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Smart options for simultaneous functionalization and pigment coloration of cellulosic/wool blends

N.A. Ibrahim[a,*], H.M. Khalil[b], E.M.R. El-Zairy[b], W.A. Abdalla[b]

[a] Textile Research Division, National Research Centre, Cairo, Dokki, Egypt
[b] Faculty of Applied Arts, Printing, Dyeing and Finishing Department, Helwan University, Cairo, Egypt

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ABSTRACT

The present innovative research work deals with the individual use of chitosan (2.5 g/kg), Aloe vera (10 g/kg), triclosan (10 g/kg), TiO_2-nanoparticles (TiO_2-NP's, 10 g/kg), silicon micro-emulsion (20 g/kg) or a water/oil-repellent agent (40 g/kg) for modifying the pigment print paste to produce functionalized cotton/wool and viscose/wool pigment prints in one step process. The imparted functional properties such as antibacterial, antibacterial/UV-protection, soft-handle or water/oil-repellency together with the change in the printing properties were evaluated. Some of the obtained pigment prints were characterized by scanning electron microscope (SEM), and energy dispersive X-rays (EDX) to confirm deposition of certain functional additives on printed fabrics. The wide-range of imparted functional properties together with the depth of the obtained pigment prints were maintained over 80% even after 15 consecutive laundering cycles. The extent of retention in functional and pigment printing properties is influenced by the type of functional additive as well as the kind of substrate.

1. Introduction

It is well known that, the most important natural fibers are cellulosic and protein fibers. They have been extensively utilized, alone and in admixtures, as textile materials. Blending of cellulosic and protein fibers results in improving the performance and quality properties, developing new textile products, minimizing the production cost as well as enhancing the possibility of imparting new functional properties. The abundant hydroxyl groups on the hydro-glucose units of cellulose are responsible for its chemicals reactivity. On the other hand, wool is made up of different amino acids, and its main functional groups include carboxyl (–COOH), amino (–NH_2) and hydroxyl (–OH) groups; thus, the wool is chemically extremely active (Hsieh, 2007; Ibrahim, 2011; Lewis, 2011).

The use of pigment for textile printing has dramatically increased over the last 50 years, about 50% share, due to ease of application on various substrates, meet the demands of fastness properties, versatility as well as no need for after washing steps, i.e. energy and water conservation as well as a reduction in environmental impact. The main components of a pigment printing paste are pigment dispersion, binding agent, thickening agent, fixing agent and some auxiliaries, e.g. emulsifier, softener, defoamer, etc. taking in consideration the ecological concern (Giesen & Eisenlohr, 1994; Ibrahim, El-Zairy, Zaky, & Borham, 2005; Uddin & Lomas, 2005; Yaman, Ozdogan, & Seventekin, 2012).

In recent years, textile products with multi-functionality have gained interest to comply with the demands for high quality, comfort and healthy life styles. Functional properties, such as antibacterial, UV-protection, self-cleaning, water and oil-repellency, softness, anti-crease, and flame proofing, all have potential industrial applications (Bajaj, 2002; Gowri, Almeida, Amorim, Carneiro, Souto, & Esteves, 2010; Hebeish & Ibrahim, 2007; Holme, 2007; Ibrahim, Eid, & El-Batal, 2012; Ibrahim, Gouda, & Zairy, 2008; Ibrahim, Mahrous, El-Gamal, Gouda, & Husseiny, 2010; Ibrahim, Refai, & Ahmed, 2010a; Schindler & Hauser, 2004; Simoncic & Tomsic, 2010).

In our present study, we develop a novel one-step process for producing cellulosic/wool pigment prints with desirable and durable functional and printing properties via incorporation of certain functional finishing agents, at proper concentration, into the pigment printing pastes followed by screen printing and microwave curing. All modified pigment prints were monitored

* Corresponding author. Tel.: +20 1001913084; fax: +20 2 333 70931.
E-mail addresses: nabibrahim49@yahoo.co.uk, nabibrahim@hotmail.com (N.A. Ibrahim).

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for printability, fastness properties, functionality, and durability to wash. In addition, mode of interactions as well as surface modification of some printed fabric samples were also confirmed by SEM and EDX analysis.

2. Experimental

2.1. Materials

Mill-scoured and semi-bleached cotton/wool (50/50, 450 g/m^2) and viscose/wool (50/50, 340 g/m^2) blended fabrics were used.

Chitosan (degree of deacetylation > 82.9%, Sigma), Ciba® Oleophobol® Co. (oil, water and stain repellent agent based on dispersion of fluoropolymers containing extender, Ciba), Knittex® FEL cross-linking agent (reactant cross-linking agent based on a modified dimethylol dihydroxy ethyleneurea, Huntsman), Ultratex® MHT conc. (softening agent based on micro emulsion concentrate of a quaternary polydimethyl siloxane, Huntsman), Invasan® (antibacterial agent based on triclosan derivative, Huntsman), DAICO® Thick. 160 (synthetic thickener based on polyacrylate, Daico, Egypt), Pigment Red 146, Pigment Blue 153 and Pigment Orange 13 (Daico, Egypt), as well as Printofix® Binder MTB-01 liquid (binding agent based on acrylate copolymer, Clariant) were of commercial grade.

Aloe gel was extracted from Aloe vera plant, available in Egypt using methanol as a solvent (Jothi, 2009). All other chemicals used in this study such as ammonium persulphate [$(NH_4)_2S_2O_8$], and acetic acid were of laboratory reagent grade.

TiO_2-nanoparticles (TiO_2-NP's) were prepared as previously reported (Bozzi, Yuranova, & Kiwi, 2005) using titanium tetraisoproproxide precursor (Sigma) with 2-propanol and nitric acid.

2.2. Methods

2.2.1. Functional finishing and pigment printing

Simultaneous functionalization and pigment printing of the nominated cellulosic/wool blends were carried out using the flat screen technique and the following print paste formulations:

Content	g/kg paste
Pigment	20
Binder	100
Thickener	20
Functional additives	
Silicon-softener	10–30
Chitosan	2.5–10
Water and oil repellent	20–60
TiO_2-NP's	5–20
Invasan®	5–20
Aloe vera	5–20
H_2O	X
Total	1000

Printed fabric samples were then simultaneously dried and fixed in a commercial microwave oven at output of 1300 W/4 min.

2.2.2. Measurements

The depth of the obtained prints, expressed as K/S values, were determined from the reflectance measurements using the Kubelka Munk equation (Judd & Wyszeck, 1975): $K/S = (1 - R)^2/2R$, where K/S is the ratio of absorption and scattering coefficient, and R is the reflectance at the wave length of maximum absorbance of the used pigment colorants.

Fastness properties to washing, rubbing and light were assessed according to AATCC Test Methods: (61-1972), (8-1972), and (16A-1972) respectively.

Antibacterial activity assessment against G +ve bacteria (*Staphylococcus aureus*) and G −ve bacteria (*Escherichia coli*) was evaluated qualitatively according to AATCC test method (147-1988) and expressed as zone of growth inhibition (ZI, mm).

UV-protection factor (UPF) was evaluated according to AS/NZS 4399-1996 standard. According to the Australian classification scheme, fabrics can be rated as providing good, very good, or excellent protection if their UPF values range from 15 to 24, 25 to 39, or above 40 respectively.

Stiffness of the treated and untreated samples was evaluated according to AATCC Test Method (D 1388-96).

Surface roughness of the treated and untreated samples was evaluated according to JIS 94 Standard, using surface roughness measuring instrument, SE 1700α (Japan).

