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Combined UV-protecting and reactive printing of Cellulosic/wool blends

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ABSTRACT

A novel approach for attaining reactive cotton/wool and viscose/wool prints with outstanding UV-protection functions was achieved via inclusion of certain UV-absorbers namely 4-hydroxybenzophenone and UV-SUN® or UV-blockers like ZnO-NPs and TiO_2-NPs along with MCT-βCD, as a reactive additive, in the printing paste formulation using Na-alginate as a thickening agent. Experimental results reveal that the inorganic UV-blockers exhibit better UV-protection functions compared with the used UV-absorbers, and the improvement in the imparted UV-protection capacity follows the decreasing order: ZnO-NPs > TiO_2-NPs > 4-hyroxybenzopherone ≥ UV-SUN® ≫ none > untreated. The enhancement in UV-protection functionality is governed by the type of substrate, cotton/wool > viscose/wool, extent of modification and loading of the used nano-metal oxides or organic absorbers onto the fabric surface as well functionality and ability of the used reactive dyes to absorb the hazardous UV-B radiation. The obtained functional prints exhibited outstanding UV-protection efficiency even after 15 washing cycles.

1. Introduction

Cellulosic fibers have a happy combination of precious inherent properties such as abundance, low cost, hydrophilicity, comfortability, easy dyeability or printability, etc. (Cook, 2001). On the other hand, wool fibers are known as superior textile material because of their warmth, lightness, softness and smoothness (Montazer, Pakdel, & Behzadnia, 2011). Blending of Cellulosic/wool fibers can be discussed in terms of: upgrading the performance and quality properties, developing novel and fashionable textile products for value addition, satisfying the end user demands, and facing global competition in textile markets taking in consideration both the economical and environmental aspects (Charankar, Verna, & Gupta, 2007; Hyde, 1998; Ibrahim, 2011, chap. 4).

UV-radiation is composed of UV-A (320–400 nm), UV-B (280–320 nm) and UV-C type (200–280 nm). Excessive exposure to UV-B radiation would cause premature skin aging and damage, sunburns, and eventually skin cancer (Abidi, Hequete, Tarimala, & Dai, 2007). Therefore special attention has been focused on imparting UV-protection functionality especially for light weight apparels without adversely affecting their comfort properties (Ibrahim, Khalifa, El-Hossamy, & Tawfik, 2010, 2011). UV-protection ability of clothing is affected by fabric construction, i.e. weight, porosity and thickness, chemical composition of fabric material, color, textile auxiliaries and finishing process (Abidi et al., 2007; Alvarez & Lipp, 2003; Ibrahim, Refai, Youssef, & Ahmed, 2005; Riva & Algaba, 2006; Sarkar, 2004; Xin & Daoud, 2004).

The efficiency of UV-protection of a textile material is defined by its ultraviolet protection factor (UPF). The higher the UPF value, the greater is the protection category according to the Australian/New Zealand standard classification (AS/NZS 4399, 1996).

In recent years, considerable R & D efforts have been devoted to add or to improve the UV-protection function of textiles against the harmful UV-radiation, especially the UV-A and UV-B the main cause of skin cancer, via using UV-absorbers and/or inorganic blockers such as TiO_2, ZnO, Al_2O_3 and SiO_2 (Abidi et al., 2007; Akrman & Prikryl, 2008; Cheng, Li, Yuen, & Hu, 2006; Czajkowski, Paluszkiewicz, Stolarski, Kazmierska, & Grzesiak, 2006; Gorensek, Urbas, Strand, & Parac-Osterman, 2007; Grancaric, Tarbuk, Dumitrescu, & Biscan, 2006; Ibrahim, Amr, Eid, Mohamed, & Fahmy, 2012; Ibrahim, Eid, & El-Batal, 2012; Ibrahim, Eid, Hashem, Refai, & El-Hossamy, 2010; Ibrahim, El-Gamal, Gouda, & Mahrous, 2010; Ibrahim, El-Zairy, El-Zairy, & Khalil, 2011; Ibrahim, El-Zairy, & Eid, 2010; Ibrahim, Khalifa, et al., 2010, 2011; Ibrahim, Refai, & Ahmed, 2010; Montazer & Seifollahzadeh, 2011; Paul et al., 2010; Wang & Hauser, 2010). The inorganic UV-blockers are more preferred due to their non-toxicity and chemical stability under high temperature and UV-radiation exposure (Yang, Zhu, & Pan, 2004).

Herein, we report the feasibility of enhancing both the printing properties and UV-protecting functionalities of cotton/wool and viscose/wool fabric blends in one step to increase the value

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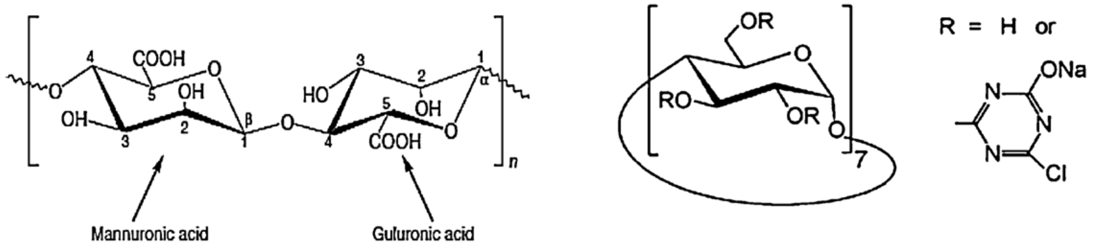
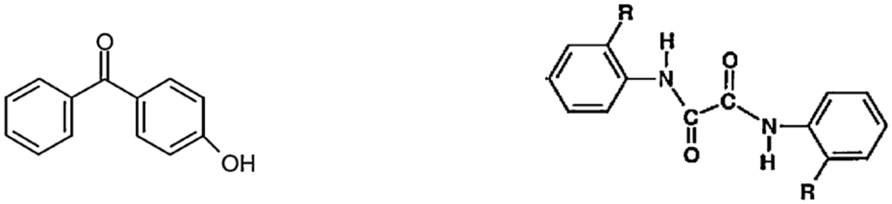


