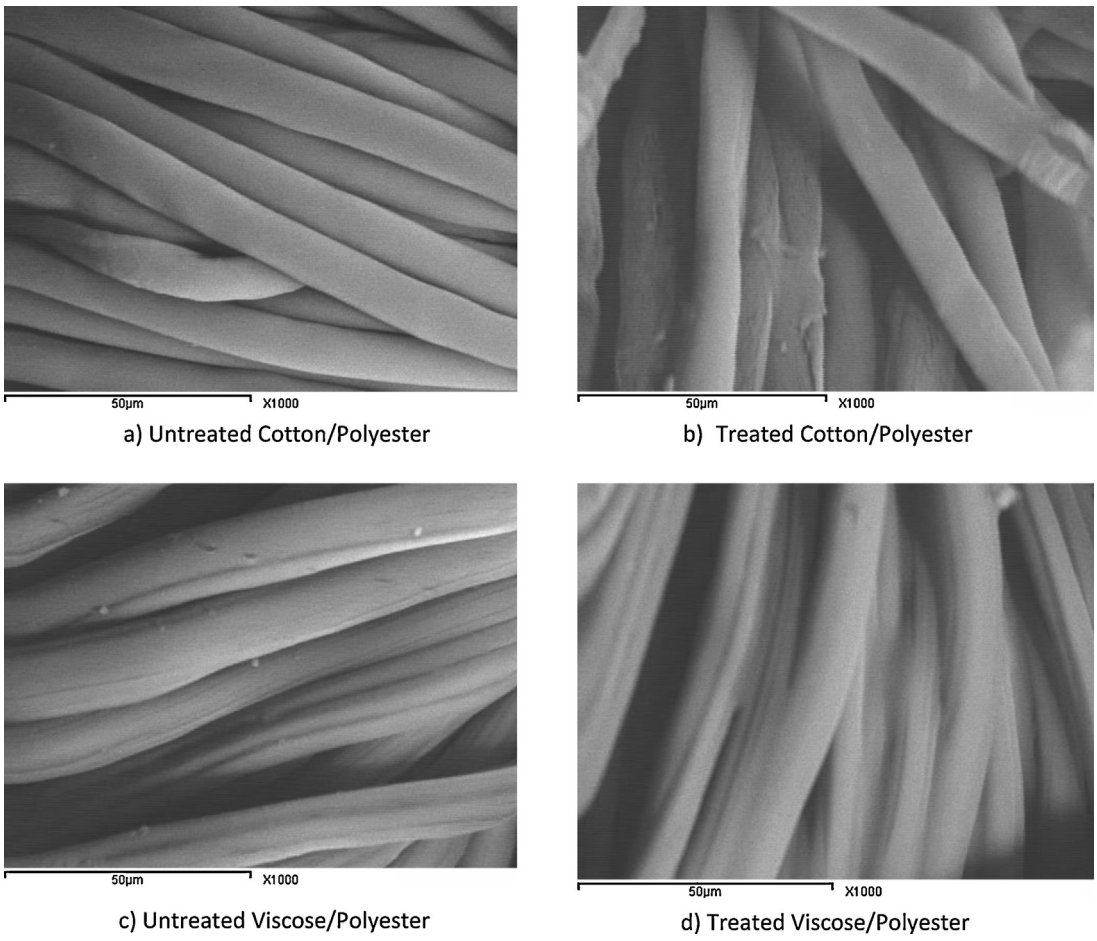


Fig. 3. SEM images of untreated and treated cotton/polyester (a&b), untreated and treated viscose/polyester (c& d). Treatment sequence: (i) crosslinking formulation: citric acid (20 g/l); NaH_2PO_2 (10 g/l); MCT-βCD (10 g/l); nonionic wetting agent (2 g/l); wet pick up (80%); drying at 100°/3 min; curing at 170°/2 min. (ii) Post-treatment with: Neem seed oil (5% owf) in alcoholic solution; LR (20/1); at 30 °C/for 30 min followed by air drying.

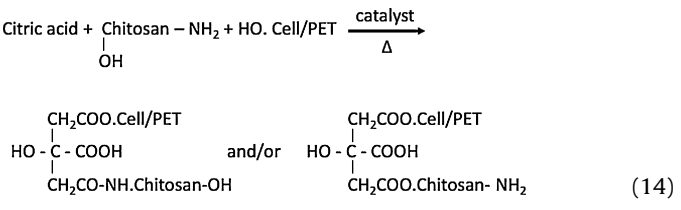
in the inner cavity of the loaded βCD thereby enhancing the extent of entrapping and retaining as well as controlling the release of the nominated active ingredients, (vii) the imparted antibacterial activity is governed by type of the active ingredient and follows the decreasing order: 4-hydroxybenzophenone > Lavander-oil > Neem-seed oil ≫ None > untreated, keeping other parameters constant, (viii) the variation in the imparted antibacterial activity of the loaded-active ingredients reflects the differences among them in chemical composition, active ingredients, mode of loading and releasing, (ix) the upgrading of the antibacterial activity of the Neem-loaded substrates is due to its bioactive components such as gedunin, azadirachtin, mahmoodin (Biswas, Chattopadhyay, Banerjee, & Bandyopadhyay, 2002), (x) the biological activity of Lavender oil is attributed to its active constituents such as linalool and its acetate and their positive impacts on inhibiting the synthesis of DNA, RNA, proteins and polysaccharides in bacterial cells (Kalemba & Kunicka, 2003), (xi) 4-hydroybenzophenone-loaded substrates showed the most powerful antibacterial activity among the utilized active ingredients which reflects the positive impact of exiting benzophenone chromophoric groups to the very active radical states on killing microorganisms (Hong & Sun, 2008), and (xii) the inactivation of G+ve bacteria was higher than that of G−ve bacteria, most probably attributed to the presence of outer cell wall membrane in the G−ve bacteria acts as a barrier.

