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Cellulosic/wool pigment prints with remarkable antibacterial functionalities

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ABSTRACT

Several bio-active agents namely choline chloride, triclosan derivative, PEG-600 and 4-hydroxybenzophenone were successfully included into solvent-free pigment formulations, in a single-stage process, followed by screen printing and microwave-fixation to obtain antibacterial functionalized cellulosic/wool pigment prints. Results obtained signify that both the improvement in functionalization and coloration properties are governed by type of antibacterial agent, kind of substrate as well as pigment colorant. The imparted antibacterial activity of the loaded bio-active agents follows the decreasing order: G+ve (*Staphylococcus aureus*) > G−ve (*Escherichia coli*), keeping other parameters constant. The imparted functional and coloration properties showed no significant decrease even after 15 washings. Mode of interactions among the nominated substrates, the pigment paste constituents and the bioactive agents were also proposed.

1. Introduction

In recent years, there has been a growing need to develop cost-effective, value added, eco-safe, functional and durable textile products (Holme, 2007; Ibrahim, Eid, & El-Batal, 2012; Powell & Cassill, 2006; Wang & Wang, 2009). Special focus has been given to the implementation of emerging technologies such as bio-, nano- and/or plasma technologies in textile wet processes to cope with the ever-increasing environmental, health and quality concerns (Abdel-Aziz, Eid, & Ibrahim, 2014; Hartwgi, 2002; Hebeish & Ibrahim, 2007; Ibrahim, Eid, Hashem, Refai, & El-Hossamy, 2010; Ibrahim, El-Badry, Eid, & Hassan, 2011; Ibrahim, Eid, Youssef, El-Sayed, & Salah, 2012; Jegannathan & Nielsen, 2013; Nierstrasz & Warmoeskerken, 2003, chapter 4; Nithya, Radhai, Rajendran, Jayakumar, & Vaideki, 2012; Sawhney et al., 2008; Shaikh, 2010). Taking these facts into account, much of our R&D efforts have been focused on developing functionalized textile products with desirable, durable functional and improved coloration properties using proper functional finishing and/or printing formulations and a facile single–stage process that can be adopted on a practical large scale (Ibrahim, Abo-Shosha, Fahmy, El-Sayed, & Hebeish, 2008; Ibrahim, Amr, Eid, & El-Sayed, 2010; Ibrahim, Refaie, & Ahmed, 2010; Ibrahim, Rehim, & El-Batal, 2010; Ibrahim, Khalifa, El-Hossamy, & Tawfik, 2010; Ibrahim, El-Gamal, Gouda, & Mahrous, 2010; Ibrahim, El-Zairy, El-Zairy, & Khalil, 2010; Ibrahim, Fahmy, Rehim, Sharaf, & Abo-Shosha, 2010; Ibrahim, El-Zairy, El-Zairy, Eid, & Ghazal, 2011; Ibrahim, El-Zairy, El-Zairy, & Ghazal, 2011; Ibrahim, Eid, & El-Zairy, 2011; Ibrahim et al., 2013; Ibrahim, Amr, Eid, Almetwally, & Mourad, 2013; Ibrahim, El-Zairy, Abdalla, & Khalil, 2013; Ibrahim, Abdalla, El-Zairy, & Khalil, 2013; Ibrahim, El-Zairy, El-Zairy, & Ghazal, 2013; Ibrahim, Eid, Elmaaty, & El-Aziz, 2013; Ibrahim, Abou Elmaaty, Eid, & Abd El-Aziz, 2013; Ibrahim, Khalil, El-Zairy, & Abdalla, 2013; Ibrahim, Eid, Abd El-Aziz, & Abou Elmaaty, 2013)

Herein, we report the technical feasibility of upgrading both the functional properties and pigment coloration of cotton/wool and viscose/wool blended fabrics in one-step via incorporation of certain functional additives namely choline chloride, PEG-600, and triclosan derivative, 4-hydroxybenzophenone into the solvent-free formulations.

2. Experimental

2.1. Materials

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

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Arkofix® NDF Liquid C (low formaldehyde-reactant resin based on modified N-methylol dihydroxyethylene urea, Clariant), Ruco® BAC MED (nonionic antibacterial finishing agent, based on diphenyl alkane derivative of triclosan-Rudolf Chemie), Printofix® Binder MTB-01 liquid (acrylate based copolymer, anionic, Clariant), Printofix® Thickener 160 EG liquid (synthetic thickening agent based on ammonium polyacrylate, Clariant), Pigment Red 146, Pigment Blue 153 and Pigment Orange 13 (Daico- Egypt) were of commercial grade.

All other chemicals used in this study such as polyethylene glycol (PEG-600), choline chloride, 4-hydroxybenzophenone as well as ammonium persulfate [$(NH_4)S_2O_8$] were of laboratory reagent grade.

2.2. Methods

2.2.1. Functionalization and coloration in one step

Combined functionalization and pigment coloration of the nominated blends were carried out using the flat screen printing technique and the following print past formulations.

