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A smart approach for enhancing dyeing and functional finishing properties of cotton cellulose/polyamide-6 fabric blend

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ABSTRACT

Polyamide-6/cotton fabric blend was modified by chemical treatments using citric acid (30 g/L) as acrosslinker, an acrylate binder (10 g/L), Na-hypophosphite (6 g/L) as a catalyst in the presence of basic dye or pigment colorant (15 g/L) employing a pad-dry-cure technique (wet-pickup 80%, 80 °C/5 min and 180 °C/2 min respectively). Combined modifying and dyeing of the treated fabric samples resulted in a significant improvement in the extent of coloration along with a remarkable improvement in the imparted functional properties namely UV-B protection and antibacterial function. The change in *K*/*S* value as well as in the fastness properties ratings of the obtained dyeings along with variation in their functional properties depend on the ester-crosslinker/catalyst concentration, type and concentration of the coloring agent as well as thermo-fixation temperature. Mode of interaction was reported, and surface modification was also confirmed by SEM analysis.

1. Introduction

Textile materials provide an excellent media for growing micro-organisms, because of their large surface, ability to retain moisture along with other basic requirements such as nutrients, oxygen and appropriate temperature (Hou, Zhou, & Wang, 2009; Kim & Sun, 2001; Purwar & Joshi, 2004). On the other hand, over exposure to the harmful UV-B radiation, in the wave length region 280–315 nm, can result in the greatest skin damage (Ibrahim, Refai, Youssef, & Ahmed, 2005; Veatch & Gatewood, 2002). Accordingly, enhancing functional properties of textile materials such as antimicrobial, anti-UV, anti-radiation and antitoxic chemicals has attracted much attention in recent years to cope with the growing awareness of health and hygiene concerns (Bajaj, 2002; Hebeish & Ibrahim, 2007; Holme, 2007; Ibrahim et al., 2005; Ibrahim, Refaie, & Ahmed, 2010; Veatch & Gatewood, 2002).

Currently, blends of man-made with natural fibers, e.g. polyamide-6/cotton, have been produced by using warp and weft of separate fibers during weaving to get union fabrics with combined desirable performance properties contributed by both blend components. Solid shades are difficult to achieve on union fabrics (Choudhury, 2006).

In this study, a new approach has been made to study the feasibility of carrying out basic or pigment dyeing and ester-crosslinking of polyamide-6/cotton blend in one step and to evaluate the impact of the combined treatments on the functional and dyeing properties of the treated fabric samples.

2. Experimental

2.1. Materials

Mill-scoured and bleached plain woven polyamide-6 (weft)/cotton (warp) blended fabric (50/50, 75 g/m^2) was used.

Cationic dyes used: Astrazon® Red GLTN 200% micro (C.I.Basic Red 18:1) and Astrozon® Blue F2RL 200% (C.I.Basic Blue 147) were kindly supplied by DyStar.

Pigment-prepartions used: Imperson® Orange K-G and Imperon® Blue K-RR were kindly supplied by DyStar. Pintofix® 83 (anionic self crosslinking acrylate based copolymer dispersion, Clariant) was used as a binding agent. All other used chemicals namely citric acid, Na-hypophosphite, Na-carbonate, and acetic acid were of laboratory reagent grade.

Hosptapal® CV-ET (nonionic wetting agent based on alkyl aryl polyglycol ether, Clariant) was of commercial grade.

2.2. Methods

2.2.1. Ester-crosslinking/dyeing in one step

The blended fabric samples were padded twice to a wet-pick up of 80% with an aqueous formulations containing citric acid (0–40 g/L), as a crosslinker, Na-hypophosphite (0–8 g/L), as a

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catalyst, Imperon® N82 binder (10 g/L), non-ionic wetting agent (2 g/L), along with the basic dye or the pigment colorant (5–20 g/L), followed by drying at 80 °C/5 min, curing at 180 °C/2 min in a circulating air oven. The cured fabric samples were then washed at 50 °C for 15 min in presence of 2 g/L wetting agent and 2 g/L Na-carbonate, to remove excess and unfixed reactants, then finally thoroughly rinsed; dried at 80 °C/3 min, and conditioned for evaluation. Typical formulations used in this study are given in the text.