The data in Table 4 also signify that the durability of the imparted antibacterial properties to wash, after 15 laundering cycles, was slightly decrease as a direct consequence of the removal of physically absorbed or unfixed active ingredients.

On the other hand the SEM images Fig. 3(a–d) illustrate the surface morphology of untreated Fig. 3(a and c) and treated substrates Fig. 3(b and d) with MCT-βCD in presence of citric acid as a crosslinking agent followed by post-treated with Neem oil. It can be obviously seen a thin layer homogeneously coated the treated substrates surfaces which indicate the existence of MCT-βCD along with Neem oil onto the surface of the treated substrates

3.6. *Effect of loading chitosan onto the blended substrates*

For a given set of finishing conditions and within the range examined, 0–5 g/l, Fig. 4a and b demonstrate that: (i) increasing the chitosan concentration up to 5 g/l brings about a significant increase in the *N*% (Fig. 4a) along with a gradual decrease in the WRA (Fig. 4b) regardless of the used substrate, (ii) the enhancement in the *N*% is attributed to the increase of the amount of loaded chitosan onto the treated substrates, with its primary amine and amine acetyl groups, according to the following tentative mechanism (Oktem, 2003; Ibrahim et al., 2005),



(14)

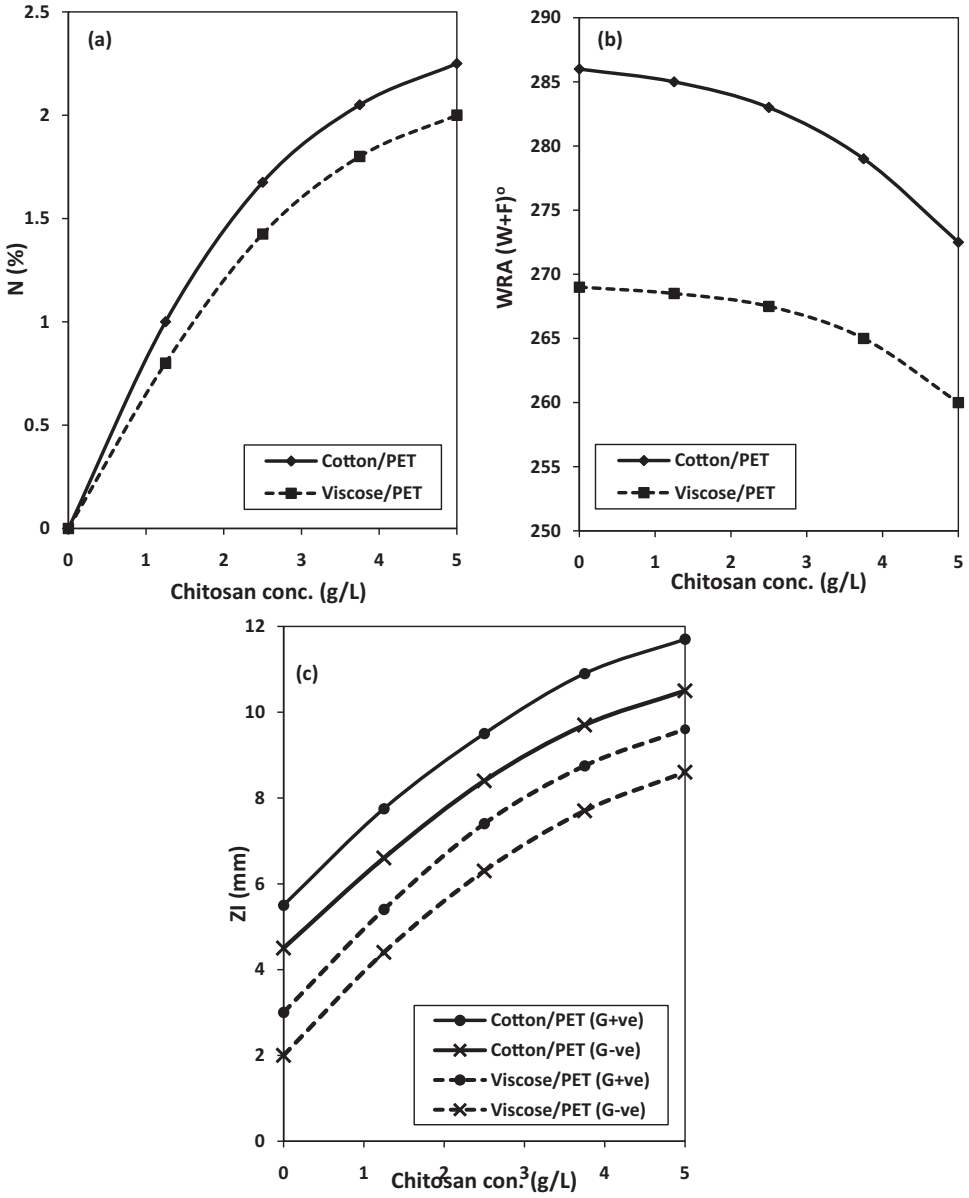
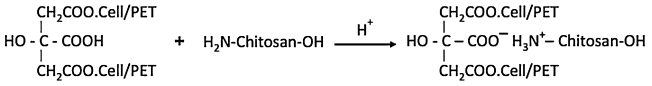