Constituent	g/kg
Pigment colorant	20
Binding agent	100
Thickening agent	20
Arkofix® NDF	10
$(NH_4)_2S_2O_8$	2
Functional additive:	
choline chloride	5
Ruco® BAC	20
PEG-600	20
Or 4-hydroxybenzophenone	5
H_2O	X
Total	1000

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

2.3. Measurements

Antibacterial efficacy of the functionalized pigment prints against G +ve bacterial (*Staphylococcus aureus*) and G −ve bacteria (*Escherichia coli*) was evaluated qualitatively according to the AATCC Test Method (147-1988), and expressed as zone of growth inhibition (ZI, mm).

UV-protection factor (UPF) was assessed according to the Australian/New Zealand Standard Method 135-2000.

Depth of the obtained pigment prints was measured using an automatic filter spectrophotometer and expressed as K/S values, $K/S = (1 - R)^2/2R$, where R is the reflectance, K and S are the absorption and scattering coefficient, respectively (Judd & Wyszeck, 1975).

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

Surface roughness of the obtained pigment prints in the absence and presence of PEG-600 was evaluated according to JIS 94 standard, using surface roughness measuring instrument, SE 1700 α (Japan).

Durability to wash was performed according to ASTM Standard Test Method (D737-96).

Scanning electron microscope (SEM) images of nominated samples were evaluated using a JEOL, JXA-840A (Japan).

3. Results and discussion

With a view towards upgrading the antibacterial activity of cellulosic/wool pigment prints, the present research article has focused on investigating the technical feasibility of carrying out concurrent functionalization and pigment coloration in a single-stage process via individual inclusion of proper active ingredients namely choline chloride, triclosan derivative, PEG-600 and 4-hydroxybenzophenone (Fig. 1) into the solvent-free pigment formulations. Discussion of the obtained results follows.

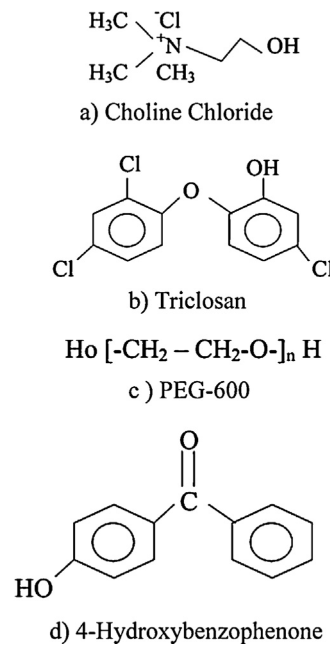
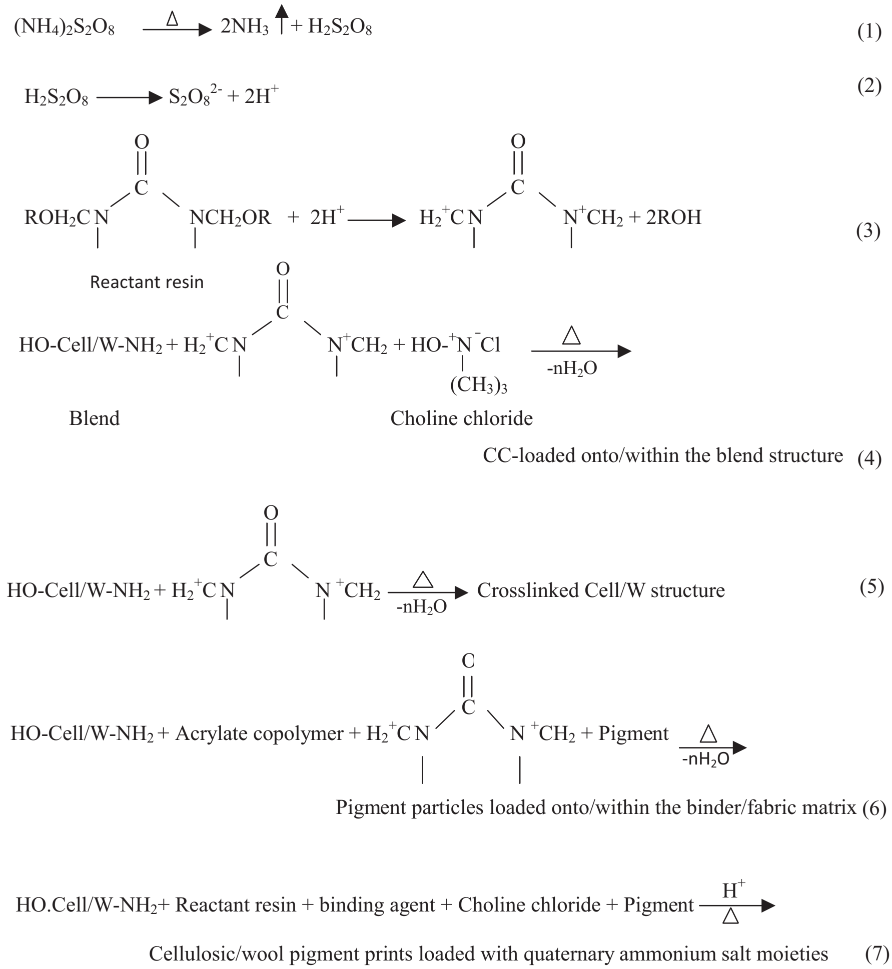


Fig. 1. Chemical structures of chemicals: (a) choline chloride, (b) triclosan, (d) PEG-600 and (c) 4-hydroxybenzophenone.

