



A cleaner production of ultra-violet shielding wool prints



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ABSTRACT

There is an urgent need to reduce the environmental impacts of textile wet processes taking in consideration product and environmental quality as well as economic concerns. Substitution of hazardous chemicals at the source and/or shortening the production steps are potential options which could be used to move towards cleaner production process and to cope with ever-increasing demands for eco-friendly textile products. In this research the possibility of enhancing both the ultra-violet shielding and coloration properties of wool fabric in a single-stage using β -cyclodextrin or monochlorotriazinyl β -cyclodextrin as well as certain ultra violet absorbers or blockers as additives to other environmentally benign printing paste components was investigated. The modified one-step coloration and functionalization method, using safer textile auxiliaries, less energy, and water consumption, proved to have positive impacts on the depth of the obtained prints and their fastness properties as well as on their ability to shield the harmful ultra-violet B-radiation without seriously affecting the environment. The enhancement in the imparted properties is governed by type of cyclodextrin, degree of fixation onto/within the wool structure, type and extent of immobilization of the used ultra violet protector, type of dye and its mode of interaction, as well as degree of interactions among the nominated printing paste components and the wool active sites during the steam fixation step. The imparted ultra-violet protection properties to the modified wool prints show obviously improved durability to wash compared to the unmodified ones.

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1. Introduction

Cyclodextrins (CDs) are non-toxic cyclic oligosaccharides having the capacity to form non-covalent host-guest inclusion complexes with a variety of guest molecules. The extent of formation, stabilization, protection as well as the controlled release of the functional guest molecules are governed by the type of host CD, i.e. α -, β - or γ -CD, along with the appropriate size and structure of functional additive (Buschmann et al., 2001; Del Valle, 2004). Among the three major CDs, β -cyclodextrin (β -CD) appears to be the most useful complexing agent taking in consideration its size, availability as well as production cost (Pinho et al., 2014; Szejtli, 2003; UL-Islam, 2013a).

Recently, the potential applications of textile auxiliaries based on β -CD derivatives in the textile domains have been attracted a lot of attention especially in the fields of textile coloration and/or

functionalization to impart new and desirable functional properties such as UV-protection (Ibrahim et al., 2013a; Perrin et al., 2007), antibacterial (Ibrahim et al., 2013b; Pinho et al., 2014; Racu et al., 2012), anti-insect, antistatic, cosmeo textiles etc (Lo Nastro et al., 2003; Szejtli, 2003; UL-Islam et al., 2013b) as well as in effluent treatment (Ducoroy et al., 2008).

Moreover, considerable efforts recently have been devoted to implement cleaner production measures (Niinimäki and Hassi, 2011; Roy Choudhury, 2013; Taylor, 2006), and upgrade the functional and coloration properties of wool-based textiles (Ghahen et al., 2014; Ibrahim, 2011; Ibrahim et al., 2012), taking in consideration the growing demands for comfort, health, hygiene, easy care and durable high grade products (Ibrahim et al., 2013c; Kelly and Johnston, 2011) while ensuring a remarkable protection against physico-chemical and/or microbial attacks (Montazer and Pakdel, 2011; Radetic, 2013; Zhang et al., 2014). In this contribution, β -cyclodextrin (β CD) or monochlorotriazinyl β -cyclodextrin (MCT- β CD) has been incorporated in the printing formulations of wool fabric along with certain functional additives to obtain wool prints with remarkable UV-protective property.

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2. Materials and methods

Plain weave 100% mill-scoured and semi-bleached wool fabric (W-XH, where XH = $-\text{NH}_2$, $-\text{OH}$ and/or $-\text{SH}$) 220 g/m² was used.

Cavasol[®] W7MCT [monochlorotriazinyl β -cyclodextrin, MCT- β CD, average molecular weight ~1560, degree of substitution (0.3–0.6 per anhydroglucose unit), Wacker, Germany], Cavasol[®] W7 [beta cyclodextrin with seven glucose units, Wacker, Germany], Dialgin[®] LV-100 [Na-alginate of low viscosity, BF-Goodrich Diamalt, GmbH, Germany], UV-SUN[®] CEL LIQ [UV-absorber based on oxalanilidin, Huntsman, USA], Ludigol[®] [Oxidizing agent based on m-nitrobenzene sulfonic acid sodium salt, BASF-Germany], and Arkofix[®] NDF liquid C [low formaldehyde-reactant resin based on modified N-methylol dihydroxyethylene urea, Clariant], were of commercial grade.

In addition, commercial disperse dyes [Disperse Blue 183, and Disperse Red 74 Sinochem Ningbo, China], reactive dyes [Reactive Red 198 (hetero-bifunctional) and Reactive Blue 19 (vinyl sulfone), OH young, Korea], and acid dyes [Acid Red 266 and Acid Blue 40 (Thai Ambica, Thailand)] were used in this study.