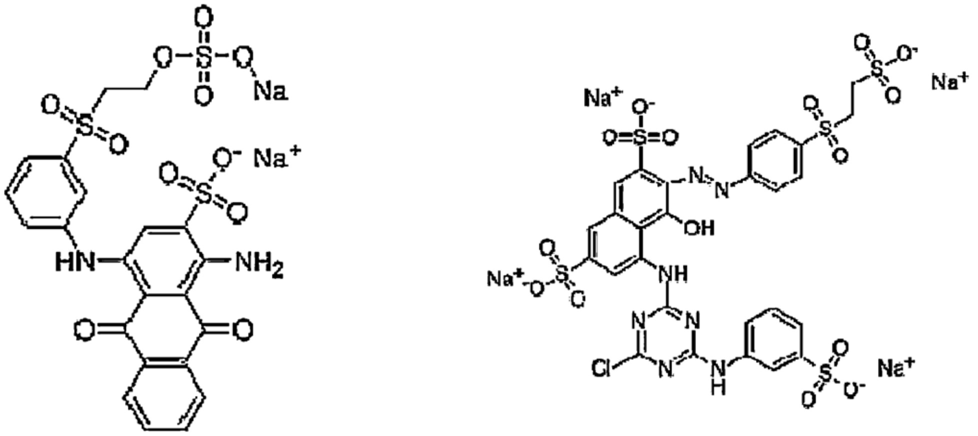
(a) Structural units of sodium alginate

(b) MCT- β-CD



(c) 4-hydroxybenzophenone

(d) Oxalanilides



(e) Reactive Blue 19

(f) Reactive Red 198

Fig. 1. Chemical structure of Na-alginate (a), MCT-βCD (b), 4-hydroxybenzophenone (c), oxalanilides (d), Reactive Blue 19 (e), and Reactive Red 198 (f).

addition and diversification. To achieve this goal, printing formulations, using Na-alginate as a thickening agent, were modified via incorporation of certain functional additives namely MCT-βCD, 4-hydroxy benzophenone, UV-SUN® CEL LIQ UV-absorber, ZnO-nanoparticles, and TiO_2-nanoparticles. Factors affecting both the printing and functional properties of the treated substrates such as type and concentration of additive, kind of substrate, as well as the used dyestuff were investigated.

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 in this study.

Cavasol® W7MCT [monochlorotriazinyl β-cyclodextrin, MCT-βCD, average molecular weight ~1560, degree of substitution (0.3–0.6 per anhydroglucose unit), Wacker, Germany], Dialgin® LV-100 [Na-alginate of low viscosity, BF-Goodrich Diamalt, GmbH, Germany], UV-SUN® CEL LIQ [UV-absorber based on oxalanildin, Huntsman, USA], Ludigol® [oxidizing agent based on m-nitrobenzene sulfonic acid sodium salt, BASF, Germany], and zinc-oxide nanoparticles [ZnO-NPs, dispersion, 50 wt.% in water, average particle size <35 nm, Aldrich], titanium iso-propoxide (AR, Grade, Sigma), and 4-hydroxybenzophenone (AR, Grade, Aldrich) were used.

Commercial reactive dyes namely Reactive Red 198 and Reactive Blue 19 [OH Young, Korea] were used as received.

Chemical structures of the used Na-alginate, MCT-βCD, 4-hydroxybenzophenone, UV-absorber and reactive dyestuffs are given in Fig. 1.

2.2. Methods

2.2.1. Preparation of TiO_2-NPs

TiO_2-nano sol was synthesized by mixing titanium isopropoxide (1%), as a precursor, with 100 ml of water containing nitric acid (1%) at room temperature to prepare the stock solution. The mixture was vigorously stirred for 20 h prior to using (Sundaresan, Sivakumar, Vigneswaran, & Ramachandran, 2011).

2.2.2. Combined functional finishing and printing

Blend Cellulosic/wool fabric samples were modified/printed using the flat screen technique and the following print paste formulations:

Constituent	g/kg paste
Dye	20 g
Na-alginate (10%)	500 g
Urea	100 g
Na-bicarbonate	20 g
MCT-βCD	10 g
Ludigol®	10 g
Functional additive:	
4-Hydroxybenzophenone (in acetone solvent)	0–15 g
UV-Sun® CEL	0–15 g
ZnO-NPs	0–5 g
or TiO_2-NPs	0–7.5 g
H_2O	X g
Total	1000 g

Printed fabric samples were then dried at 85 °C for 5 min and steam fixed at 110 °C for 20 min using Ariolt® CSL-Steamer-Italy, rinsed thoroughly, soaped for 15 min at 60 °C in the presence of 2 g/L Leomin® W (nonionic wetting agent and detergent-BASF), then thoroughly rinsed and finally dried at 85 °C for 5 min.

2.2.3. Testing

The depth of the obtained prints, expressed as K/S was measured at the wavelength of the maximum absorbance using an automatic-filter spectrophotometer, and calculated by the Kubelka–Munk equation (Judd & Wyszeck, 1975):

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

where K, S, and R are the absorption coefficients, the scattering sufficient and the reflectance at the wavelength of maximum absorbance of the used dye respectively.

Fastness properties to washing, crocking, perspiration and light of printed fabric samples were evaluated according to AATCC test methods: (61-1972), (8-1972), (15-1973) and (16A-1972) respectively.