2.2.2. Measurements

The color strength, K/S, of the obtained dyeings was measured at the wave length of maximum absorbance with an automatic filter spectrophotometer and calculated with the Kubelka–Munk equation (Garland, 1993):

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

where K is the absorption coefficient, S is the scattering coefficient, R is the reflectance of the dyed samples.

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

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

Fastness properties to washing, rubbing and perspiration were assessed according to AATCC tests methods: (61-1972), (8-1972) and (15-1973) respectively.

The obtained results of the above-mentioned testing methods are the average of triplicate test.

3. Results and discussion

To study the technical feasibility of combined dyeing and functional finishing of polyamide-6/cotton fabric blend as well as to attain proper dyeing and functional properties, citric acid (CA)/NaH_2PO_2 concentration, fixation temperature as well as type and concentration of the used basic dye and pigment colorant have been investigated. Results obtained along with their appropriate discussion follow.

3.1. CA/NaH_2PO_2 concentration

For a given set of dyeing and crosslinking conditions and within the range examined, Fig. 1a and b demonstrates that: (i) increasing the CA/NaH_2PO_2 concentration from zero up to 30/6 g/L is accompanied by a remarkable increase in the K/S values of the obtained basic dyeings along with a significant improve in the UPF values of the dyed/finished fabric samples, regardless of the used basic dye (Ibrahim, Abo-Shosha, Elnagdy, & Gaffar, 2002; Martel, Weltrowski, Ruffin, & Morecellet, 2002), (ii) the enhancement in the K/S values (Fig. 1a) could be discussed in terms of higher extent of dye adsorption, diffusion and penetration as well as fixation onto and/or within the fabric structure via the remaining free carboxylic acid groups that are available to react with the basic dye molecules (Ibrahim et al., 2002; Ibrahim, Eid, Hashem, Refai, & El-Hossamy, 2010), (iii) remarkable improvement in the UV-protection properties can be discussed in terms of the higher ability of the used basic dyes to absorb the harmful UV-β radiation, as well as the lower amount of transmitted UV radiation through the darker dyeing (Holme, 2003), (iv) further increase in CA/NaH_2PO_2 concentration, i.e. beyond (30/6 g/L), has practically a slight or no further improvement, (v) the enhancement in both K/S (Fig. 1a) and UPF (Fig. 1b) values in the absence of CA/NaH_2PO_2 reflects the positive impact of the used acrylate binder due to its ability to form crosslinked polymer network under curing conditions in which the positively charged dye molecules becomes embedded/trapped and/or fixed onto the negatively charged active sites (El-Ghoul et al., 2007), i.e. COOH groups of the treated substrate thereby enhancing both the K/S value as well as the UV-absorption capacity of the dyed fabric samples, and (vi) the variation in the aforementioned properties upon using different basic dyes reflects the differences between them in molecular size, chemical structure, hue, basicity, extent of fixation as well as in maintaining their ability to absorb UV-B radiation.