Water and oil repellency were evaluated according to AATCC Test Method 22-1989.

Scanning electron microscope (SEM) images of some selected samples were obtained with a JEOL, JXA-840A electron probe micro-analyzer, equipped with energy disperse X-ray spectroscopy (EDX) for the composition analysis.

Durability to washing was evaluated for some selected samples according to ASTM Standard Method (D 737-96).

3. Results and discussion

Factors affecting the imparted functional properties and pigment printing properties of cotton/wool and viscose/wool blended fabrics brought about by individual incorporation of certain functional finishing agents, namely chitosan, Aloe vera, triclosan derivative, TiO_2-NP's, silicon softener and water-oil repellent into the pigment paste formulation, using different pigment colorants, followed by screen printing and microwave curing were thoroughly investigated. Discussion of the obtained results follows.

3.1. Type and concentration of functional finishing agent

Fig. 1a shows the influence of chitosan concentration on the extent of pigment coloration, expressed as K/S value. For a given set of printing paste formulation and curing conditions, it is clear that increasing chitosan concentration up to 2.5 g/kg paste results in a remarkable improvement in the depth of obtained pigment prints, regardless of the used substrate. This improvement in K/S values is a direct consequence of enhancing the extent of encapsulation, fixation and adhesion of the dispersed pigment particles, which have no affinity for any fiber, onto the substrate via enhancing the film forming properties and providing an extra active sites, i.e. –NH_2 and –OH groups, for cross-linking and pigment particles accommodation (Giesen & Eisenlohr, 1994; Ibrahim et al., 2005; Ibrahim, El-Zairy, El-Zairy, & Khalil, 2010; Yaman et al., 2012). Further increase in the chitosan concentration, beyond 2.5 g/kg, is accompanied by a gradual decrease in the depth of the obtained prints most probably due to the gradual increase in the pigment print paste viscosity as well as a reduction in paste uptake/binder film formation and subsequent pigment entrapment during the microwave curing step. On the other hand, the extent of pigment fixation follows the decreasing order cotton/wool > viscose/wool reflects the differences between them in fabric structure, weight, porosity, thickeners, morphology, amount and availability of the chemical groups of the substrate components, which influence the extent of fixation and adhesion strength of the binder-to-fiber, as well as extent of undue penetration of dispersed pigment particles (Ibrahim, Abdalla, El-Zairy, & Khalil, 2013; Ibrahim, El-Zairy, Abdalla, & Khalil, 2013).

Fig. 1b shows that increasing Aloe vera gel, a naturally occurring biopolymer, concentration up to 10 g/kg pigment paste is

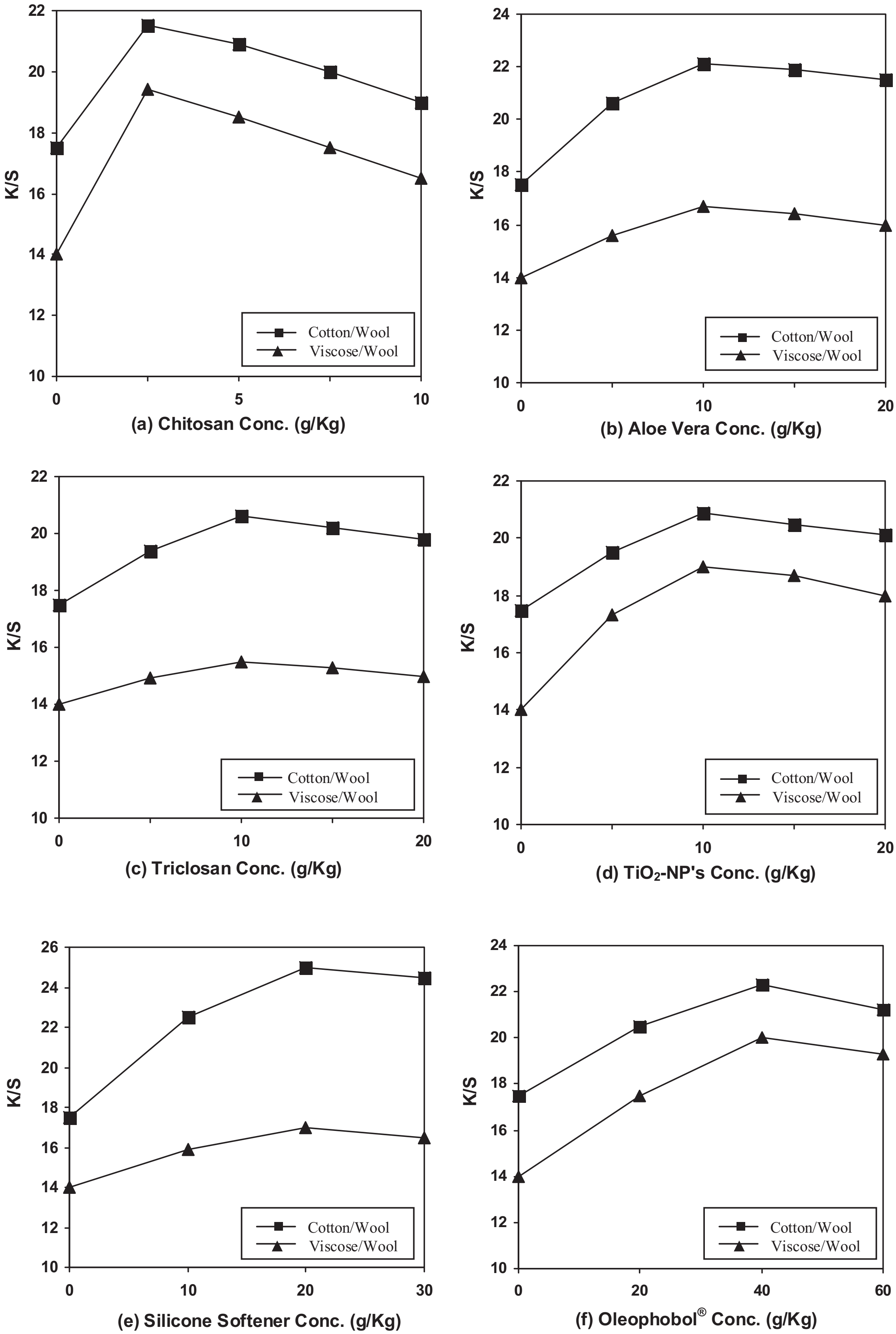

Fig. 1. Effect of chitosan (a), Aloe vera (b), triclosan (c), TiO_2-NP's (d), silicone softener (e), and Oleophobol® (f) concentration on the depth of the obtained prints. Printing paste components: Pigment Red 146(20 g/kg); synthetic thickener(20 g/kg); Printofix®Binder – MTB (100 g/kg); cross-linker (10 g/kg); and $(NH_4)_2S_2O_8$ (2 g/kg). Microwave fixation: 1300 W/4 min.

accompanied by a noticeable increase in the *K*/*S* values of the obtained pigment prints irrespective of the used substrate. The enhancement in the *K*/*S* value is determined by type of substrate: cotton/wool (*K*/*S* = 22.0) > viscose/wool (*K*/*S* = 16.63). This remarkable increase in the *K*/*S* values most probably reflects the positive impacts of potentially active chemical constituents of Aloe vera gel such as carbohydrates, anthraquinones, organic compounds and lipids, proteins, enzymes and amino acids along with their active groups, e.g. –OH, –COOH, –NH_2 groups (Hamman, 2008; Moghaddasi & Verma, 2011), on enhancing the extent of formation of flexible three dimension binder film that encapsulates and entraps pigment particles and adheres them to fabric surfaces during microwave fixation step with a consequent darker depth of shades. Further increase in Aloe vera gel concentration up to 20 g/kg is followed by a slight decrease in the fixation of the pigment particles, regardless of the used cellulosic/wool blended substrate.