UV-protection factor (UPF) was evaluated according to AS/NZS 4399-1996 standard.

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

The durability to wash (after 15 launder cycles) was determined according to AATCC test method 135-2000.

3. Results and discussion

Since the main target of the present work is to search for the proper printing formulation for enhancing both the printing properties and the UVB-protection capacity of Cellulosic/wool blends namely cotton/wool and viscose/wool fabrics, a wide range of parameters have been studied. Results obtained along with appropriate discussion follow.

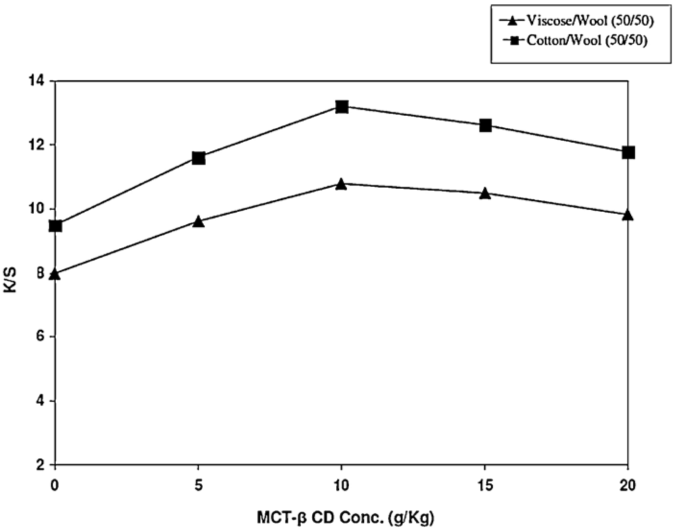


Fig. 2. Effect of MCT-βCD concentration on printability with Reactive Blue 19.

3.1. MCT-βCD concentration

Fig. 2 shows that inclusion of MCT-βCD, with its hydrophilic outer surfaces and internal hydrophobic hollow interior, into the printing formulation up to 10 g/kg brings about a significant improvement in K/S values of the obtained prints regardless of the used substrate. This enhancement in the depth of the obtained prints reflects the positive impacts on grafting and immobilization of MCT-βCD moieties onto the printed substrates through covalent bonds formation [Eq. (1)] thereby enhancing their hydrophilicity, increasing the number of active sites (Denter & Schollmeyer, 1996), i.e. hydroxyl groups, and producing modified structure more readily printable with the used Remazol dye which, in turn facilitated and increased the extent of dye fixation [Eqs. (2), (3) and (5)] according to the tentative scheme of reactions (Scheme 1) (Ibrahim, 2011, chap. 4; Ibrahim & El-Zairy, 2009; Ibrahim, El-Zairy, et al., 2010; Savarino, Viscardi, Quagliotto, Montoneri, & Barni, 1999; Szejtli, 2003; Xia & Lin, 2004).

Additionally, further increase in MCT-βCD concentration, i.e. beyond 10 g/kg, has practically a negative impact on the depth of the obtained prints. This can be attributed to the increase in the viscosity of printing pastes, side interaction with MCT-βCD along with partial hydrolysis of MCT-βCD [Eqs. (4) and (6) respectively], thereby hindering the mobility of dye molecules as well as their extent of fixation onto the fabric surface, i.e. lower depth of shade. Therefore, 10 g/kg MCT-βCD seems to be a proper concentration.

It was also interesting to note that, the extent of printing is governed by the type of substrate and follows the decreasing order: cotton/wool > viscose/wool, probably due to their differences in fabric construction, i.e. weight, thickness, and porosity, extent of modification and subsequent undue penetration of dye molecules (Ibrahim, Abo-Shosha, Allam, & El-Zairy, 2010; Ibrahim, El-Zairy, et al., 2011).

3.2. Inclusion of UV-absorbers

As far as the change in K/S values of the printed substrates as a function of type and concentration of the used UV-absorbers namely 4-hydroxybenzophenone and UV-SUN® CEL, Fig. 3a discloses that: (i) increasing both of the used functional additives concentration up to (5 g/kg) results in a significant improvement in the depth of the obtained prints irrespective of the used substrate, (ii) further increase in concentration, i.e. beyond 5 g/kg, is accompanied by a slight decrease in K/S values, and (iii) the extent

i) Loading of MCT-βCD onto the substrate

$$\text{HX-Cell/ W-XH} + \text{YMCT-}\beta\text{CD} \sim (\text{OH})_n \xrightarrow[\text{Steam}]{\text{OH}^-}$$

Blend (I)　　MCT-βCD

$$(\text{HO})_n - \beta\text{CD} - \text{MCT} - \text{X} - \text{Cell./W-X-MCT-}\beta\text{CD} \sim (\text{OH})_n + \text{n HY} \quad (1)$$

Modified substrate (II)

ii) Formation of vinyl sulphone

$$\text{D.SO}_2\text{.CH}_2\text{.CH}_2\text{.OSO}_3\text{Na} \xrightarrow[\text{Steam}]{\text{OH}^-} \text{D. SO}_2\text{.CH} = \text{CH}_2 + \text{HOSO}_3\text{Na} \quad (2)$$

Remazol dye　　Vinyl form

iii) Nucleophilic addition

$$\text{(I) and/or (II) +n D. SO}_2\text{ CH} = \text{CH}_2 \xrightarrow[\text{Steam}]{\text{OH}^-}$$

Modified/printed substrate (3)

$$\text{n D. SO}_2\text{.CH} = \text{CH}_2 + \text{MCT- }\beta\text{CD} \sim (\text{OH})\text{n} \xrightarrow[\text{Steam}]{\text{OH}^-}$$

$$\text{n DSO}_2\text{ CH}_2\text{ CH}_2\text{.O} \sim (\beta\text{CD} - \text{MCT}) \quad (4)$$