3.1. Choline chloride

As far as the changes in the antibacterial activity and coloration properties of the simultaneously functionalized and pigment printed viscose/wool and cotton/wool blends as a function of including choline chloride (CC) into the pigment formulations, Table 1 shows that: (i) incorporation of CC in the printing paste results in a significant improvement in the depth of the obtained prints, expressed as K/S values, along with a reasonable enhancement in their fastness properties, (ii) the above mentioned improvement in printing properties reflects the positive impacts of the used cationic quaternary ammonium salt on modifying the fabric surface and creating additional positive active centers thereby affording active sites for subsequent pigment particles fixation and accommodation onto/into the binding agent/fabric matrix during the microwave fixation step (Ibrahim, Eid, Elmaaty, et al., 2013), (iii) the extent of improvement in the printing properties, K/S values and fastness properties, is determined by type of pigment colorant, i.e. form, size, chemical structure, color, hue, functionality, compatibility with other ingredients as well as location, degree of fixation and entrapment onto/within the resultant three-dimensionally linked network (Ibrahim, El-Zairy, Zaky, & Borham, 2005; Ibrahim, Eid, Elmaaty, et al., 2013; Ibrahim, Abou Elmaaty, et al., 2013; Ibrahim, Khalil, et al., 2013), (iv) the remarkable improvement in the imparted antibacterial activity to the obtained pigment prints is attributed to the ability of the anchored CC moieties to interact with cytoplasmic membrane of bacteria, cause membrane leakage, induce protein inactivation, affect the DNA molecules of bacteria, cause a loss in ability to replicate and even cell death (Ibrahim, Eid, Elmaaty, et al., 2013; Lam, Kan, & Yuen, 2012), (v) the antibacterial efficacy against the examined bacteria follows the decreasing order G+ve > G−ve reflecting the differences between the two types in membrane structure, response



Scheme 1. Reaction scheme for concurrent functionalization and pigment coloration (Cardamone, Marmer, Blanchard, Lambert, & Bulan-Brady, 1996; Cardamone & Turner, 2000; Ibrahim, Eid, Elmaaty, et al., 2013; Ibrahim, Khalil, et al., 2013; Wartelle & Marshall, 2005).

Table 1
Effect of inclusion of choline chloride into the pigment printing formulations.

Pigment	Substrate	Choline Chloride (5 g/kg)	***K/S***[a]	Incr. in ***K/S*** (%)	ZI (mm)[b]		WF[c]		RF[d]		LF[e]
					G +ve	G −ve	Alt.	St.	Dry	Wet	
Pigment Red 146	V/W	−ve	13.94	0.00	0.00	0.00	3	3–4	3–4	3	3–4
	C/W		17.28	0.00	0.00	0.00	3–4	4	4	4	3–4
	V/W	+ve	15.61	11.31	22.5	21.0	4–5	4–5	4	4	4
	C/W		20.19	16.84	21.0	20.0	4–5	4–5	4–5	4	4
Pigment Blue 153	V/W	−ve	11.09	0.00	0.00	0.00	3–4	4	3	3	4
	C/W		11.60	0.00	0.00	0.00	4	4	3	3	4
	V/W	+ve	13.50	21.73	21.8	20.5	4	4–5	4	4	5
	C/W		14.37	23.89	20.5	19.0	4–5	4–5	4	4	5
Pigment Orange 13	V/W	−ve	6.04	0.00	0.00	0.00	3	3–4	3	3	4
	C/W		6.75	0.00	0.00	0.00	4	4	4	4	4
	V/W	+ve	8.56	41.72	21.0	20.0	4	4	4	4	5
	C/W		9.85	45.93	18.0	16.5	4–5	4–5	4–5	4	5

V/W: viscose/wool, C/W: cotton/wool.
Printing paste constituents: pigment colorant (20 g/kg); binder (100 g/kg); thickener (20 g/kg); crosslinker (10 g/kg); catalyst (2 g/kg); choline chloride (5 g/kg); fixation at 1300 W for 4 min.
(−ve): in the absence; (+ve): in the presence of choline chloride.
[a] *K/S*: color strength.
[b] ZI: zone of inhibition; G +ve: (*S. aureus*); G −ve: (*E. coli*).
[c] WF: wash fastness; Alt: alteration; St: staining on cotton.
[d] RF: rubbing fastness.
[e] LF: light fastness.

Table 2
Effect of inclusion of Ruco®-BAC into the pigment printing formulations.