Fig. 1c illustrates the effect of incorporating triclosan derivative, at different concentration (0–20 g/kg pigment paste) in the printing paste on the *K*/*S* values of the obtained pigment prints. Within the range examined the so-obtained results indicate that increasing triclosan concentration up to 10 g/kg results in increasing the *K*/*S* value of the cotton/wool prints from 17.48 up to 20.52 and viscose/wool prints from 14.02 up to 15.52. This can be discussed in terms of better encapsulation, binding and fixation of pigment particles onto the fabrics surface via the cross-linked binder film. Further increase in triclosan derivative concentration results in a slight decrease in the depth of the obtained prints; i.e. less extent of pigment fixation.

As far as the changes in the *K*/*S* values of the obtained pigment prints as a function of the TiO_2-NP's concentration, Fig. 1d shows that the maximum values of *K*/*S* (20.92 and 19.00) for cotton/wool and viscose/wool respectively, attained at a TiO_2-NP's concentration 10 g/kg pigment paste. It may be due to the positive role of TiO_2-NP's, as a co-catalyst, in enhancing the extent of cross-linking of the binder film thereby improving the performance of capturing and entrapping pigment particles with subsequent adhesion to and fixation onto the fabrics surface (Ibrahim, Refai, et al., 2010; Nazari, Montazer, & Rahimi, 2009; Nazari, Montazer, Rashidi, Yazdanshenas, & Abbasinejad, 2009; Wang & Chen, 2005). Further increase in TiO_2-NP's, beyond 10 g/kg, has a slight negative impact on the depth of the obtained prints as manifested by a decrease in the *K*/*S* values irrespective of the used substrate.

On the other hand, Fig. 1e shows that inclusion of the quaternary polydimethyl siloxane softener Ultratex® HMT up to 20 g/kg, into the pigment printing paste along with other ingredients is accompanied by a significant increase in *K*/*S* value of the printed cellulosic/wool substrates, most probably due to the better accommodation and fixation of the pigment particles within the binder and/or the softener film onto the printed fabrics surface (Ibrahim et al., 2005; Schindler & Hauser, 2004). Further increase in the softener film has practically no significant effect.

Moreover, Fig. 1f shows the effect of the used water/oil repellent agent, Ciba® Oleophobol, concentration on the *K*/*S* values of the obtained pigment prints. It is clear that depth of the printed fabric samples is gradually increased as the water/oil repellent concentration increase up to 40 g/kg then decreases slightly. This enhancement in *K*/*S* values could be discussed in terms of the formation of water/oil repellent polymer film alone or in combination with other components, i.e. binder and cross-linker, during the microwave curing step, thereby increasing the extent of fixation of pigment particles onto the coated fabric surface (Ibrahim, Amr, Eid, & El Sayed, 2010; Schindler & Hauser, 2004). Further increase in the water/oil repellent agent results in a marginal decrease in the depth of the obtained prints.

Based on the aforementioned studies, incorporation of chitosan (2.5 g/kg), Aloe vera gel (10 g/kg), triclosan derivative (10 g/kg), TiO_2-NP's (10 g/kg), silicone softener (20 g/kg), or the water–oil repellent agent (40 g/kg) into the pigment printing paste formulation followed by screen printing and microwave fixation at 1300 W/4 min seems to be a proper concentration for obtaining the higher depth of the obtained pigment prints, keeping other parameters constant.

3.2. Combined functional finishing and pigment printing in one step

Results of the foregoing section made it possible to obtain pigment prints with darker depth of shade along with expected functional properties by including the nominated functional additives, at the proper concentrations, into the print paste. With this in mind, systematic study was carried out to investigate the impact of using the nominated additives along with different pigment colorants on the functional and printing properties of the simultaneously finished and printed cellulosic/wool fabrics.

3.2.1. Antimicrobial finishing/pigment printing

The antimicrobial and pigment properties of printed cotton/wool and viscose/wool blended fabrics in the absence and presence of chitosan (2.5 g/kg), Aloe vera (10 g/kg) or triclosan derivatives (10 g/kg) were assessed and presented in Table 1. For a given set of printing conditions, the data in Table 1 signify that: (i) incorporation of any of the nominated active ingredients into the printing paste results in a remarkable improvement in the antibacterial activity, expressed as ZI value, against the G +ve (*S. aureus*) and G −ve (*E. coli*) bacteria, (ii) the extent of improvement in the imparted antimicrobial properties is governed by the type of functional additive: chitosan > Aloe vera > triclosan ≫ none, kind of substrate: cotton/wool > viscose/wool, as well as pigment colorant: Pigment Orange 13 > Pigment Red 146 > Pigment Blue 153, keeping other parameters fixed, (iii) the variation in the antibacterial activity of the obtained pigment prints using chitosan, Aloe vera or triclosan could be discussed in terms of the differences among them in: chemical structure, active ingredients, i.e. amino groups in chitosan, antiseptic agent (lupeol, salicylic acid, urea nitrogen, cinnamonic acid, phenols and sulfur) in Aloe vera or a chlorinated bis-phenols as in case of triclosan (Ibrahim, El-Zairy, et al., 2010; Moghaddasi & Verma, 2011; Orhan, Kut, & Gunesoglu, 2007; Zemljic, Strand, Sauperl, & Kleinschek, 2009), compatibility with other ingredients in the printing paste, extent of fixation and loading onto the printed fabric surface as well as, (iv) the difference in mode of antibacterial action, i.e. by interfering with bacterial metabolism and/or binding with DNA to inhibit mRNA synthesis due to the polycationic nature of chitosan especially in acidic medium (Kong, Chen, Xing, & Park, 2010; Zitao, Chen, Jinmin, Yanliu, & Donghui, 2003), via an electrochemical mode of action of penetrate and disrupt the cell walls of bacterial as in case of using Aloe vera thereby preventing the bacteria from functioning or reproducing (Jothi, 2009; Sarkar, Purushottam, & Chanuhan, 2003), or by inhibiting fatty acid biosynthesis through the blocking of lipid bio-synthesis as in case of using triclosan derivative (Ibrahim, Abdalla, et al., 2013; Ibrahim, El-Zairy, et al., 2013; Ibrahim, Hashem, El-Sayed, El-Husseiny, & Elanany, 2010; Orhan, Kut, & Gunesoglu, 2009).