Inclusion complex (easily washable)

iv) Nucleophilic substitution and addition

$$\text{HX} - \text{Cell/W-XH} + \text{n MCT} - \beta\text{CD} \sim (\text{OH})\text{n} + \text{n DSO}_2\text{.CH} = \text{CH}_2 \xrightarrow[\text{Steam}]{\text{OH}^-}$$

printed substrate anchoring – βCD moieties (5)

v) Side interactions

$$\text{YMCT-}\beta\text{CD} \sim (\text{OH})_n \xrightarrow[\text{Steam}]{\text{OH}^-}$$

Partially hydrolyzed MCT-βCD (6)

$$\text{D.SO}_2\text{.CH=CH}_2 \xrightarrow[\text{Steam}]{\text{OH}^-} \text{D. SO}_2\text{CH}_2 - \text{CH}_2\text{OH} \quad (7)$$

Partially hydrolyzed dye

where Cell. = Cellulose, W = wool, X-H = - OH, -NH_2 and/or- SH, Y = Cl

Scheme 1. The proposed reactions mechanism.

of improvement in the *K*/*S* values is governed by type of additive: 4-hydroxybenzophenone > UV-SUN® CEL, and kind of substrate cotton/wool > viscose/wool keeping other parameters constant.

Enhancement in the depth of the obtained prints upon adding the nominated UV-absorbers, up to 5 g/kg, to the printing formulations may probably be due to: (i) formation of an inclusion complex:

$$\beta\text{CD} + \text{UV-absorber} \rightleftharpoons \beta\text{CD-UV-absorber} \quad (8)$$

in the inner cavity of the loaded βCD ring thereby hindering the extent of formation of [βCD–dye inclusion complex] and increasing the availability and accessibility of dye molecules to interact chemically with the available dyeing sites onto the fabric surface, and (ii) the probability of side interactions among the used additives (4-hydroxybenzophenone or UV-SUN® CEL, a bi-reactive oxalic acid di-anilide derivative), the dye molecules and the substrate cannot be ruled out, thus finally resulting in more dye fixation (Ibrahim & El-Zairy, 2009; Ibrahim, Gouda, Husseiny, El-Gammal, & Mahrous, 2009; Szejtli, 2003). On the other hand, the slight decrease in *K*/*S* values upon using higher additive concentration, i.e. >5 g/kg, may also simply be attributed to a shortage in and blocking of available and accessible active dyeing sites onto the fabric surface.

Fig. 3b shows the anti-UV radiation properties of the modified/printed fabric samples as a function of type and concentration of the nominated UV-absorbers. It is clear that incorporation of

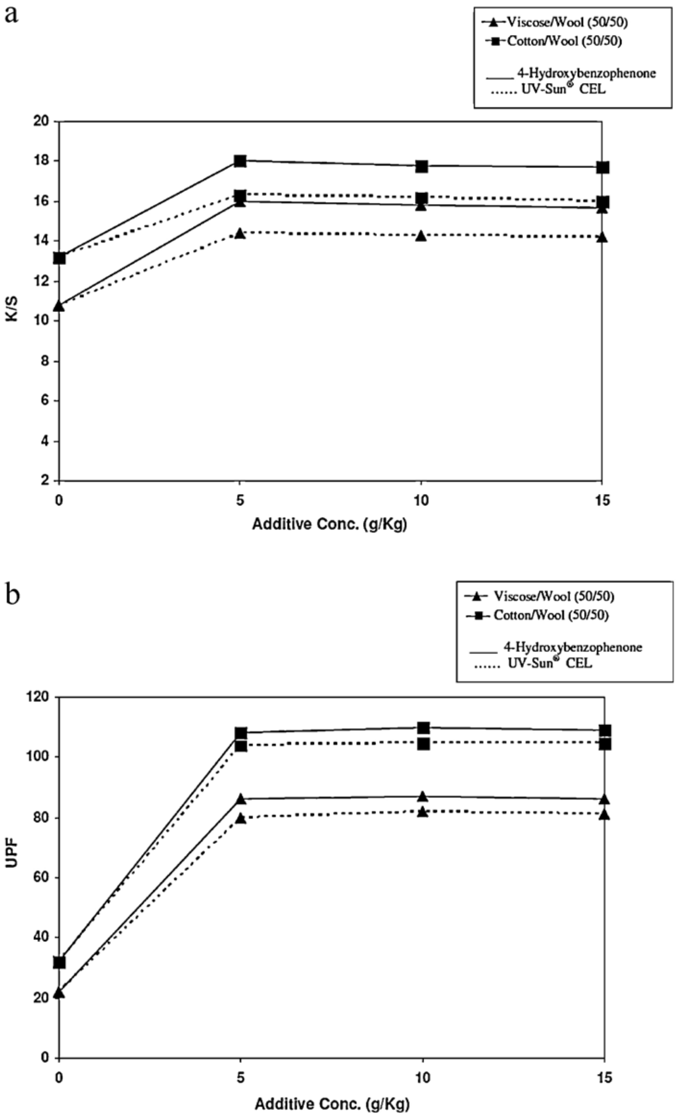
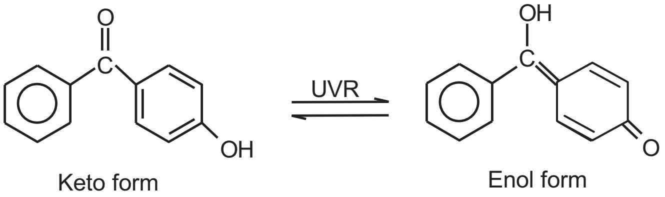


Fig. 3. Effect of functional additive concentration on *K*/*S* (a) and UPF values (b) of printed fabric samples.

a benzophenone moiety, by loading 4-hydroxybenzophenone, or an oxalanilide moiety, by loading UV-SUN® onto/into the fabric structure as a functional additive, 5 g/kg, results in an outstanding enhancement in the UPF properties regardless of the used substrate. The extent of upgrading the UV-protective functionality is governed by type of additive: 4-hydroxybenzophenone ≥ UV-SUN® CEL, as well as type of substrate: cotton/wool > viscose/wool. Further increase in the UV-absorber concentration has practically no effect on the imparted UV-B protection functionality.