ZnO-nanoparticles [50% wt. % in water, particle size <35 nm, avg., Aldrich], Ti-tetraisopropoxide [analytical grade, sigma], 4-hydroxybenzophenone [analytical grade, Aldrich], and other laboratory, grade chemicals such as citric acid, acetic acid, nitric acid, Na-bicarbonate and PEG-600 were employed.

2.1. Synthesis of TiO₂-NPs

Synthesis of TiO₂-NPs sol, using Ti-isopropoxide as precursor, was carried out according to a previously reported method (Ibrahim et al., 2013a).

2.2. Concurrent functionalization and coloration

The wool fabric samples were prepared in 15 × 5 cm² swatches. Concurrent anti-UV functionalization and coloration of wool fabric samples was performed using the flat screen technique and the following print paste formulations:

Constituent	g/kg paste
a- Disperse dye	20
Na-alginate (10%)	500
Citric acid	10
DMDHEU (35%)	10
β CD (Cavasol [®] W7)	15
PEG-600 (without using carrier)	20
b- Acid dye	20
Na-alginate (10%)	500
Citric acid	10
DMDHEU (35%)	10
β CD (Cavasol [®] W7)	15
PEG-600	20
c- Reactive dye	20
Na-alginate (10%)	500
MCT- β CD (Cavasol [®] W7-MCT)	15
Na-bicarbonate	10
Ludigol [®]	10
PEG-600 (without using urea)	20
d- Functional additive	
UV-Sun [®] CEL	0–15
4-Hydroxybenzophenone	0–15
ZnO-NPs (<35 nm)	0–9
Or TiO ₂ -NPs (<10 nm)	0–15
e- H₂O	X
Total	1000 g

Functionalized/printed samples were then dried at 100 °C for 5 min, steam fixed at 110 °C for 20 min using Ariolt[®] CSL-steamer-Italy, rinsed thoroughly, soaped for 15 min at 50 °C in the presence of 2 g/L Na-carbonate and 2 g/L nonionic wetting agent, then thoroughly rinsed and finally dried at 100 °C for 5 min.

2.3. Measurements

The color strength of the obtained prints, expressed as K/S, was calculated by the following equation, Kubelka-Munk equation (Judd and Wyszeck, 1975): $K/S = (1-R)^2/2R$ where R = surface reflectance, K: light absorption, S: light scattering.

The effectiveness in shielding harmful UV-radiation, expressed as ultraviolet protection factor (UPF), was measured in vitro using a Labsphere[®] UV-100F UV-Transmission Analyzer and evaluated according to AS/NZS 4399-1996 standard. According to this standard, fabrics with a UPF values in the range 15–24, 25–39 and above 40 are classified as having good, very good, and excellent UV-protection, respectively.

Fastness properties to washing, rubbing, perspiration and light of the obtained wool prints were assessed according to AATCC Test Methods: (61–1972); (8–1972); (15–1973) and (16A-1972) respectively.

The durability to wash (after 15 launder cycles) was evaluated according to AATCC Test Method 135–2000.

Energy dispersive X-ray (EDX) spectra of selected samples was evaluated using a JEOL, JXA-840A electron probe microanalyzer equipped with disperse X-ray spectroscopy for the composition analysis.

3. Results and discussion

For enhancing the UV-shielding efficiency and printing properties of wool in a one step, CDs (β -CD and MCT- β CD) along with other selected active ingredients namely UV-SUN[®], 4-hydroxybenzophenone, TiO₂-NPs and ZnO-NPs were incorporated into the printing formulations under proper printing and fixation conditions. Variables studied include: type and concentration of CD and UV-absorber, type of dyestuff and fixing agent. Results obtained along with appropriate discussion follow.

3.1. CD concentration

For a given set of printing formulations/conditions and within the range examined (0–20 g/kg), Fig. 1a shows that i) increasing β -CD concentration up to 15 g/kg has a positive impact on the depth of the obtained prints, irrespective of the used dye, i.e. better K/S values (Ibrahim and El-Zairy, 2009; Perrin et al., 2007), ii) further increase in β -CD concentration has practically no effect on the color yield of the obtained prints, and iii) the enhancement in the depth of the obtained wool prints is determined by the type of dyestuff, disperse > acid, and reflects the differences between the nominated disperse and acid dyes in molecular size, chemical structure, functional groups, a chromogen component and hue, compatibility with other ingredients, extent of transferring from the printing paste film toward the wool surface during the steam fixation step, affinity to the wool, ability to interact with the wool active sites at acidic pH and/or to form guest-host inclusion complexes with the grafted β -CD moieties (Buschmann et al., 2001; Del Valle, 2004; Lo Nostro et al., 2003).

It is worth mentioning that the concurrent loading of β -CD onto the wool substrate and better fixation of the used acid and disperse dyestuffs during the steam fixation step using DMDHEU, as a fixing agent, and citric acid, as a catalyst, could be explained by the

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