On the other hand, incorporation of chitosan, Aloe vera or triclosan derivative into the pigment printing paste is accompanied by an improvement in both the depth of the obtained prints along with their fastness properties, regardless of the used pigment colorant. This improvement in printing properties, i.e. *K*/*S* and fastness properties reflects the positive role of the aforementioned functional additives in enhancing the extent of fixation and

Table 1
Antibacterial/printing properties of printed cellulosic/wool blended fabrics using different pigment colorants along with antimicrobial additives in the printing paste.[a]

Pigment	Substrate	Additive	ZI[b] (mm)		K/S[c]	WF[d]		RF[e]		LF[f]
			G +ve	G −ve		Alt	St.	Dry	Wet	
Pigment Red 146	Cotton/wool	Chitosan	22.0 (00.0)	20.0 (00.0)	21.61 (17.48)	4–5(4)	4–5(4)	4–5(4)	4(3–4)	4–5(3–4)
		Aloe vera	19.5	17	22	5	5	5	5	5
		Triclosan	15.5	13	20.52	5	5	5	5	5
	Viscose/wool	Chitosan	19.0 (00.0)	18.0 (00.0)	19.43 (14.02)	4(3–4)	4(3–4)	4(3–4)	4(3)	4(3)
		Aloe vera	16	14.5	16.63	5	5	5	4	4
		Triclosan	13.5	11.5	15.52	5	5	5	4	4
Pigment Blue 153	Cotton/wool	Chitosan	21.0 (00.0)	18.0 (00.0)	13.22 (11.60)	4–5(4)	4–5(3–4)	4–5(3)	4(3)	4–5(4)
		Aloe vera	18	16	16.39	5	5	5	4	5
		Triclosan	14	12	14.78	5	5	4	4	5
	Viscose/wool	Chitosan	18.0 (00.0)	16.0 (00.0)	12.52 (11.25)	4–5(4)	4–5(3–4)	4–5(3)	4(3)	4–5(4)
		Aloe vera	14	13	15.55	5	5	5	4	5
		Triclosan	12	10	13.34	5	5	4	4	5
Pigment Orange 13	Cotton/wool	Chitosan	24.0 (00.0)	22.0 (00.0)	8.61 (6.75)	5(4)	4–5(4)	4–5(4)	4(3–4)	5(4)
		Aloe vera	20.5	19	10.35	5	5	5	5	5
		Triclosan	18	16	9.93	5	5	5	5	5
	Viscose/wool	Chitosan	20.5 (00.0)	18.5 (00.0)	8.31 (6.24)	4–5(3)	4(3)	4(3)	4(3)	4(3–4)
		Aloe vera	16.5	15	10.03	4	4	4	4	4
		Triclosan	14.5	12.5	9.52	4	4	5	5	4

Values in parenthesis are the values of the pigment prints in the absence of the aforementioned additives.

[a] Printing paste components: pigment colorant (20 g/kg); synthetic thickener (20 g/kg); binder (100 g/kg); cross-linker (10 g/kg); catalyst (2 g/kg) in the absence and presence of chitosan (2.5 g/kg), Aloe vera (10 g/kg) or triclosan (10 g/kg). Microwave fixation at 1300 W/4 min.

[b] ZI: zone of inhibition.

[c] K/S: color strength.

[d] WF: wash fastness; Alt: alteration; St.: staining on cotton.

[e] RF: rubbing fastness.

[f] LF: light fastness.

Table 2
Antibacterial/UV-protecting and printing properties of printed cellulosic/wool blended fabrics using different pigment colorants along with TiO_2-NP's in the printing paste.[a]

Pigment	Substrate	TiO_2-NP's(10 g/kg)	ZI[b] (mm)		UPF[c]	K/S[d]	WF[e]		RF[f]		LF[g]
			G +ve	G −ve			Alt	St.	Dry	Wet	
Pigment	Cotton/wool	Without	0	0	63	17.48	4	4	4	3–4	3–4
Red		With	16	15	80	20.91	5	5	5	4	4
146	Viscose/wool	Without	0	0	74	14.02	4	4	4	3	3
		With	13	11.5	99	19.03	5	5	4	4	4
Pigment	Cotton/wool	Without	0	0	60	11.6	4	4	3	3	4
Blue		With	23	20	76	13.89	5	5	5	4	5
153	Viscose/wool	Without	0	0	85	11.25	4	4	3	3	4
		With	18	17	118	13.4	5	5	5	4	5
Pigment	Cotton/wool	Without	0	0	81	6.75	4	4	4	3–4	4
Orange		With	21	18	95	9.87	5	5	5	4	5
13	Viscose/wool	Without	0	0	98	6.24	3	3	3	3	3–4
		With	15	13	137	8.98	4	4	4	4	4

[a] Printing paste components: pigment colorant (20 g/kg); synthetic thickener (20 g/kg); binder (100 g/kg); cross-linker (10 g/kg); catalyst (2 g/kg) in the absence and presence of TiO2-NP's (10 g/kg). Microwave fixation at 1300 W/4 min.
[b] ZI: zone of inhibition.
[c] UPF: ultraviolet protection factor.
[d] K/S: color strength.
[e] WF: wash fastness; Alt: alteration; St.: staining on cotton.
[f] RF: rubbing fastness.
[g] LF: light fastness.

accommodation of extra pigment particles within the cross-linked network formed onto the fabric surface during the microwave fixation step. Moreover, the variation in the printing properties upon using the aforementioned additives may be attributed to their differences in chemical structure, functional groups, extent of fixation and interaction among other ingredients during the fixation step as well as the differences among the used pigments in particle size, chemical composition, location and extant of distribution, color, hue as well as subsequent immobilization onto the fabric surface (Ibrahim et al., 2005; Uddin & Lomas, 2005; Yaman et al., 2012).

Furthermore, the imparted antibacterial properties as well as the extant of pigment printing, in general, depend on the fabric structure, its functional groups, availability and accessibility of its active sites, mode of interaction and extent of modification, as well as location and extent of distribution of the formed film incorporating different ingredients, especially the antibacterial pendant groups and the pigment particles.

Table 1 also clearly indicates that the effectiveness against the most common causes of bacterial infection, i.e. *E. coli* and *S. aureus* bacteria, follows the decreasing order G +ve > G −ve, irrespective of the used functional additive. This reflects the differences between the nominated bacteria in cell wall structure, sensitivity to disruption and/or in response to inactivation (Gouda & Ibrahim, 2008; Gupta, Bajpai, & Bajpai, 2008).

3.2.2. *Antibacterial/anti-UV/pigment printing*

To evaluate the dual role of TiO_2-NP's as antibacterial and anti-UV agent, TiO_2-NP's (10 g/kg) were included into the pigment printing paste followed by screen printing and microwave fixation. The data in Table 2 indicate that incorporate of TiO_2-NP's into the printing paste results in (i) a remarkable improvement in the antibacterial activity, expressed as ZI values, as well as in the UV-protecting properties, expressed as UPF values, of the printed fabric samples, (ii) an improvement in both the depth of the obtained pigment prints along with their fastness properties, regardless of

Table 3
Softness and printing properties of printed cellulosic/wool blended fabrics using different pigment colorants along with silicone softener in the printing paste.[a]

Pigment	Substrate	Silicon softener (20 g/kg)	Surface roughness (mm)	Stiffness	K/S[b]	WF[c]		RF[d]		LF[e]
						Alt	St.	Dry	Wet	
Pigment	Cotton/wool	Without	29.05	3833	17.48	4	4	4	4	4
Red		With	15.96	1340	25.02	5	5	5	5	5
146	Viscose/wool	Without	22.54	2519	14.02	4	4	4	3	3
		With	13.41	1114	16.9	4	4	4	4	5
Pigment	Cotton/wool	Without	26.95	4100	11.6	4	4	3	3	4
Blue		With	14.98	1768	17.64	5	4	5	4	5
153	Viscose/wool	Without	23.11	1866	11.25	4	4	3	3	4
		With	14.03	1458	15.81	5	5	4	4	5
Pigment	Cotton/wool	Without	25.49	2880	6.75	4	4	4	3–4	4
Orange		With	14.1	2099	9.47	5	5	5	5	5
13	Viscose/wool	Without	21.68	2548	6.24	3	3	3	3	3–4
		With	13.25	1865	9.06	4	4	4	4	4

[a] Printing paste components: pigment colorant (20 g/kg); synthetic thickener (20 g/kg); binder (100 g/kg); cross-linker (10 g/kg); catalyst (2 g/kg) in the absence and presence of silicon softener (20/kg). Microwave fixation at 1300 W/4 min.
[b] K/S: color strength.
[c] WF: wash fastness; Alt: alteration; St.: staining on cotton.
[d] RF: rubbing fastness.
[e] LF: light.