Excellent UPF values of 4-hydroxybenzophenone loaded fabric samples reflects their higher degree of UV-B absorption capacity and ability to dissipate energy through the subsequent change of the UV-absorber structure from keto to enol form as follows (Hong & Sun, 2008):



(9)

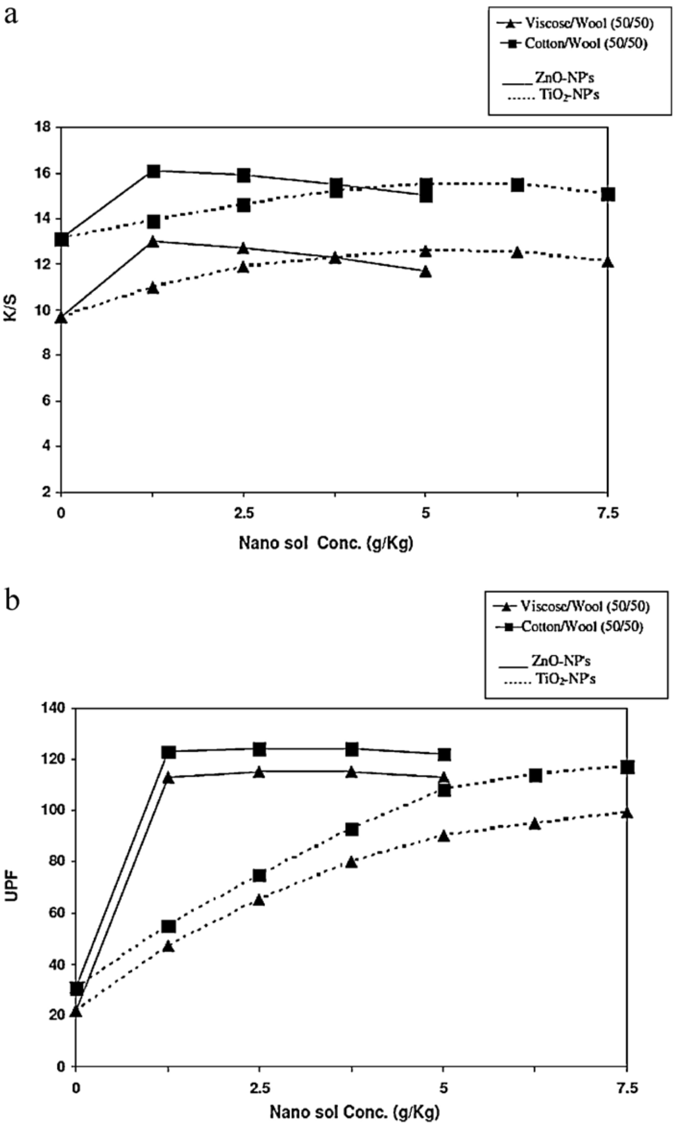
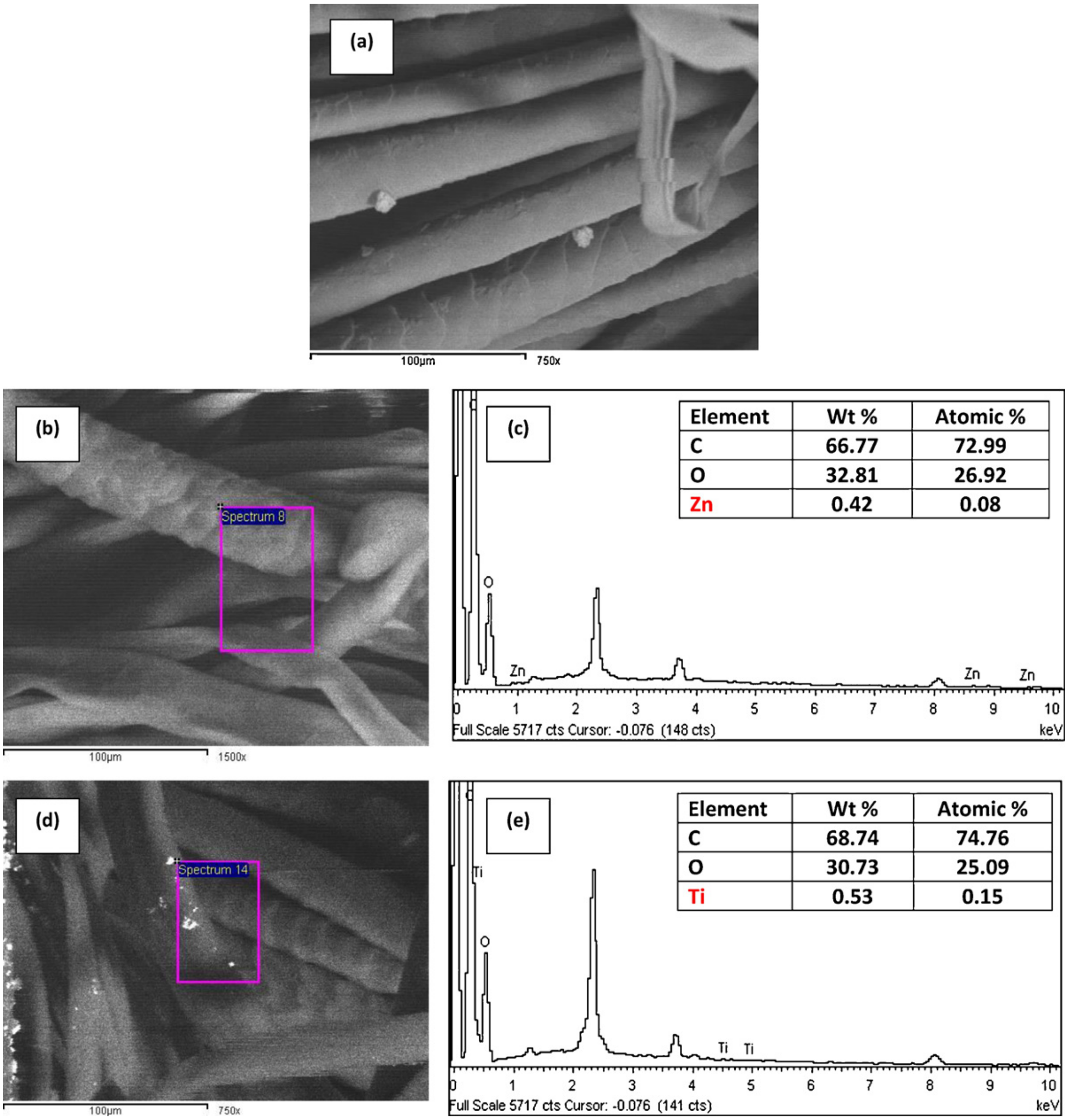