Pigment	Substrate	Triclosan derivative (20 g/kg)	***K/S***[a]	Incr. in ***K/S*** (%)	ZI (mm)[b]		WF[c]		RF[d]		LF[e]
					G +ve	G −ve	Alt.	St.	Dry	Wet	
Pigment Red 146	V/W	−ve	13.94	0.00	0.00	0.00	3	3–4	3–4	3	3–4
	C/W		17.28	0.00	0.00	0.00	3–4	4	4	4	3–4
	V/W	+ve	16.22	16.35	19.5	18.0	3–4	4–5	4	4	4–5
	C/W		20.30	17.48	17.5	16.0	4	4–5	4	4	4–5
Pigment Blue 153	V/W	−ve	11.09	0.00	0.00	0.00	3–4	4	3	3	4
	C/W		11.60	0.00	0.00	0.00	4	4	3	3	4
	V/W	+ve	13.27	19.66	16.5	15.0	4–5	4–5	4	4	5
	C/W		13.93	20.09	13.0	11.5	4–5	5	4	4	5
Pigment Orange 13	V/W	−ve	6.04	0.00	0.00	0.00	3	3–4	3	3	4
	C/W		6.75	0.00	0.00	0.00	4	4	4	4	4
	V/W	+ve	10.18	68.54	12.5	11.0	3–4	4	4	4	5
	C/W		10.85	79.64	10.0	8.0	4–5	4–5	4	4	5

Printing paste constituents: pigment colorant (20 g/kg); binder (100 g/kg); thickener (20 g/kg); crosslinker (10 g/kg); catalyst (2 g/kg); Ruco®-BAC (20 g/kg); fixation at 1300 W for 4 min.
For explanation of abbreviations see footnote to Table 1.

for inactivation as well as amenability to damage and destruction (Ibrahim, Gouda, El-shafei, & Abdel-Fatah, 2007; Ibrahim, Eid, et al., 2010; Ibrahim, Eid, Elmaaty, et al., 2013), (vi) the enhancement in the extent of coloration and functionalization is governed by type of substrate, e.g. fabric structure, weight, thickness, cellulose component, amorphous/crystalline regions, extent of penetration/diffusion/modification, degree of immobilization and fixation of CC and/or pigment particles during the fixation step (Ibrahim, El-Zairy, Abdalla, et al., 2013; Ibrahim, Khalil, et al., 2013), (vii) the depth of the obtained prints follows: C/W > V/W order most probably due to the undue-penetration of printing paste components within the V/W structure, and (viii) the antibacterial activity of the functionalized pigment prints follows the decreasing order V/W > C/W reflecting the higher extent of modification and immobilization of quaternary ammonium active sits onto/within the V/W structure and/or onto/into the binder/fabric matrix.

Based on the abovementioned results, the following reaction scheme (Scheme 1) represents the most likely scenario illustrating the reactions and/or interactions among the cellulosic/wool blend [HO-Cell./W-NH_2], choline chloride, binding agent, cross linking agent, pigment colorant and the catalyst at 1300 W for 4 min.

On the other hand, loading of the used cationic bioactive agent, CC, onto the negatively charged active sites, —COOH groups, cannot be phased out.

3.2. Triclosan derivative

As far as the changes in the antibacterial activity as well as in the coloration properties of the functionalized/pigment printed V/W and C/W blends as a function of inclusion of triclosan derivative, Ruco®-BAC, into the pigment printing pastes along with other constituents followed by screen printing and microwave curing, the data in Table 2 indicate that: (i) inclusion of triclosan derivative, 20 g/kg, into the printing formulations brings about a significant increase in the depth of the obtained pigment prints, expressed as *K/S* values, along with an improvement in some of the evaluated fastness properties, regardless of the used pigment colorant and substrate, (ii) the extent of improvement in the printing properties is determined by both the type of substrate and pigment colorant as discussed earlier, (iii) the enhancement in coloration properties reflects the positive impact of adding triclosan on facilitating and enhancing the extent of binder-film formation and degree of network crosslinking onto the fabric surface thereby supporting

Table 3
Effect of inclusion of PEG-600 into the pigment printing formulations.

Pigment	Substrate	PEG-600 (20 g/kg)	***K/S***[a]	Incr. in ***K/S*** (%)	ZI (mm)[b]		WF[c]		RF[d]		LF[e]	SR[f] (μm)
					G +ve	G −ve	Alt.	St.	Dry	Wet		
Pigment Red 146	V/W	−ve	13.94	0.00	0.00	0.00	3	3–4	3–4	3	3–4	22.54
	C/W		17.28	0.00	0.00	0.00	3–4	4	4	4	3–4	29.05
	V/W	+ve	16.88	21.11	21.0	19.0	4–5	4–5	4–5	4	4–5	18.20
	C/W		21.30	23.26	18.5	17.0	4–5	4–5	5	5	5	21.29
Pigment Blue 153	V/W	−ve	11.09	0.00	0.00	0.00	3–4	4	3	3	4	23.11
	C/W		11.60	0.00	0.00	0.00	4	4	3	3	4	22.60
	V/W	+ve	15.31	38.05	20.0	18.0	4–5	4–5	4	4	5	26.95
	C/W		16.72	44.14	17.5	16.0	4–5	4–5	4	4	5	20.40
Pigment Orange 13	V/W	−ve	6.04	0.00	0.00	0.00	3	3–4	3	3	4	21.68
	C/W		6.75	0.00	0.00	0.00	4	4	4	4	4	20.56
	V/W	+ve	11.43	89.24	19.0	18.0	4	4	4–5	4	4–5	25.49
	C/W		12.90	91.11	16.5	15.0	4–5	4–5	5	4–5	4–5	22.37