Fig. 4. Effect of chitosan concentration on %N (a), WRA (b) and ZI (c) of the finished substrate. Finishing formulation: citric acid (20 g/l); NaH_2PO_2 (10 g/l); chitosan (0–5 g/l); nonionic wetting agent (2 g/l); wet-pickup (80%); drying at 100 °C/3 min; curing at 170 °C/2 min.



(15)

$$\mathrm{HO-Cell/PET + H_2N-Chitosan-OH \xrightarrow{\triangle} loaded\ chitosan\ onto\ the\ substrate} \quad (16)$$

$$\mathrm{Citric\ acid + HO-Chitosan-NH_2 \xrightarrow[\triangle]{catalyst} crosslinked\ chitosan\ deposits} \quad (17)$$

and (iii) the decrease in the extent of ester-crosslinking, expressed as WRA values, is a direct consequence of side interactions among the chitosan, the cross-linking agent and the substrate [Eq. (14)] as well as the deposition of the cross-linked chitosan onto the fabric surface [Eq. (17)].

On the other hand, the increasing in chitosan concentration up to 5 g/l results in a gradual improvement in the imparted antibacterial activity (Fig. 4c). The improvement in the antibacterial efficacy of chitosan-loaded substrates is attributed to the polycationic nature of the chitosan thereby interfering with bacterial metabolism by stacking the cell's surface and/or via inhibition of mRNA synthesis by binding with DNA (Gao & Cranston, 2008; Zemljic, Strand, Sauper, & Kleinschek, 2009).

Moreover, the G+ve bacteria are more susceptible to the antibacterial effect of chitosan compared to the G−ve one. The variation in the antibacterial activity is determined by type of the substrate, i.e. chemical composition, blending ratio, amorphous to crystalline regions, the add-on of bio-active polymer, chitosan, location and extent of distribution onto the treated substrates and follows the descending order: cotton/polyester > viscose/polyester, keeping other parameters constant.

4. Conclusions

A combined easy care, antibacterial, and/or anti-UV protection finish is developed for upgrading the quality and functionality of cellulosic/polyester blended fabrics. From the present study the following conclusions can be made:

- Treatment of the used substrates using Ag-NP's/PVP or ZnO-NP's/HBPAA (40 g/l) along with citric acid (20 g/l) and Na-hypophosphite (10 g/l) followed by padding, drying and curing at 170 °C/2 min results in a significant improvement in the antibacterial or antibacterial/UV-protection properties respectively.
- Combined basic dyeing using basic blue 9 (20 g/l) along with other ingredients brings about a remarkable improvement in both the UPF and ZI values of the imparted functional properties.
- Post treatment of the obtained basic dyeings with the nominated hybrids causes further improvement in the imparted function properties.
- Incorporation of Neem seed-oil, Lavender-oil or 4-hydroxybenzophenone (5% owf) into the hydrophobic cavities of βCD-loaded substrates is accompanied by a noticeable increase in the imparted antibacterial activity against both G+ve and G−ve bacteria.
- Inclusion of chitosan (up to 5 g/1) into the finishing formulations enhances the antibacterial efficacy of the treated substrates.
- The extent of improvement in the imparted functional properties as well as the decrease in the easy care property of the finished substrates are governed by the type of substrate, type and amount of loaded active ingredients as well as treatment sequence.
- The imparted antibacterial properties against the G+ve (*S. aureus*) and G−ve (*E. coli*) bacteria follow the decreasing order: G+ve > G−ve regardless of the used finishing regime.
- After 15 washing cycles, the imparted functional properties are not seriously affected.
- SEM and EDX analysis confirm the surface modification of the selected samples as well as the presence of Ag or Zn elements onto it.

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