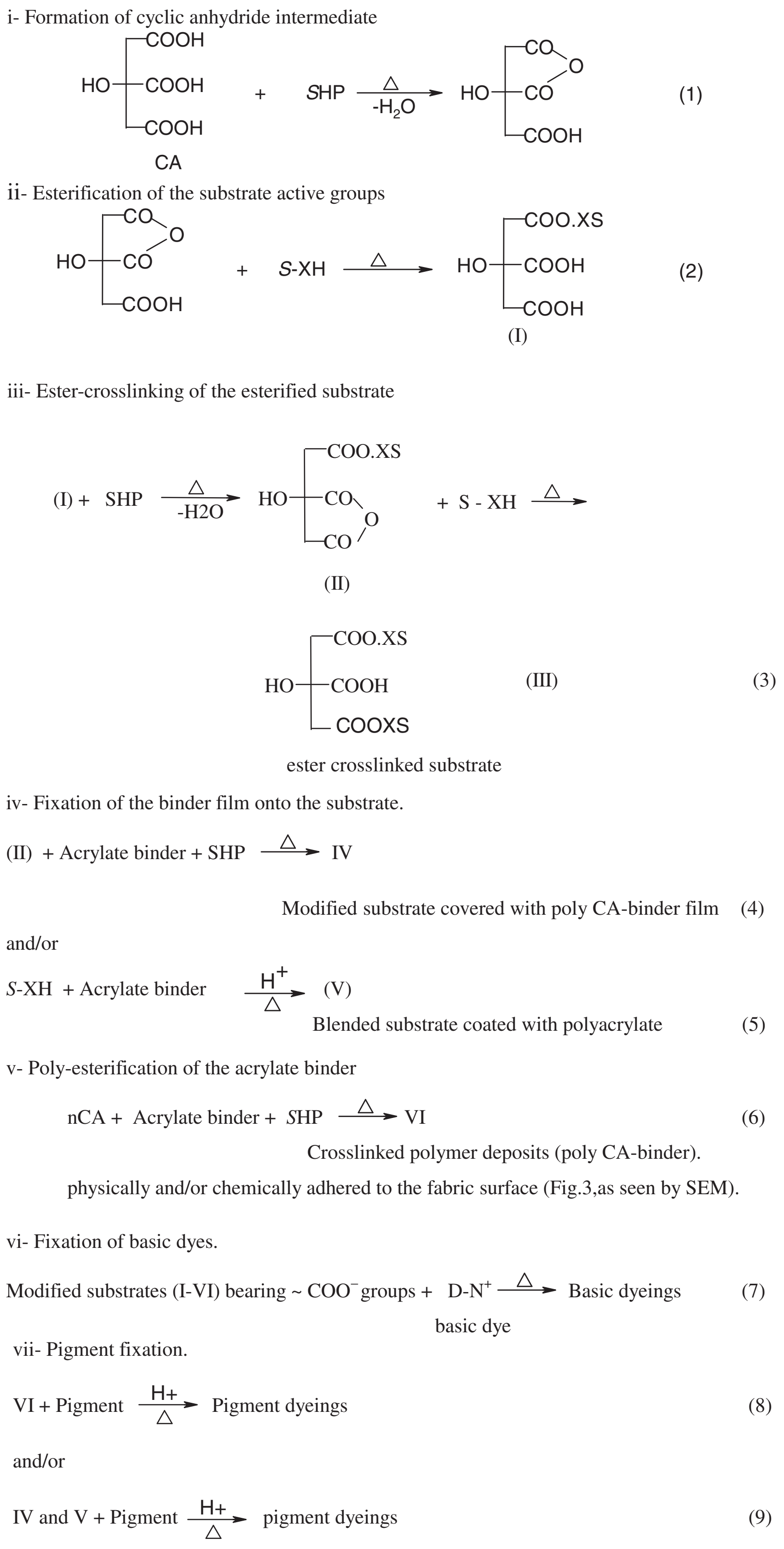
On the other hand Fig. 2a and b shows that incorporation of both the CA and NaH_2PO_2 in the dyeing/finishing formulation allowed better pigment-coloration along with higher UV-protection than the used binder alone. These results can be explained by the surface modification of the treated substrate via formation of poly CA-binder that physically and/or chemically adhered to the surface of the blended fabric upon treatment which improved the extent of pigment particles entrapment and fixation (El-Ghoul et al., 2007; Holme, 2003; Ibrahim, El-Gamal, Hassan, & Abo-El-Maged, 2007), i.e. higher K/S values (Fig. 2a) which in turn upgrades the ability to absorb the harmful UV-B radiation, i.e. higher UPF values (Fig. 2b). However, no significant difference was observed by further increase in CA/NaH_2PO_2 concentration, i.e. beyond 30/6 g/L. In the case of control, i.e. in the absence of the CA/NaH_2PO_2, the presence of the acrylate binder caused an improvement in both the K/S and UPF values as discussed before. Besides, Fig. 2a and b displays that the extent of improvement in the K/S as well as in the UPF values is governed by the nature of the pigment, i.e. particle size, degree of dispersion, chemical structure, extent of agglomeration, hue and extent of becoming embedded trapped and/or fixed onto the modified fabric surface (Ibrahim et al., 2007).