Table 4
Water/oil repellency and printing properties of printed cellulosic/wool blended fabrics using different pigment colorants along with the water/oil repellent agent in the printing paste.[a]

Pigment	Substrate	Water/oil repellent (40 g/kg)	Repellency rating		Surface roughness (mm)	K/S[b]	WF[c]		RF[d]		LF[e]
			Water	Oil			Alt	St.	Dry	Wet	
Pigment Red 146	Cotton/wool	Without	0	0	29.05	17.48	4	4	4	3–4	3–4
		With	80	7	20.19	22.38	5	5	5	5	4
	Viscose/wool	Without	0	0	22.54	14.02	4	4	4	3	3
		With	70	5	16.85	20.03	5	5	4	4	4
Pigment Blue 153	Cotton/wool	Without	0	0	26.95	11.6	4	4	3	3	4
		With	80	7	20.58	13.75	5	5	4	4	5
	Viscose/wool	Without	0	0	23.11	11.25	4	4	3	3	4
		With	70	5	18.54	13.44	5	5	4	4	5
Pigment Orange 13	Cotton/wool	Without	0	0	25.49	6.75	4	4	4	3–4	4
		With	80	7	18.34	9.69	5	5	5	5	5
	Viscose/wool	Without	0	0	21.68	6.24	3	3	3	3	3–4
		With	70	5	16.3	9.4	4	4	4	4	4

[a] Printing paste components: pigment colorant (20 g/kg); synthetic thickener (20 g/kg); binder (100 g/kg); cross-linker (10 g/kg); catalyst (2 g/kg) in the absence and presence of the water/oil repellent agent (40/kg). Microwave fixation at 1300 W/4 min.
[b] K/S: color strength.
[c] WF: wash fastness; Alt: alteration; St.: staining on cotton.
[d] RF: rubbing fastness.
[e] LF: light fastness.

the used pigment colorant, (iii) the enhancement in the imparted antibacterial functional property as well as the printing properties is determined by the type of substrate and follows the decreasing order: cotton/wool > viscose/wool, keeping other parameters constant and (iv) the change in the pigment printing properties is governed by the type of pigment colorant as mentioned before.

The imparted multifunctional properties, anti-bacterial/anti-UV, reflects the dual role of loaded TiO_2-NP's in (i) generation of

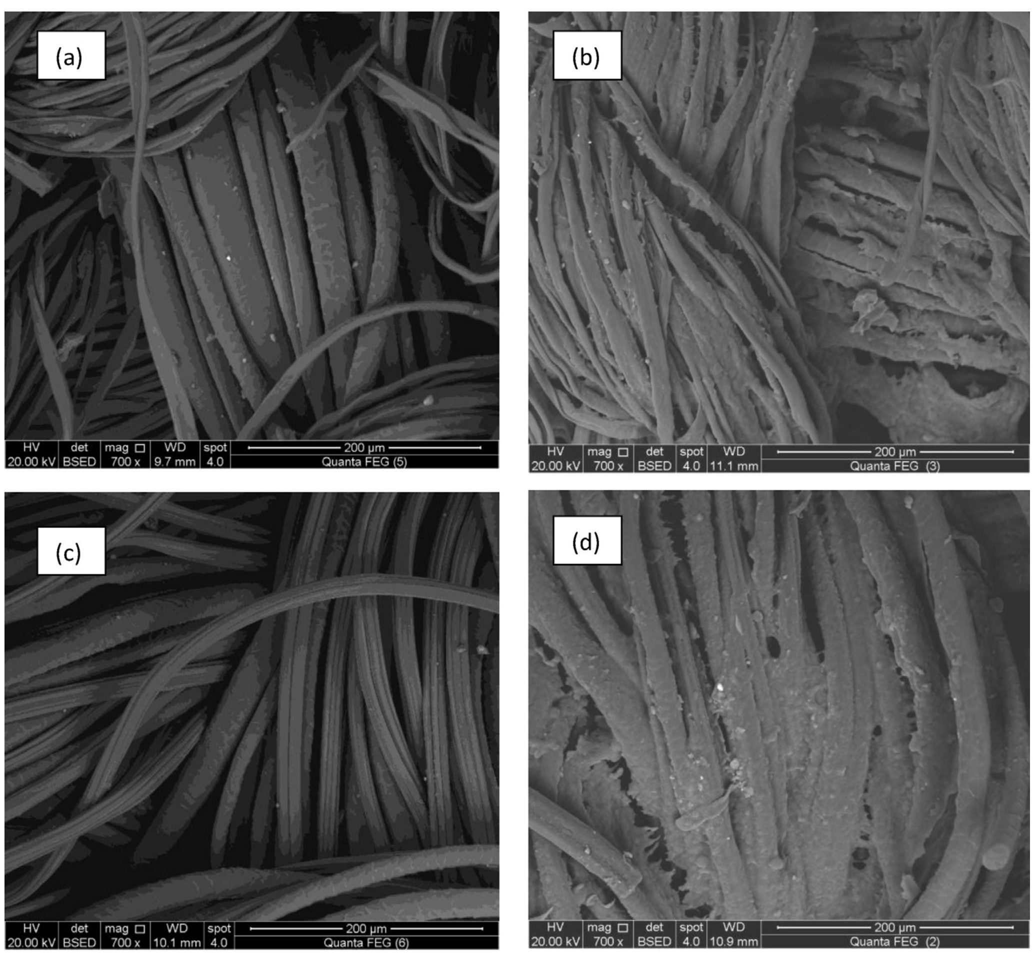

Fig. 2. SEM of untreated cotton/wool fabric (a), SEM of treated cotton/wool fabric with Aloe vera (b), SEM of untreated viscose/wool fabric (c), and SEM of treated viscose/wool fabric with Aloe vera (d).