Fig. 4. Effect of nano sol type and concentration on *K*/*S* (a) and UPF values (b) of printed fabric samples.

Therefore, 5 g/kg UV-absorber seems to a proper concentration for attaining higher depth of shades along with excellent UPF-values, regardless of the used substrate.

3.3. *Influence of UV-blocking additive*

The effect of type and concentration of the added nano-sols namely ZnO-NPs and TiO_2-NPs on the *K*/*S* values of the printed fabric samples was also investigated (Fig. 4a). Within the range examined, it was observed that increasing concentration of ZnO-NPs up to 1.25 g/kg or TiO_2-NPs up to 5 g/kg in the reactive printing formulation along with other components results in an improvement in the depth of the obtained prints. This can be discussed in terms of better binding and fixation of the dye molecules onto/into the fabric structure via the interaction of the deposited and/or immobilized nano-particles onto/within the substrate with the functional groups and solubilizing groups of the dye, e.g. $-NH_2$, $-NH$, $-SO_3Na$, etc. On the other hand, the positive role of deposited nano-particles on decreasing the electrostatic repulsion between the blended fibers and the dye and/or water absorption features of fabrics which in turn resulted in enhanced extent of dye uptake



Element	Wt %	Atomic %
C	66.77	72.99
O	32.81	26.92
Zn	0.42	0.08

Element	Wt %	Atomic %
C	68.74	74.76
O	30.73	25.09
Ti	0.53	0.15

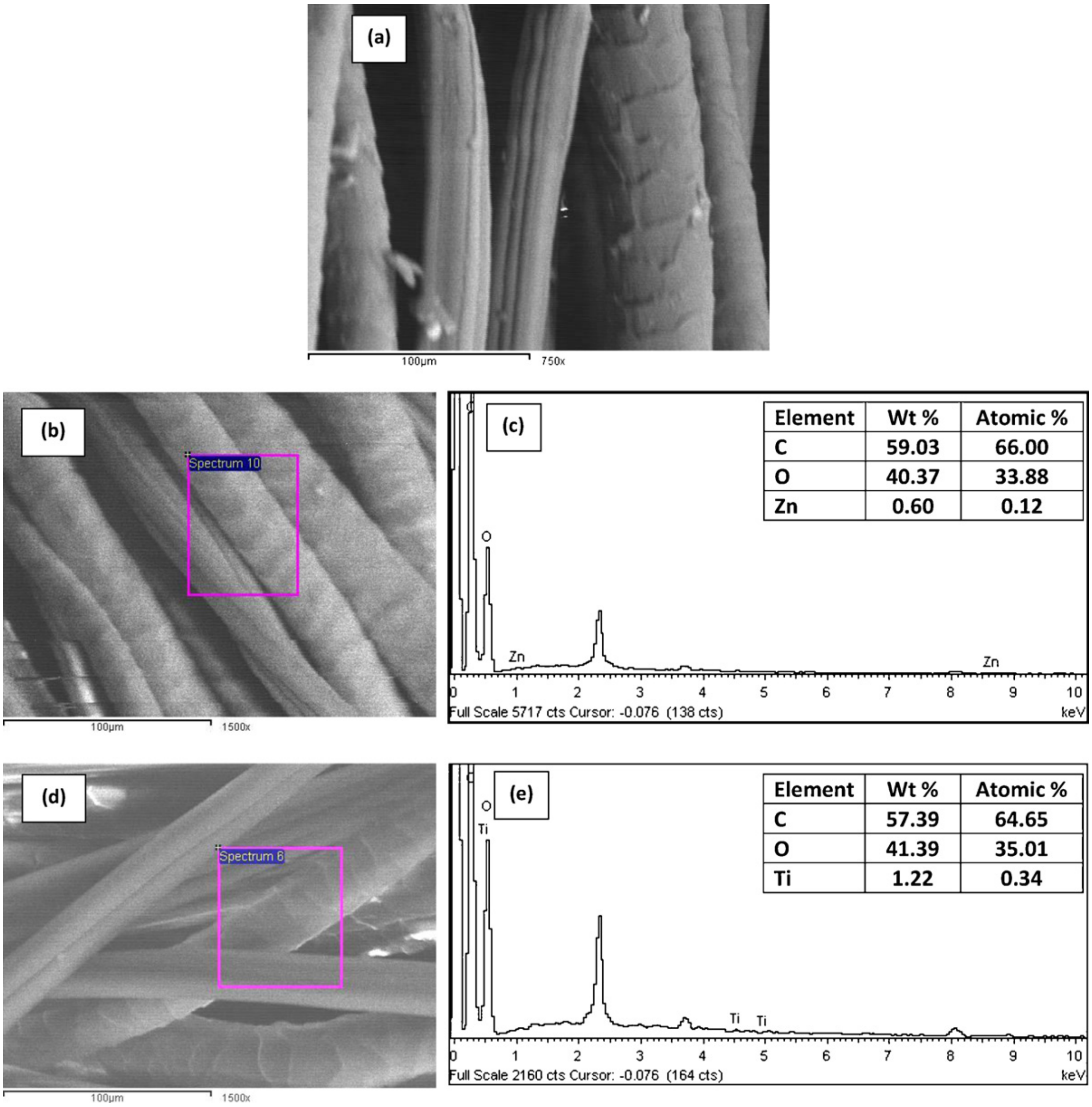
Fig. 5. SEM of untreated wool/cotton fabric (a), SEM of treated wool/cotton fabric with ZnO-NPs (b), EDX image and element content of ZnO-NPs loaded substrate (c), SEM of treated wool/cotton fabric with TiO_2-NPs (d), and EDX image and element content of TiO_2-NPs loaded substrate (e).