3.2. Tentative mechanism

The significant increase in K/S values as well as the remarkable improvement in the imparted UV-protection properties of the simultaneously dyed/finished fabric samples, suggest that, presence of the used substrate (S-XH) along with citric acid (CA), as a crosslinking agent, NaH_2PO_2 (SHP), as a catalyst, Imperon® binder (IB), and the basic dye or pigment colorant at proper curing conditions would be expected to promote the following reactions and/or interactions (Scheme 1) (El-Ghoul et al., 2007; Ibrahim et al., 2002, 2007; Abo-Shosha, Ibrahim, Elnagdy, & Gaffour, 2002):where ∼XH = –OH groups (of cotton cellulose), ∼CONH and/or terminal-NH_2 and –COOH groups at the end of each chain (Bozic, Kokol, & Guebtiz, 2009) (of polyamide-6 component).

3.3. Fixation temperature

The variation in the K/S value as well as the subsequent improvement in the UPF values as a function of thermofixation temperature are shown in Figs. 4(a, b) and 5(a, b). For a given dyeing/finishing formulations, Figs. 4 and 5 display that: (i) raising the thermofixation temperature from 120 °C up to 180 °C results in a remarkable improvement in the extent of basic dyeing (Fig. 4a) as well as in the extent of pigment fixation, expressed as K/S values (Fig. 5a), (ii) The degree of fixation of the used basic dyes is governed by the extent of dye cations adsorption at the fabric surface, subsequent diffusion into the fabric structure as well as the extent of interaction with the accessible anionic dye sites, –COOH groups, onto and/or within the fabric structure (El-Ghoul, 2007; Ibrahim et al., 2002), (iii) the



Scheme 1. Tentative mechanism.

extent of improvement in the *K*/*S* value of the obtained pigment dyeings is governed by formation and fixation of a crosslinked polymer network, i.e. poly (CA-binder) under curing conditions in which pigment particles become embedded and trapped onto the fabric surface (Ibrahim et al., 2007), and (iv) the enhancement in the UV-protection functionality of the obtained basic and pigment dyeings reflects the positive impacts of the developed method on modifying the fabric structure through ester-crosslinking and surface coating, i.e. reduction in the amount of transmitted UV-B radiation, as well as on enhancing the extent of basic dyes and

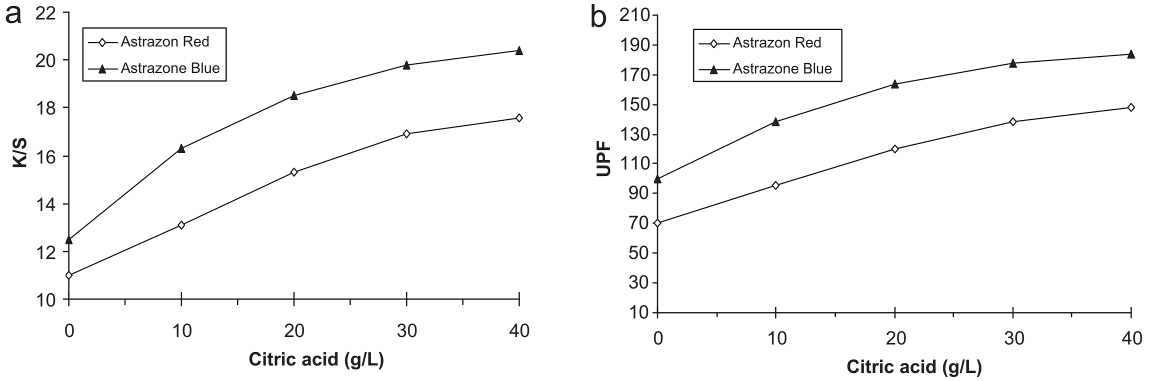


Fig. 1. Effect of citric acid concentration on the *K*/*S* (a) and the UPF (b) values of the treated fabric samples (citric acid (0–40 g/L); NaH_2PO_2 (20%ow of the citric acid); Imperon® N82 (10 g/L); basic dye (10 g/L), acetic acid (2 mL/L); wet-pickup (80%); drying at 80 °C/5 min; curing at 180 °C/2 min).