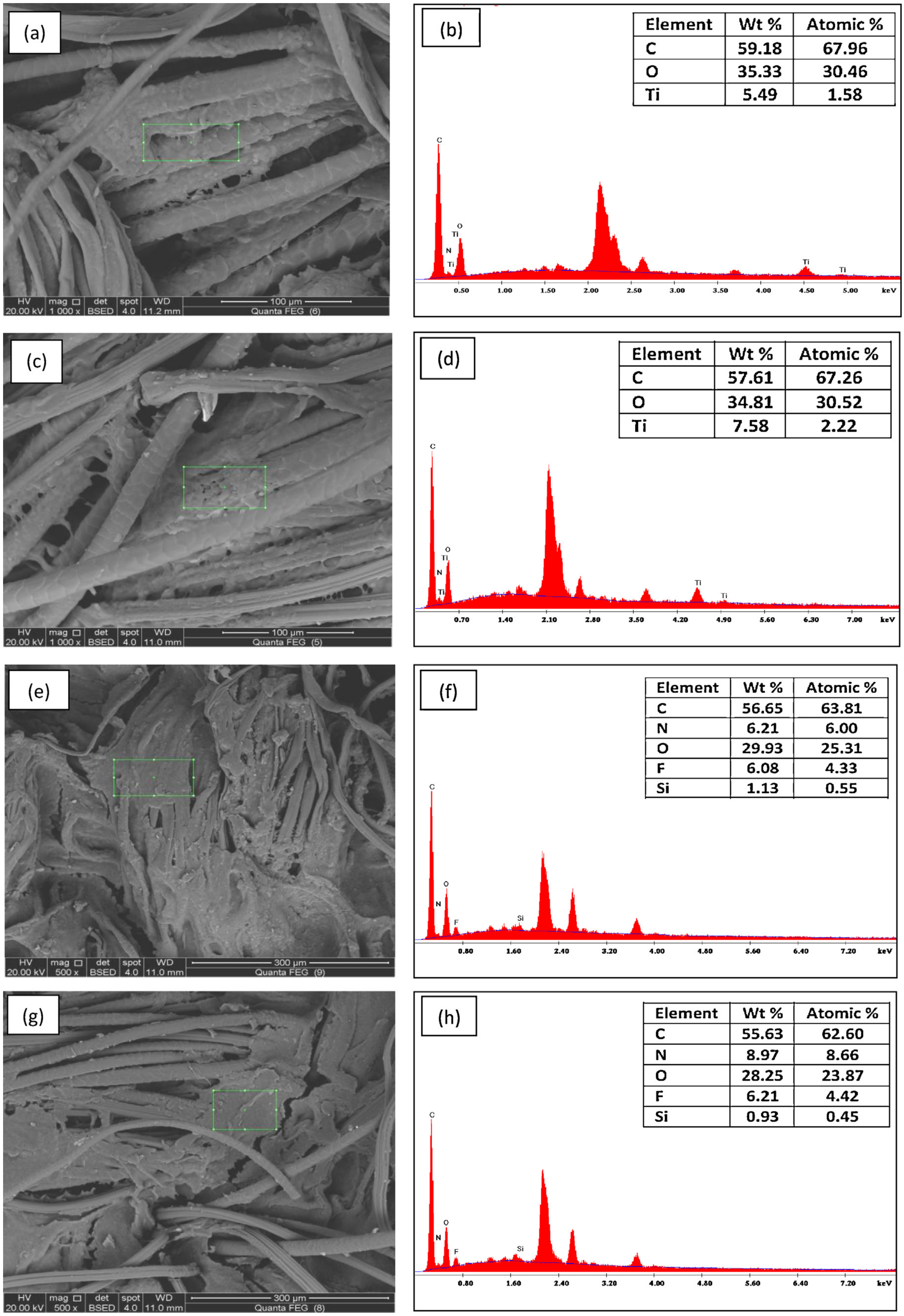

Fig. 3. EDX image and element content of TiO_2-NP's loaded cotton/wool blend (a, b) and viscose/wool blend (c, d), and EDX image and element content of water/oil repellent loaded cotton/wool blend (e, f) and viscose/wool blend (g, h).

Table 5
Durability of the imparted functional and coloration properties to wash using different printing paste.[a]

Functional finish	Additive	Substrate	ZI[b] (mm)		UPF[c]	Roughness (mm)	Repellency rate		K/S[d]
			G +ve	G −ve			Water	Oil	
None	None	C/W	0	0	63 (50)	29.05 (25.52)	0	0	17.48 (13.15)
		V/W	0	0	74 (60)	22.54 (20.08)	0	0	14.02 (10.62)
Antibacterial	Chitosan (2.5 g/kg)	C/W	22.0 (19.5)	20.0 (17.5)	–	–	–	–	21.61 (17.75)
		V/W	19.0 (17.0)	18.0 (16.0)	–	–	–	–	19.43 (16.22)
	Aloe vera (10 g/kg)	C/W	19.5 (17.5)	17.0 (15.0)	–	–	–	–	22.00 (18.92)
		V/W	16.0 (14.0)	14.5 (13.0)	–	–	–	–	16.63 (13.32)
	Triclosan (10 g/kg)	C/W	19.0 (17.0)	18.0 (16.5)	–	–	–	–	20.52 (16.85)
		V/W	13.5 (11.5)	11.5 (10.0)	–	–	–	–	15.52 (12.48)
Antibacterial and anti-UV	TiO_2-NP's(10 g/kg)	C/W	16.0 (14.5)	15.0 (13.5)	80 (68)	–	–	–	20.91 (17.38)
		V/W	13.0 (11.0)	11.5 (10.0)	99 (87)	–	–	–	19.03 (16.00)
Soft-handle	Softener (20 g/kg)	C/W	–	–	–	15.96 (17.65)	–	–	25.02 (22.01)
		V/W	–	–	–	13.41 (11.23)	–	–	16.90 (13.87)
Water/oil repellent	Water/oil repellent (40 g/kg)	C/W	–	–	–	20.91 (23.30)	80 (70)	7 (5)	22.38 (19.22)
		V/W	–	–	–	16.85 (18.20)	70 (50)	5 (4)	20.03 (16.88)

C/W: cotton/wool blend; V/W: viscose/wool blend. Values in parenthesis are the values of some pigment prints properties after 15 washing cycles.
[a] Printing paste components: Pigment Red 146 (20 g/kg); synthetic thickener (20 g/kg); Printofix® Binder MTB (100 g/kg); cross-linker (10 g/kg); catalyst (2 g/kg). Microwave fixation at 1300 W/4 min.
[b] ZI: zone of inhibition
[c] UPF: UV-protection factor
[d] *K/S*: color strength.

extremely reactive species, e.g. superoxide ions, hydroxyl radicals, etc., thereby enhancing the extent of attacking the bacterial cell membrane, losing of its essential functions and destroying it (Chen & Wang, 2006; Ibrahim, Amr, Eid, Mohammed, & Fahmy, 2012b; Ibrahim, Refai, et al., 2010), as well as (ii) scattering and absorbing the harmful UV-B radiation (Abidi, Hequete, Tarimala, & Dai, 2007; Ibrahim, Amr, et al., 2012; Ibrahim, El-Zairy, et al., 2013; Ibrahim, Refai, et al., 2010).

It is also clear from Table 2 that: (i) the nominated G +ve bacteria are more susceptible to the action of the loaded TiO_2-NP's than the G −ve bacteria, regardless of the used substrate, (ii) the darker the depth of the shade, the greater is the UV-protection, irrespective of the used pigment colorant, (iii) the UPF-values of the functionalized pigment prints is governed by the extent of loading TiO_2-NP's onto the substrate: viscose/wool > cotton/wool, as well as the kind of pigment colorant, (iv) the enhancement in the pigment printing properties upon inclusion of TiO_2-NP's into the printing paste could be ascribed to the positive role of the TiO_2-NP's as a co-catalyst for cross-linking and intensifying the extent of polymerization and fixation of the binder film onto fabrics surface and subsequent fixation and entrapment of extra pigment particles (Chen & Wang, 2006; Dastjerdi & Montazer, 2010; Nazari, Montazer, & Rahimi, 2009; Nazari, Montazer, Rashidi, et al., 2009), and (v) the slight improvement in the light fastness properties of the obtained pigment prints could be attributed to the UV light- absorption capacity of the loaded TiO_2-NP's.