on the blend components cannot be ruled out (Montazer et al., 2011).

It was also revealed from Fig. 4a that the *K*/*S* values of the printed blends governed by type of substrate, i.e. cotton/wool > viscose/wool, as well as kind of nano metal oxide, ZnO-NPs > TiO_2-NPs. This reflects the differences between ZnO and TiO_2-NPs in shape, molecular size distribution and content, extent of location, distribution and fixation, their binding capacity, and ability to form metal chelates with the dye thereby darkening the shade without adversely affecting the hue, as in case of using ZnO-NPs (Ibrahim, El-Gamal, et al., 2010; Ibrahim, Mahrous, El-Gamal, Gouda, & Husseiny, 2010). On the other hand further increase in nano metal oxide concentration has a negative impact on the *K*/*S* values, most probably due to blocking and/or shortage in dye active sites on the fabric surface and/or hindering the mobility and transfer of the dye molecules from the printing paste film toward the fabric surface during the steam fixation step, i.e. lower extent of printing.

Fig. 4b illustrates the influence of incorporating ZnO-NPs or TiO_2-NPs, as a UVR-blocker, at different concentrations in the printing paste on the UPF values of the obtained printings. It can be seen from Fig. 4b that increasing the nano ZnO-sol concentration up to 1.25 g/kg or nano TiO_2-sol concentration up to 5 g/kg in the printing paste results in a remarkable improvement in the UPF value, >50+, regardless of the used substrate, clearly indicating that the treated substrates possessed excellent UV-blocking and protection properties.

The imparted extraordinary performance of UV-protection to the obtained printings reflects the positive impact of nano-sized ZnO and TiO_2 on enhancing the UV-blocking property due to their increased surface area as well as intense absorption in the UV-region (Bringer & Hofer, 2004; Ibrahim, Amr, et al., 2012; Yang et al., 2004). On the other hand, the extent of improvement in the UV-blocking activity of the fabrics, as indicated by UPF values, is determined by: the absorption capacity of the used nano-metal oxides in the UV-region of 280–400 nm, extent of excitation of their



Element	Wt %	Atomic %
C	59.03	66.00
O	40.37	33.88
Zn	0.60	0.12

Element	Wt %	Atomic %
C	57.39	64.65
O	41.39	35.01
Ti	1.22	0.34

Fig. 6. SEM of untreated wool/viscose fabric (a), SEM of treated wool/viscose fabric with ZnO-NPs (b), EDX image and element content of ZnO-NPs loaded substrate (c), SEM of treated wool/viscose fabric with TiO_2-NPs (d), and EDX image and element content of TiO_2-NPs loaded substrate (e).

electrons to cross the band gap, so as to produce pairs of electrons, holes and subsequent their ability to combine with other holes or electrons, thereby acting as a UV-protector (Yang et al., 2004). In addition, the UPF values, keeping other parameters constant, were affected by the type of substrate and followed the decreasing order: cotton/wool > viscose/wool which could be discussed in terms of differences between the two substrates in physical aspects of fabric, extent of printing as well extent of loading and distribution of the nano-sized metal oxides.

It is also evident from Fig. 4b that further increase in the prepared sol concentration has practically no significant positive effect on the imparted UV-blocking activity, expressed as UPF values.

3.4. SEM micrographs and EDX spectrum

The SEM images of the untreated and treated cotton/wool (Fig. 5a, b and d) and viscose/wool (Fig. 6a, b and d) show the deposition of the metal oxide-nanoparticles onto the treated fabric samples. Moreover, the existence of elementary Zn (Figs. 5c and 6c) or Ti (Figs. 5e and 6e) as detected by EDX confirms the loading of nominated metal oxides nanoparticles onto the top layer of the treated fabric samples. The extent of loading ZnO-NPs and TiO_2-NPs is governed by type of substrate, extent of modification as well as degree of fixation onto the fabrics surface.