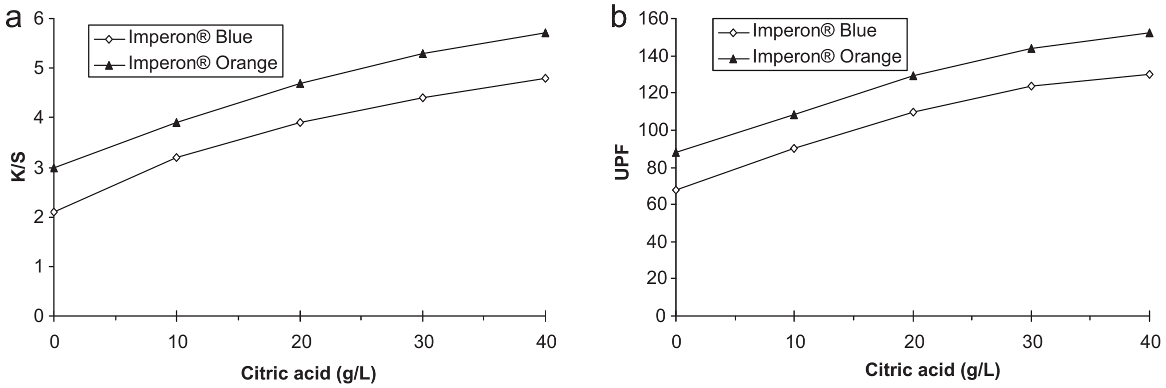


Fig. 2. Effect of citric acid concentration on the *K*/*S* (a) and the UPF (b) values of the treated fabric samples (citric acid (0–40 g/L); NaH_2PO_2 (20%ow of the citric acid); Imperon® N82 (10 g/L); pigment colorant (10 g/L), acetic acid (2 mL/L); wet-pickup (80%); drying at 80 °C/5 min; curing at 180 °C/2 min).

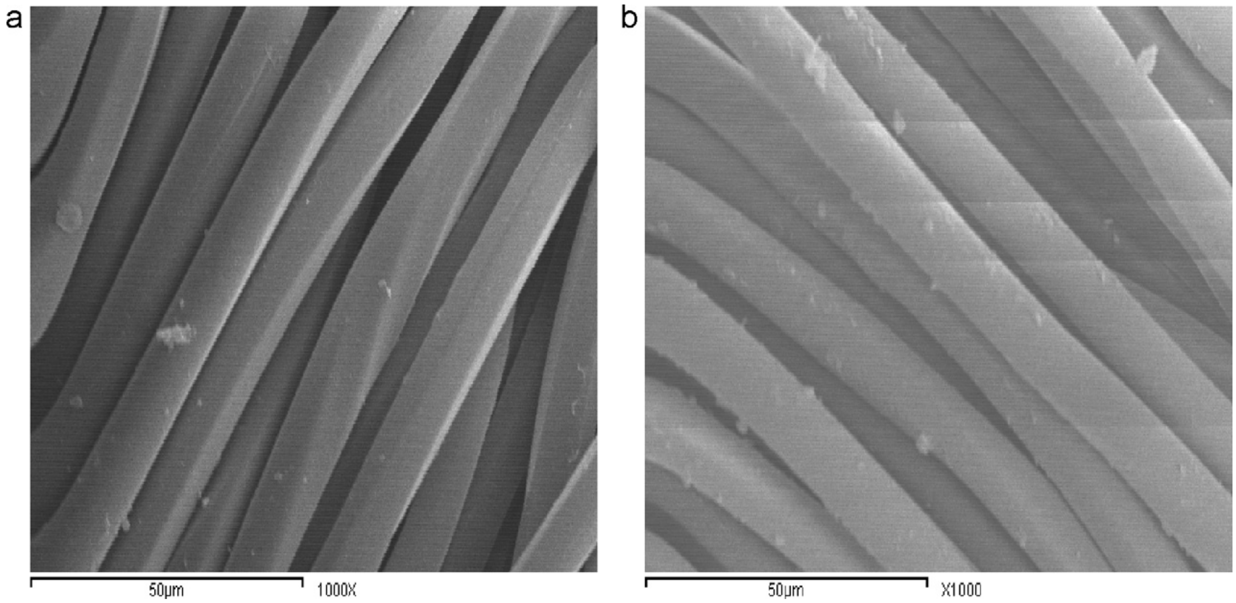


Fig. 3. SEM micrographs of (a) untreated blend and (b) finished blend with CA + acrylate binder using NaH_2Po_2 catalyst.

pigment colarants fixation, i.e. higher ability to absorb the harmful UV-B radiation (Figs. 4b and 5b) (Ibrahim, Mahrous, El-Gamal, Gonda, & Husseiny, 2010a; Veatch & Gatewood, 2002).