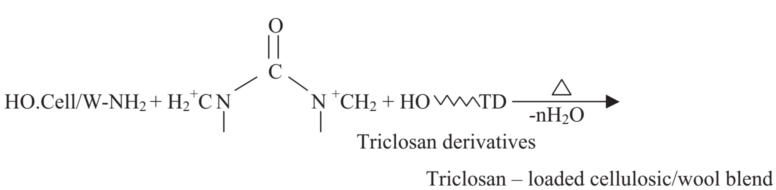
Printing paste constituents: pigment colorant (20 g/kg); binder (100 g/kg); thickener (20 g/kg); crosslinker (10 g/kg); catalyst (2 g/kg); PEG-600 (20 g/kg); fixation at 1300 W for 4 min.
For explanation of abbreviations see footnote to Table 1.
[f] SR: Surface roughness

Table 4
Effect of inclusion of 4-hydroxybenzophenone into the pigment printing formulations.

Pigment	Substrate	4-Hydroxy-benzophenone (5 g/kg)	***K/S***[a]	Incr. in ***K/S*** (%)	ZI (mm)[b]		WF[c]		RF[d]		LF[e]	UPF[f]
					G +ve	G −ve	Alt.	St.	Dry	Wet		
Pigment Red 146	V/W	−ve	13.94	0.00	0.00	0.00	3	3–4	3–4	3	3–4	65
	C/W		17.28	0.00	0.00	0.00	3–4	4	4	4	3–4	73
	V/W	+ve	16.20	16.21	16.5	15.5	4	4–5	4–5	4	4–5	90
	C/W		21.07	21.93	15.0	13.0	4	4–5	5	5	4–5	98
Pigment Blue 153	V/W	−ve	11.09	0.00	0.00	0.00	3–4	4	3	3	4	75
	C/W		11.60	0.00	0.00	0.00	4	4	3	3	4	88
	V/W	+ve	13.05	17.67	14.0	12.0	5	5	4	4	5	95
	C/W		14.50	25.00	12.5	11.0	4–5	4–5	4	4	5	103
Pigment Orange 13	V/W	−ve	6.04	0.00	0.00	0.00	3	3–4	3	3	4	87
	C/W		6.75	0.00	0.00	0.00	4	4	4	4	4	98
	V/W	+ve	9.40	55.63	12.5	10.5	4–5	4–5	4–5	4–5	4–5	110
	C/W		10.79	59.85	10.0	9.0	4–5	4–5	4–5	4–5	4–5	122

Printing paste constituents: pigment colorant (20 g/kg); binder (100 g/kg); thickener (20 g/kg); crosslinker (10 g/kg); catalyst (2 g/kg); 4-Hydroxybenzophenone (5 g/kg); fixation at 1300 W for 4 min.
For explanation of abbreviations see footnote to Table 1.
[f] UPF: UV-protection factor.

and helping the entrapment, accommodation and fixation of more pigment particles onto/within the modified binder film/fabric matrix during the fixation step (Ibrahim, Eid, Elmaaty, et al., 2013; Ibrahim, Khalil, et al., 2013), i.e. darker depth of shade and better fastness properties, (iii) the % increase in *K/S* values follow the decreasing orders: C/W > V/W and pigment orange 13 > pigment Blue 153 > pigment Red 146, keeping other parameters constant, (iv) immobilization of triclosan derivative onto/within the fabric and/or within the crosslinked network/fabric matrix with the help of the reactant resin:



(8)

via ionic interaction with wool component active sites:

via ionic interaction with wool component active sites:

$$HO.Cell/W\text{-}NH_2 + HO\sim\sim TD \xrightarrow[\Delta]{H^+} HO.Cell/W^{\cdot}\ {}^+NH_3.{}^-O \sim\sim TD \quad (9)$$

and/or via interactions among the binder/crosslinker/substrate/pigment:

$$HO.Cell/W\text{-}NH_2 + \text{Binding agent} + \text{Reactant resin} + \text{Pigment particles} \xrightarrow[\Delta]{H^+} \text{Cellulosic/wool pigment prints loaded with triclosan moieties} \quad (10)$$

is accompanied by a noticeable improvement in the antibacterial activity of the obtained pigment prints against the nominated G+ve and G−ve bacteria and follows the decreasing order: G+ve > G−ve, most probably due to the difference in their cell walls, (v) the imparted antibacterial activity to the functionalized cellulosic/wool pigment prints in governed by type of substrate: V/W > C/W, as well as the kind of pigment colorant: pigment Red 146 > pigment Blue 153 > pigment orange 13, keeping other parameters fixed, and (vi) antibacterial functionality of triclosan-loaded cellulosic/wool pigment prints most probably attributed to its ability to inhibit biosynthesis of fatty acid through blocking lipid biosynthesis thereby hindering both the building of cell membranes and reproduction (Cardamone et al., 1996; Lam et al., 2012; Orhan, Kut, & Gunesoglu, 2008).