3.2.3. Soft-handle finishing and pigment printing in one step

For given set of soft-finishing and pigment printing of the nominated substrates using different pigment colorants, the data in Table 3 demonstrate that: (i) inclusion of the silicone softener in the printing paste, 20 g/kg, results in a significant improvement in the smoothness along with a remarkable reduction in the stiffness of the produced pigment prints, (ii) the positive variation in the aforementioned surface properties reflects the positive role of silicone film as a lubricating agent between the fibers in the yarn and between the yarns of the fabric, thereby imparting softness and minimizing stiffness (Wahle & Falkowski, 2002; Habereder & Bereck, 2002; Hashem & Ibrahim, 2002; Ibrahim, Gouda, Husseiny, El-Gammal, & Mahrous, 2009), (ii) the extent of reduction in fiber friction which results in soft yarn and improved fabric handle, in the presence and absence of silicone softener, is governed by the type of substrate and its components and follows the decreasing order: viscose/wool > cotton/wool, (iii) the enhancement in the printing properties, i.e. *K*/*S* and fastness properties, reflects the positive role of the silicone micro emulsion in leading to better extent of binding film orientation, formation and/or distribution on the fabric surface thus creating a proper condition for accommodation and anchoring of pigment particles as well as their fixation during the microwave curing step (Ibrahim et al., 2005).

3.2.4. Concurrent water/oil repellent and pigment printing

Table 4 shows that printing of the nominated substrates in the presence of the water/oil repellent additive (40 g/kg) followed by screen printing and microwave fixation is accompanied by a remarkable increase in water/oil repellent ratings 70/6, and 50/5 for cotton/wool and viscose/wool fabric respectively. The type of pigment colorant has practically no effect on the imparted repellent properties. The imparted functional properties are governed by type of substrate and follow the decreasing order: cotton/wool > viscose/wool fabric. The improvement in the repellent properties is attributed to the formation of a hydrophobic/oleophobic polymer film on the printed fabric surface thereby lowering the fabric surface energy and hence repellent properties (Abo-Shosha, El-Hilw, Aly, & Amr, 2009; Ibrahim, Amr, et al., 2010). Incorporation of the nominated water/oil repellent in the printing paste has a positive impact on the depth of the obtained prints along with a slight enhancement in the fastness properties ratings as a direct consequence of increasing the extent of entrapment and entanglement of the pigment particles within the cross-linked polymer film onto the fabric surface.

On the other hand, the data so obtained signify that inclusion of the used water/oil-repellent results in a remarkable reduction in the roughness, i.e. promoting surface smoothening, of the obtained pigment prints as a direct consequence of the deposition of a hydrophobic smooth film on the fiber and fabric surface. The extent of improvement in surface smoothening is governed by type of substrate i.e. viscose/wool > cotton/wool, keeping other parameters constant.

3.2.5. SEM images and EDX spectra

The SEM was used to observe the cotton/wool and viscose/wool blended fabrics before (Fig. 2a and c) and after printing (Fig. 2b and d) respectively in the presence of certain functional additives namely Aloe vera, TiO_2-NP's (Fig. 3a and c) and the water/oil repellent (Fig. 3e and g) respectively. According to the given SEM images, the pigment printed fabric surfaces were clearly covered with deposited printing paste and loaded with the pigment particles along with the nominated active ingredients; endow the fabric functionalization and coloration.

On the other hand, EDX spectra of pigment printed cotton/wool and viscose/wool fabric samples and loaded with TiO_2-NP's (Fig. 3b and d) or the water/oil repellent (Fig. 3f and h) confirmed the existence of titanium element or silicon and fluorine elements respectively on the obtained pigment prints. The results were reported based on both the weight percentages (%). Once again, the distribution of the deposited printing paste onto the fabric surface is influenced by type and morphology of untreated substrate.

3.2.6. Durability to wash

The durability of the imparted functional properties as well as the retained depth of shade, expressed as *K/S* values, of some pigment prints until 15 laundering cycles were determined according to ASTM Standard Test (D737-96) and demonstrated in Table 5. For a give set of printing condition, the data in Table 5 signify that: (i) inclusion of the nominated functional additives in the printing paste results in a significant improvement in the imparted functional properties along with an enhancement in the depth of the obtained pigment prints, (ii) the durability to wash, after 15 washing cycles, was slightly decreased, which can be discussed in terms of desorption and/or removal of physically absorbed or unfixed active ingredients and pigment particles, (iii) the extent of retention of the imparted properties as well as the pigment particles onto the printed substrate are governed by type of functional additive, kind of substrate, along with the ability to form a durable three-dimensional cross-linked sheath or film containing both the active species and the pigment particles on the fabric surface and (iv) the obtained functionalized pigment prints exhibited very sufficient: antibacterial and/or UV-blocking properties, soft-handle, or water/oil repellency in addition to high depth of shades even after 15 washing cycles.

4. Conclusions

- Functionalized cotton/wool and viscose/wool pigment prints were achieved by individual including of chitosan (2.5 g/kg), Aloe vera (10 g/kg), triclosan (10 g/kg), TiO_2-NP's (10 g/kg), silicone softener (20 g/kg) or the water/oil repellent agent (40 g/kg) in the print paste, followed by screen printing and microwave fixation at 1300 W/4 min.
- The enhancement in the imparted functional properties such as antibacterial, antibacterial/UV-protection, soft-handle or water-repellency with the improve in the printing properties is governed by both the type of the functional additive and the kind of substrate.
- The functionalized pigment prints were found to have good functionality and printability even 15 consecutive laundering cycles.
- Finally, the obtained results have important practical implications for the establishment of simultaneous functional finishing and pigment printing in one step process talking both the environmental and economical aspects in concern.

References

Abidi, N., Hequete, E., Tarimala, S., & Dai, I. I. (2007). Cotton fabric surface modification for improved UV-radiation protection using sol–gel process. *Journal of Applied Polymer Science*, *104*, 111–117.

Abo-Shosha, M. H., El-Hilw, Z. H., Aly, A. A., & Amr, A. (2009). New textile water repellent based on reaction of toluene 2,4-diisocyanate with stearyl alcohol. *AATCC Review*, *9*(7), 38–42.

Bajaj, P. (2002). Finishing of textile materials. *Journal of Applied Polymer Science*, *83*, 631–659.

Bozzi, A., Yuranova, T., & Kiwi, J. (2005). Self cleaning of wool-polyamide and polyester textiles by TiO2-rutile modification under daylight irradiation at ambient temperature. *Journal of Photochemistry and Photobiology. A, Chemistry*, *172*, 27–34.

Chen, C. C., & Wang, C. C. (2006). Crosslinking of cotton cellulose with succinic acid in the presence of titanium dioxide nano-catalyst under UV-irradiation. *Journal of Sol–Gel Science and Technology*, *40*, 31–38.

Dastjerdi, R., & Montazer, M. (2010). A review on the application of inorganic nano-structured materials in the modification of textiles: Focus on anti-microbial properties. *Colloids and Surfaces B: Biointerfaces*, *79*, 5–18.

Giesen, V., & Eisenlohr, R. (1994). Pigment printing. *Review Progress Coloration*, *24*, 26–30.

Gouda, M., & Ibrahim, N. A. (2008). New approach for improving antibacterial function to cotton fabric. *Journal of Industrial Textiles*, *37*, 327–339.

Gowri, S., Almeida, L., Amorim, T., Carneiro, N., Souto, A. P., & Esteves, M. F. (2010). Polymer nanoparticles for multifunctional finishing of textiles – A review. *Textile Research Journal*, *80*, 1290–1306.

Gupta, P., Bajpai, M., & Bajpai, S. K. (2008). Investigation of antibacterial properties of silver nanoparticles-loaded poly (acrylamide-co-itaconic acid)-grafted cotton fabric. *Journal of Cotton Science*, *12*, 280–286.

Habereder, P., & Bereck, A. (2002). Part 2: Silicone softeners. *Review Progress Coloration*, *32*, 125–136.

Hamman, J. H. (2008). Composition and application of Aloe vera leaf gel. *Molecules*, *13*, 1599–1616.