It is understandable that, the improvement in the above-mentioned properties, by raising the thermofixation temperature, is a direct consequence of (El-Ghoul, 2007; Ibrahim et al., 2002; Martel et al., 2002): (i) increasing the catalyst function as well as the rate of anhydride formation, (ii) enhancing the extent of fabric modification via esterification, (iii) creation of new active sites onto and/or within the modified substrate, i.e. –COOH active sites, (iv) helping the extent of basic dye fixation, (v) improving the efficiency of binder-film formation as well as pigment particles fixation, and

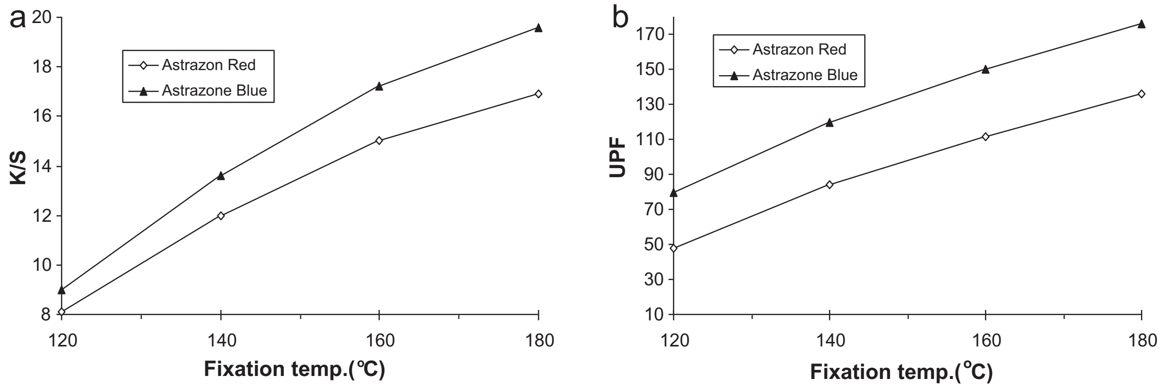


Fig. 4. Effect of fixation temperature on the *K*/*S* (a) and the UPF (b) values of the treated fabric samples (citric acid (30 g/L); NaH_2PO_2 (6 g/L); Imperon® N82 (10 g/L); basic dye (10 g/L), acetic acid (2 mL/L); wet-pickup (80%); drying at 80 °C/5 min; curing time 2 min).

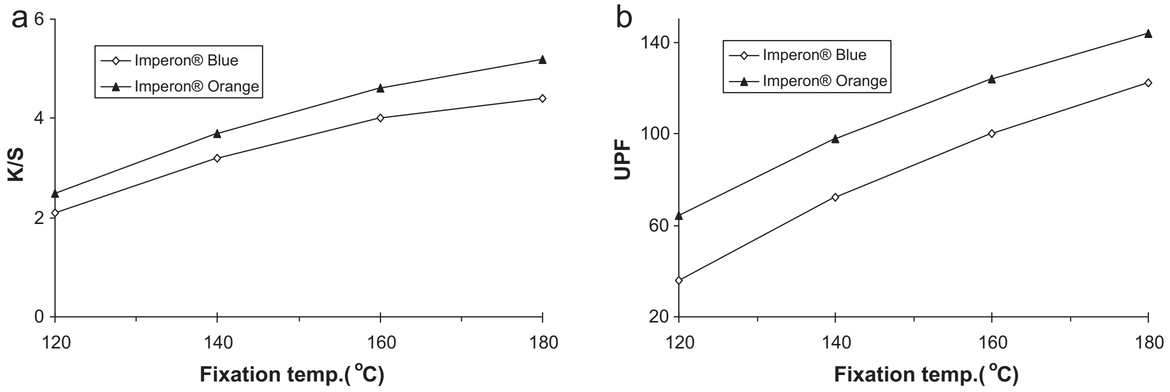


Fig. 5. Effect of fixation temperature on the *K*/*S* (a) and the UPF (b) values of the treated fabric samples (citric acid (30 g/L); NaH_2PO_2 (6 g/L); Imperon® N82 (10 g/L); pigment colorant (10 g/L), acetic acid (2 mL/L); wet-pickup (80%); drying at 80 °C/5 min; curing at 2 min).