3.3. PEG-600

The effect of incorporation of PEG -600, 20 g/kg, into the pigment printing pastes on antibacterial functionality and pigment printability of the used cellulosic/wool blended fabrics is given in Table 3. For a given set of concurrent finishing and pigment printing conditions, it is clear that: (i) inclusion of PEG-600, as a bio-active agent and as a substituent for urea for ecological reasons, in the printing formulations is accompanied by significant increase in the depth of the obtained prints along with an improvement in their fastness properties, (ii) this improvement in printing properties reflects the ability of PEG-600 to facilitate and increase the extent of pigment transfer from the thickening paste to the fibre surface, participate in side interactions with the used binding and/or crosslinking agents thereby enhancing the extent of polymerization and crosslinking, improve location and extent of distribution as well as adhesion and loading of binder film onto the fabric surface thereby affording more accessible sites for consequent entrapment and fixation of extra pigment particles onto/within the fibre/fabric matrix, i.e. higher *K/S* values and

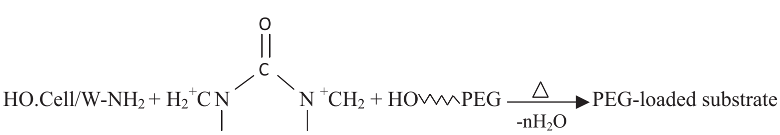
Table 5
Durability to wash.

Bio-active agent	Substrate											
	V/W						C/W					
	Without			15 washes			Without			15 washes		
	[a]K/S	[b]ZI (mm)		K/S	ZI (mm)		K/S	ZI (mm)		K/S	ZI (mm)	
		G +ve	G −ve		G +ve	G −ve		G +ve	G −ve		G +ve	G −ve
Choline chloride (5 g/kg)	15.61	22.5	21.0	13.00	18.5	17.0	20.19	21.0	20.0	16.91	17.0	15.0
Ruco®-BAC (20 g/L)	16.22	19.5	18.0	13.82	15.5	14.5	20.30	17.5	16.0	17.11	14.5	13.0
PEG-600 (20 g/kg)	16.88	21.0	19.0	14.46	17.0	15.0	21.30	18.5	17.0	18.02	15.0	14.0
4-Hydroxy-benzophenone(5 g/kg)	16.20	16.5	15.5	13.70	14.0	12.5	21.07	15.0	13.0	17.65	12.5	11.0

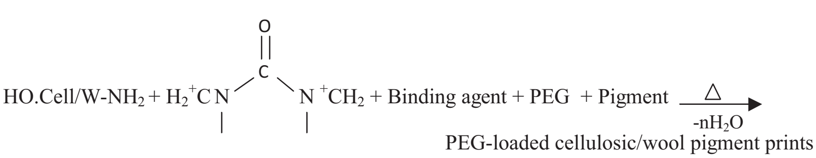
Printing paste constituents: Pigment Red 146 (20 g/kg); binder (100 g/kg); thickener (20 g/kg); crosslinker (10 g/kg); catalyst (2 g/kg); fixation at 1300 W for 4 min.
For explanation of abbreviations see footnote to Table 1.

better fastness properties, (iii) differences in printing properties would be expected to rely on nature of the substrate, C/W > V/W, as well as pigment colorant as mentioned before (iv) fixation of PEG-600 moieties onto/within the printed substrates during the microwave fixation step brings about a remarkable enhancement in their antibacterial efficacy, (v) the imparted antibacterial activity follows the decreasing orders: V/W > C/W prints, and pigment Red 146 > pigment Blue 153 > pigment orange 13, keeping other variables constant, (vi) antibacterial functionality of PEG-loaded pigment prints most probably attributed to a physico-chemical phenomenon and its ability to disrupt cell membrane equilibrium by causing dual hydrophobic–hydrophilic behavior (Gupta & Bhaumik, 2007; Vigo & Leonas, 1999), (vii) the effectiveness against *E coli* (G−ve) and *S. aureus* (G+ve) follows the decreasing order: G+ve > G−ve, and (viii) the imparted softness properties, expressed as a decrease in SR values, as compared with unloaded-PEG ones, is attributed to the lubricating effect of the loaded-PEG onto/within the cellulosic pigment prints and/or the binder film/fabric matrix.