Hashem, M., & Ibrahim, N. A. (2002). Response of linen fabric to finishing treatments. *Journal Textile Association*, *63*, 189–194.

Hebeish, A., & Ibrahim, N. A. (2007). The impact of frontier sciences on textile industry. *Colourage Annual*, *54*, 41–55.

Holme, I. (2007). Innovative technologies for high performance textiles. *Coloration Technology*, *123*, 59–73.

Hsieh, Y. L. (2007). Chemical structure and properties of cotton. In S. Gordan, & Y. L. Hsieh (Eds.), *Cotton: Science, technology*. Cambridge: Woodhead, pp. 3–30.

Ibrahim, N. A. (2011). Dyeing of textile fibre blends. In M. Clark (Ed.), *Handbook of textile and industrial dyeing, vol. 2: Application of dyes* (pp. 147–172). Oxford: Woodhead Publishers. Chapter 4.

Ibrahim, N. A., Abdalla, W. A., El-Zairy, E. M. R., & Khalil, H. M. (2013). Utilization of monochloro-triazine β-Cyclodexrtin for enhancing printability and functionality of wool. *Carbohydrate Polymers*, *92*, 1520–1529.

Ibrahim, N. A., Amr, A., Eid, B. M., & El Sayed, Z. M. (2010). Innovative multifunctional treatments of ligno-cellulosic jute fabric. *Carbohydrate Polymers*, *82*, 1198–1204.

Ibrahim, N. A., Amr, A., Eid, B. M., Mohammed, Z. E., & Fahmy, H. M. (2012). Poly (acrylic acid)/poly (ethylene glycol) adduct for attaining multifunctional cellulosic fabrics. *Carbohydrate Polymers*, *89*, 648–660.

Ibrahim, N. A., Eid, B. M., & El-Batal, H. (2012). A novel approach for adding smart functionalities to cellulosic fabrics. *Carbohydrate Polymers*, *87*, 744–751.

Ibrahim, N. A., El-Zairy, E. M. R., Abdalla, W. A., & Khalil, H. M. (2013). Combined UV-protecting and reactive printing of cellulosic/wool blends. *Carbohydrate Polymers*, *92*, 1386–1394.

Ibrahim, N. A., El-Zairy, E. M. R., El-Zairy, M. R., & Khalil, H. M. (2010). Improving transfer printing and UV-blocking properties of polyester-based textiles using MCT-βCD, chitosan and ethylenediamine. *Coloration Technology*, *126*, 330–336.

Ibrahim, N. A., El-Zairy, M. R., Zaky, S., & Borham, H. A. (2005). Environmental sound synthetic pigment printing using synthetic thickening agents. *Polymer-Plastics Technology and Engineering*, *44*, 111–132.

Ibrahim, N. A., Gouda, M., Husseiny, Sh. M., El-Gammal, R. M., & Mahrous, F. (2009). UV-protecting and antibacterial finishing of cotton knits. *Journal of Applied Polymer Science*, *112*, 3589–3596.

Ibrahim, N. A., Gouda, M., & Zairy, W. M. (2008). Enhancing easy care and antibacterial functions of cellulose/wool blends. *Journal of Natural Fibers*, *5*, 347–365.

Ibrahim, N. A., Hashem, M., El-Sayed, W. A., El-Husseiny, Sh., & Elanany, E. M. (2010). Enhancing antimicrobial properties of dyed and finished cotton/polyester fabrics. *AATCC Review*, *10*, 55–63.

Ibrahim, N. A., Mahrous, F., El-Gamal, A. R., Gouda, M., & Husseiny Sh, M. (2010). Multifunctional anionic cotton dyeing. *Journal of Applied Polymer Science*, *115*, 3249–3255.

Ibrahim, N. A., Refai, R., & Ahmed, A. F. (2010). Novel approach for attaining cotton fabric with multifunctional properties. *Journal of Industrial Textiles*, *40*, 65–83.

Jothi, D. (2009). Experimental study on antimicrobial activity of cotton fabric treated with aloe gel extract from aloe vera plant for controlling the *Staphylococcus aureus* (bacterium). *African Journal of Microbiology Research*, *3*, 228–232.

Judd, D., & Wyszeck, G. (1975). *Color in business science and industry* (3rd ed.). New York: John Wiley & Sons.

Kong, M., Chen, X. G., Xing, K., & Park, H. J. (2010). Antimicrobial properties of chitosan and mode of action: A state of the art review. *International Journal of Food Microbiology*, *144*, 51–63.

Lewis, D. M. (2011). Coloration of wool. In M. Clark (Ed.), *Handbook of textiles and industrial dyeing, vol. 2: Applications of dyes* (pp. 6–7). Oxford: Woodhead Publisher. Chapter 1.

Moghaddasi, M. S., & Verma, S. K. (2011). Aloe vera their chemicals composition and applications: A review. *International Journal of Biological & Material Research*, *2*, 466–471.

Nazari, A., Montazer, M., & Rahimi, M. K. (2009). Concurrent antimicrobial and crosslinking of bleached and cationic cotton using nano-TiO_2 and BTCA. *Iranian Polymer Science and Technology Journal*, *22*, 41–51.

Nazari, A., Montazer, M., Rashidi, A., Yazdanshenas, M., & Abbasinejad, M. A. (2009). Nano-TiO_2 photo-catalyst and sodium hypophosphite for crosslinking cotton with polycarboxylic acids under UV and high temperature. *Applied Catalysis A: General*, *371*, 10–16.

Orhan, M., Kut, D., & Gunesoglu, C. (2007). Use of triclosan as antibacterial agent in textiles. *Indian Journal of Fibre & Textile Research*, *32*, 114–118.

Orhan, M., Kut, D., & Gunesoglu, C. (2009). Improving the antibacterial activity of cotton fabrics finished with triclosan by the use of 1, 2, 3, 4- butanetetracarboxylic acid and citric acid. *Journal of Applied Polymer Science*, *111*, 1344–1352.

Sarkar, R. K., Purushottam, D. E., & Chanuhan, P. D. (2003). Bacteria-resist finish on cotton fabrics using natural herbal extracts. *Indian Journal of Fiber & Textile Research*, *28*, 322–331.

Schindler, W. D., & Hauser, P. I. (2004). *Chemical finishing of textiles*. Cambridge, England: Woodhead Publisher.

Simoncic, B., & Tomsic, B. (2010). Structure of novel antimicrobial agents for textiles – A review. *Textile Research Journal*, *80*, 1721–1737.

Uddin, F., & Lomas, M. (2005). Combined crease recovery finishing and pigment printing. *Coloration Technology*, *121*, 158–163.

Wahle, B., & Falkowski, J. (2002). Softeners in textile processing, part 1: An overview. *Review Progress Coloration*, *32*, 118–124.

Wang, C. C., & Chen, C. C. (2005). Physical properties of crosslinked cellulose catalyzed with nano-titanium dioxide. *Journal of Applied Polymer Science*, *97*, 2450–2456.

Yaman, N., Ozdogan, E., & Seventekin, N. (2012). Improvement in fastnesses and color strength of pigment printed textile fabric. *Journal of Engineered Fibers and Fabrics*, *7*, 40–46.

Zemljic, L. F., Strand, S., Sauperl, O. X., & Kleinschek, K. S. (2009). Characterization of amino groups for cotton fabrics coated with chitosan. *Textile Research Journal*, *79*, 219–226.

Zitao, Z., Chen, L., Jinmin, J., Yanliu, H., & Donghui, C. (2003). Antibacterial properties of cotton fabrics treated with chitosan. *Textile Research Journal*, *73*, 1103–1106.