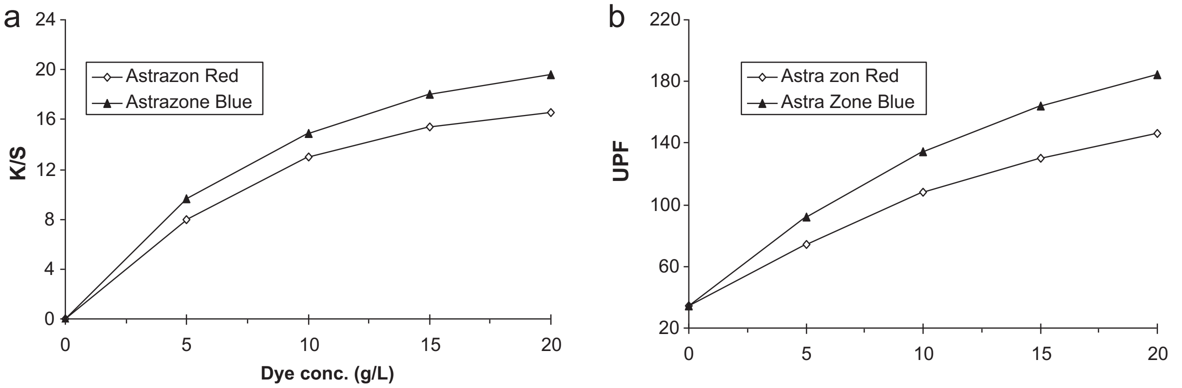


Fig. 6. Effect of basic dye concentration on the *K*/*S* (a) and the UPF (b) values of the treated fabric samples (citric acid (30 g/L); NaH_2PO_2 (6 g/L); Imperon® N82 (10 g/L); dye (0–20 g/L), acetic acid (2 mL/L); wet-pickup (80%); drying at 80 °C/5 min; curing at 180 °C/2 min).

as a consequence, (vi) upgrading the UV-protection capacity of the treated fabric samples.

3.4. Dye concentration

As shown in Figs. 6 and 7, the higher the concentration the darker the color yield of the obtained basic (Fig. 6a) and pigment (Fig. 7a) dyeings, and the better the UV-B protection functionality of these dyeings (Figs. 6b and 7b). This improvement in *K*/*S* value, regardless of the used basic dye or pigment colorant, can be explained with availability and accessibility of basic dye cations in the vicinity of the anionic active sites of the treated substrate, –COOH groups, as well as the availability and accessibility of the pigment molecules in the vicinity of the crosslinked binder network under curing conditions, i.e. higher *K*/*S* and better UPF values compared to undyed/finished fabric samples.

3.5. Functional and dyeing properties

UV-protection and antibacterial function as well as the dyeing properties of the simultaneously dyed/finished fabric samples are given in Table 1. For a given treatment conditions, the obtained data demonstrate that: (i) incorporation of the used basic dyes or the pigment colorants in the finishing formulation is accompa-