The enhancements in the above-mentioned functional and coloration properties via inclusion of PEG-600 could be explained by the following reactions/interactions among the different ingredients and the substrate (Ibrahim, Amr, Eid, Mohamed, & Fahmy, 2012):



(11)



(12)

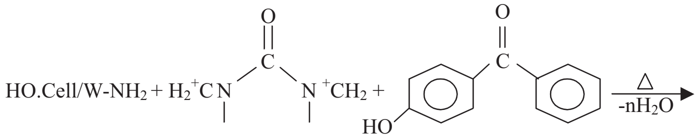
improvement in the fastness properties of the functionalized pigment prints, ii) the extent of enhancement in K/S values follows the decreasing orders: C/W > V/W, keeping the pigment colorant constant, and pigment orange 13 > pigment Blue 153 > pigment Red146, keeping the type of substrate fixed, (iii) the enhancement in the coloration properties reflects the positive impact of 4-hydroxybenzophenone on enhancing the extent of crosslinking and formation of three-dimensional linked network in which an extra pigment particles become embedded/entrapped/fixed onto the treated substrates surface during the microwave fixation step, i.e. darker depth of shade as well as better fastness properties, (iv) loading of benzophenone chromophoric group onto/within the modified pigment prints imparts a remarkable antibacterial ability against both the G+ve and G−ve bacteria under UV-light, (v) the imparted antibacterial activity most probably due to the toxic effects of the benzophenone chromophoric radicals initiated by the peroxidation of membrane lipid and/or through directly attack membrane proteins and their subsequent negative effects on membrane function (Hong & Sun, 2007; Ibrahim, Eid, Youssef, et al., 2013), (vi) the inactivation ability follows the decreasing order: G+ve > G−ve due to the presence of outer cell membrane, a barrier, in the G−ve bacteria structure, (vii) loading

The surface morphology of untreated and pigment prints loaded with PEG 600 is illustrated in Fig. 2a and b and Fig. 2c and d respectively. Fig. 2b and d clearly shows that the surfaces were coated with well distributed layer resulted from the deposition of pigment paste ingredients onto the surface of printed substrates.

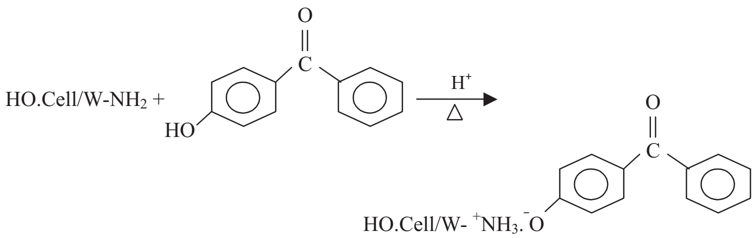
3.4. 4-Hydroxybenzophenone

Table 4presents the antibacterial, coloration and UV-protective properties of the cellulosic/wool pigment prints in the absence and presence of 4-hydroxybenzophenone (5 g/kg). The results show that: (i) adding 4-hydroxybenzophenone to the printing paste constituents results in an enhancement in the extent of pigment printing, expressed as depth of shade, *K*/*S* values, as well as an

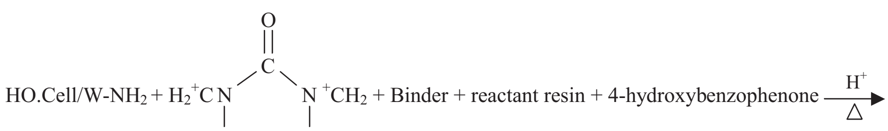
of 4-hydroxybenzophenone onto the obtained pigment prints results in a significant improvement in their UV-protection capacity, expressed as UPF values, (viii), this improvement in UPF values is attributed to the change in the structure of the nominated benzophenone from the keto to the enol form thereby increasing its ability to absorb the harmful UVB-radiation and preventing its penetration within the fabric structure (Ibrahim, El-Zairy, Abdalla, et al., 2013; Yang & Naarani, 2007; Orhan, Kut, & Gunesoglu, 2007), and (ix) the extent of upgrading the UV-protection capacity is governed by type of substrate, chemical structure of the pigment colorant and its ability to absorb the harmful UV-radiation, as well as the extent of loading the UV-absorber onto/within the fabric structure as follows:



Benzophenone-loaded cell/wool blend (13)



Benzophenone-loaded cellulosic/wool blend (14)



Benzophenone-loaded cellulosic /wool pigment prints (15)