3.5. Performance and functional properties

Effect of using different UV-absorbers such as UV-SUN® and 4-hydroxybenzophenone or UV-blockers such as ZnO-NPs and TiO_2-NPs on the printing properties and UV-protection activities of the used substrates are shown in Table 1. For a given set of printing formulations and conditions, the data so obtained signify that: (i) incorporation of the above mentioned additives individually in the printing paste results in a significant improvement in *K*/*S*, fastness properties as well as the UPF values of the obtained printings, (ii) the extent of improvement in the obtained properties is governed by type of substrate, type of reactive dye as well as kind of the UV-absorber or blocker, (iii) washing, rubbing and perspiration fastness properties of the printed fabric samples, using the nominated functional additives, were very good to excellent, regardless

Table 1
Effect of using different dyes, additives and substrates on both the printing and UV-protecting properties.

Dyestuff (20 g/kg)	Substrate	Additive	*K/S*	Incr. in *K/S* (%)	WF		RF		PF				LF	UPF[a]
					Alt	C	Dry	Wet	Acidic		Alkaline			
									Alt	C	Alt	C		
Reactive Blue 19	Cotton/wool	None	13.30	–	4	4	4	4	4	4	4	4–5	3	32 (25)[b]
		UV-Sun® CEL (5 g/kg)	16.28	22.41	4–5	5	4–5	4–5	4–5	5	4–5	4–5	4	104 (90)
		4-Hydroxybenzophenone (5 g/kg)	18.01	35.41	5	4–5	4–5	4–5	5	4–5	4–5	5	5	108 (96)
		TiO_2-NPs (5 g/kg)	15.50	16.54	4–5	5	5	4–5	4–5	4–5	4–5	5	4–5	114 (100)
		ZnO-NPs (1.25 g/kg)	16.19	21.73	4–5	4–5	4–5	5	5	5	4–5	5	4–5	122 (110)
	Viscose/wool	None	10.84	–	3–4	4	4	3	4	3–4	4	4	3	23 (15)
		UV-Sun® CEL (5 g/kg)	14.44	33.21	4–5	5	4–5	4	4–5	4–5	5	5	4–5	80 (71)
		4-Hydroxybenzophenone (5 g/kg)	16.02	48.71	4–5	4–5	5	4–5	4	4	5	5	5	88 (76)
		TiO_2-NPs (5 g/kg)	12.75	17.62	5	5	4–5	4–5	4	4	5	4–5	4–5	92 (85)
		ZnO-NPs (1.25 g/kg)	13.03	20.20	4–5	4–5	4–5	4–5	4–5	4	5	5	4–5	108 (100)
Reactive Red 198	Cotton/wool	None	4.13	–	4	3–4	4	3–4	4	3–4	4–5	4	4	32 (25)
		UV-Sun® CEL (5 g/kg)	6.57	59.08	4–5	4	4–5	4	4–5	4	4–5	4–5	4–5	87 (80)
		4-Hydroxybenzophenone (5 g/kg)	7.80	88.86	5	4–5	4–5	5	4–5	4–5	4–5	4–5	5	100 (91)
		TiO_2-NPs (5 g/kg)	7.39	78.93	5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	110 (101)
		ZnO-NPs (1.25 g/kg)	7.89	91.04	4–5	4–5	4	4	4–5	4–5	5	5	5	116 (106)
	Viscose/wool	None	3.79	–	4	4	4	4	4	4	3–4	4	4	23 (15)
		UV-Sun® CEL (5 g/kg)	6.10	60.95	4–5	4–5	4–5	4–5	4–5	5	4–5	4–5	4–5	76 (68)
		4-Hydroxybenzophenone (5 g/kg)	7.44	96.31	5	4–5	5	4–5	4–5	4–5	4–5	4–5	5	82 (72)
		TiO_2-NPs (5 g/kg)	7.08	86.81	4–5	5	4–5	4–5	4–5	5	4–5	4–5	4–5	104 (95)
		ZnO-NPs (1.25 g/kg)	7.38	94.72	5	4–5	4–5	4–5	5	4–5	4	4–5	5	109 (97)

[a] UPF of untreated substrates are:

Cotton/wool = 20
Viscose/wool = 15.

[b] Values in parentheses indicate retained UV-protection property after 15 washings.

of the used reactive dye, (iv) the presence of MCT-βCD along with the nominated reactive dyes, without any further additives, also contributed toward increasing the UPF values compared with the untreated ones (20 for cotton/wool and 15 of viscose/wool substrates), (v) the slight improvement in the light fastness reflects the positive impact of the used additives on decreasing the strength of the incident light on the fabric surface thereby minimizing or preventing the light fading of the used reactive dyes (Yang & Naarani, 2007), (vi) the extent of improvement in the UV-protective property is determined by nature of the functional additive, keeping other parameters fixed, and follows the decreasing order: ZnO-NPs > TiO_2-NPs > 4-hydroxybenzophenone > UV-SUN® ≫ none, and (vii) there is a slight decrease in the UPF values of the obtained printings even after 15 washings.

4. Conclusions

- Reactive printed Cellulosic/wool blends with an excellent UV-protection functions have been developed by including certain UV-absorbers namely 4-hydroxybenzophenone and UV-SUN® or UV-blockers like ZnO-NPs and TiO_2-NPs along with MCT-βCD in the reactive printing formulations.
- Compared with the used UV-absorbers, nano-scale metal oxides, ZnO-and TiO_2-NPs, UV-blockers exhibit better UV-protection capacity.
- The extent of improvement in UPF values of the obtained printings, as a function of type of additive, follows the decreasing order:
  ZnO-NPs > TiO_2-NPs > 4-hydroxybenzophenone ≥ UV-SUN® ≫ none > untreated.
- The depth of the obtained prints, fastness properties and their UV-protection capacities are governed by type of substrate, cotton/wool > viscose/wool, and the functionality of reactive dye, i.e. mono (Reactive Blue 19) or bi-functional (Reactive Red 198).
- After 15 washes, the printed fabrics still had an excellent UV-protection functions.
- The developed process can be easily adapted on industrial scale using the available printing equipments.

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