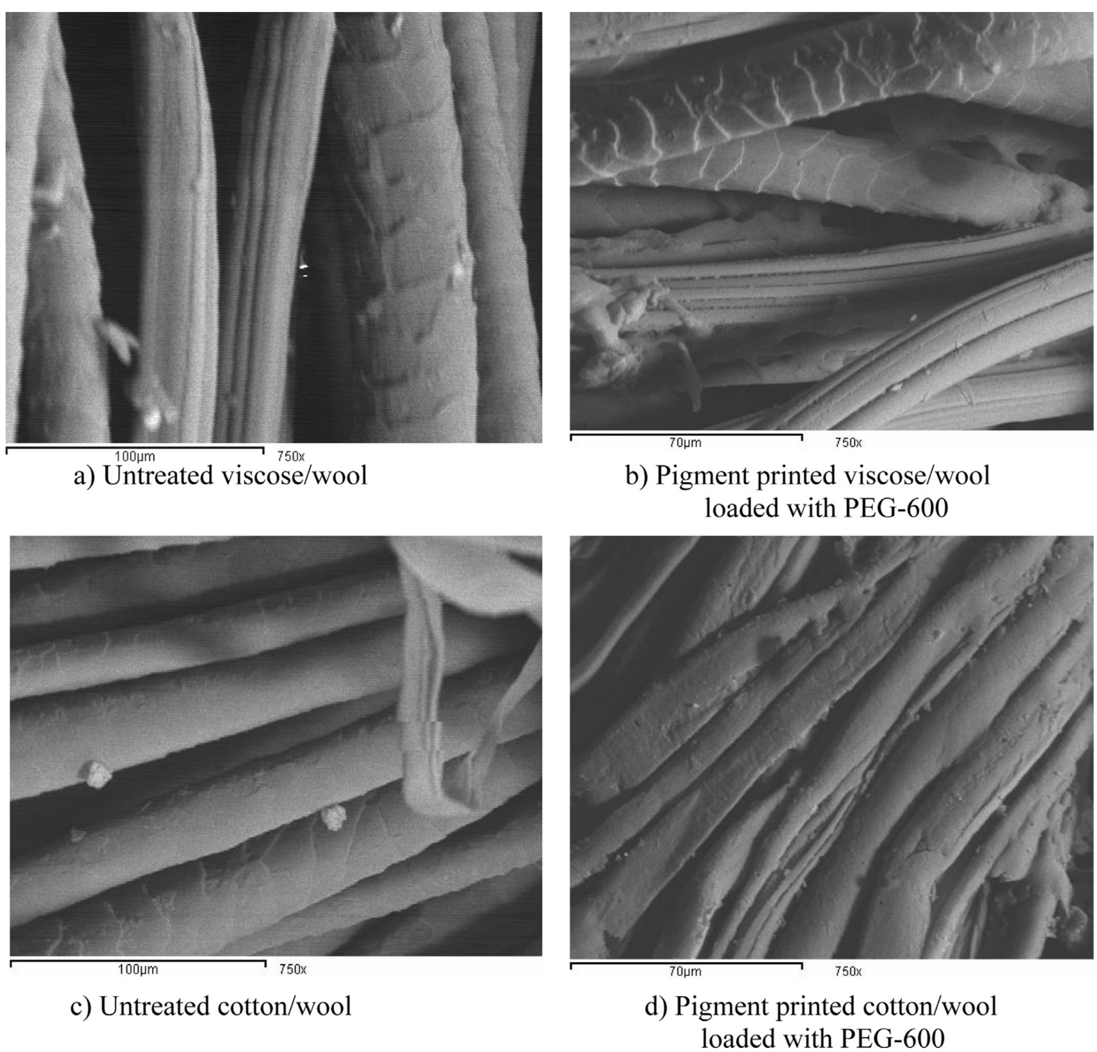


Fig. 2. SEM of untreated and pigment printed cellulosic/wool blend in loaded with PEG-600.

3.5. Durability to wash

Table 5 shows variation in the imparted functional and coloration properties after 15 consecutive washing cycles of the selected V/W and C/W pigment prints. From Table 5 it can be seen that (i) there is a reasonable decrease in both K/S and ZI values after 15 washings, regardless of the used antibacterial agent and fabric blend, (ii) this decrease is attributed to the removal of unfixed and/or physical entrapped active ingredients and pigment particles, (iii) the extent of retention of the imparted antibacterial activity as well as the depth of shade of the obtained pigments prints are determined by kind of the substrate, nature of bioactive ingredient as well as mode of interaction and fixation during the microwave fixation step, (iv) the higher the extent of fixation, the better the retained functional and coloration properties, and (v) the antibacterial efficacy remained highly effective, ≥80%, even after 15 cycles.

4. Conclusions

We have successfully developed a facile single-stage process for obtaining V/W and C/W pigment prints with remarkable and durable antibacterial activities. It was found that individual incorporation of choline chloride (5 g/kg), triclosan derivatives (20 g/kg), PEG-600 (20 g/kg) or 4-hydroxybenzophenone (5 g/kg) into free-solvent pigment pastes followed by flat screen printing and microwave fixation results in an improvement in the depth of the obtained pigment prints along with a remarkable enhancement in their antibacterial activity. The extent of improvement in the imparted functional properties, i.e. antibacterial, antibacterial/softness, or antibacterial/anti-UV, as well as the variation in the coloration properties, i.e. *K/S* and fastness, are governed by the nature of the reactive additives, the type of substrate as well as the kind of pigment colorant. The functionalized pigment prints showed a remarkable durability to wash.

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