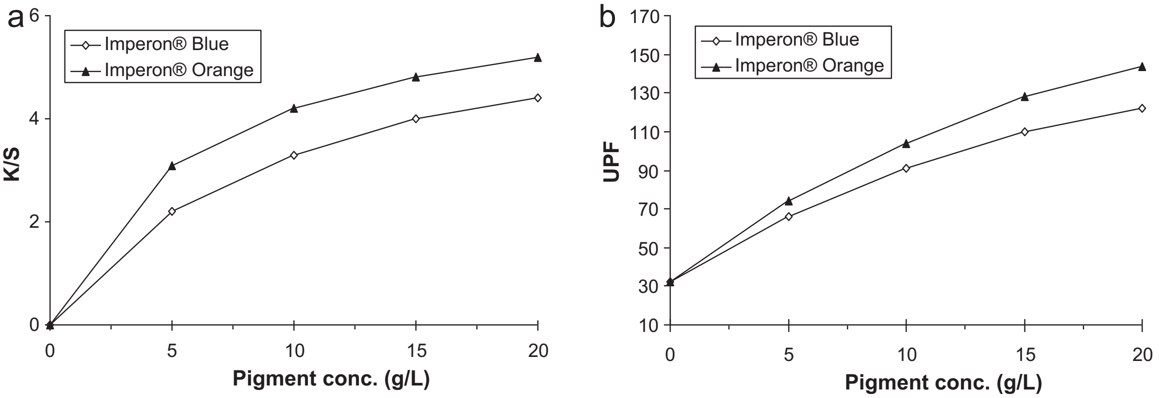


Fig. 7. Effect of pigment colorant concentration on the *K*/*S* (a) and the UPF (b) values of the treated fabric samples. citric acid (30 g/L); NaH_2PO_2 (6 g/L); Imperon® N82 (10 g/L); pigment (0–20 g/L), acetic acid (2 mL/L); wet-pickup (80%); drying at 100 °C/5 min; curing at 180 °C/2 min).

Table 1
Functional and dying properties of the obtained functional dyeings.

Dye (15 g/L)	*K*/*S*	UPF	ZI (mm)		WF		RF		PF			
			G+ve	G−ve	St.	Alt.	Dry	Wet	Acidic		Alkaline	
									St.	Alt.	St.	Alt.
Astrazone® Blue F2RL	17.90	164	10.2	9.4	3	3	3–4	3	3	3	2–3	3
Astrazone® Red GTLN	15.07	132	8.9	7.8	3	3	4	3–4	3	3	2–3	3
Imperon® Blue K-RR	3.95	110	10	9.6	5	5	5	4–5	5	5	5	5
Imperon® Orange KG	4.83	128	9.4	8.6	5	5	5	4–5	5	5	5	5
None[a]	–	36	3.6	2.9	–	–	–	–	–	–	–	–
Untreated	–	22	0	0	–	–	–	–	–	–	–	–

Citric acid (30 g/L); NaH_2PO_2 (6 g/L); Imperon® N82 (10 g/L); acetic acid (2 mL/L); dye (15 g/L); wet-pickup (80%); drying at (80 °C/5 min); curing at (180 °C/2 min). *K*/*S*: color strength; UPF: UV-protection sector; ZI: zone of inhibition; G+ve: *St. aurous*; G−ve: *E. coli*. WF: Wash fastness; St. staining on cotton, Alt.: Alteration; PF: Perspiration fastness.

[a] None: in absence of dye.

nied by a significant improvement in the color yield, *K*/*S*, of the obtained dyeings along with a subsequent enhancement in their functional properties namely UV-B protection, expressed as UPF value, as well as antibacterial properties against G+ve and G−ve bacteria, expressed as zone of inhibition, regardless of the used dye or pigment colorant, (ii) the *K*/*S* values as well as the fastness ratings are determined by the dye or pigment nature, molecular size, state of aggregation, functionality, mode of interaction and fixation as well as type of the formed bonds, (iii) fastness to washing, rubbing and perspiration of the obtained pigment dyeings are in the range 4–5 to 5, and better than the obtained basic dyeings (2–3 to 4), (iv) the extent of improvement in the UPF values of the obtained dyeings is determined by the extent of modification of the fabric structure as well as fixation of the incorporated dye or pigment along with their ability to reduce the UV-B transmission and/or absorption, (v) the enhancement in the antibacterial properties of the obtained dyeings most probably due to the inhibition effect of the free –COOH groups onto the finish/fabric matrix (Ibrahim, Eid, et al., 2010) as well as inactivation effect of the used basic dyes and pigment colorants, and (vi) inactivation efficiency of G+ve bacteria (*St. aureus*) was higher than that of G−ve bacteria (*E. coli*) most probably due to the high sensitivity of the outer membrane of G+ve one (Maillard, 2002).

4. Conclusion

A new approach for enhancing the dyeing and functional properties of polyamide-6/cotton fabric blend has been investigated. The most appropriate conditions for combined dyeing and functional finishing were citric acid (30 g/L), NaH_2PO_2 (6 g/L), acrylate binder (10 g/L), acetic acid (2 mL/L), dye or pigment (15 g/L), wet-pickup (80%), drying at 80 °C/5 min and curing at 180 °C/2 min. Inclusion of the nominated basic dyes or pigment colorants in the finishing formulation results in a remarkable improvement in the imparted UV-protection and anti-bacterial properties of the obtained dyeings. The extent of improvement in the dyeing properties, i.e., *K*/*S* and fastness ratings, as well as the gained functional properties are governed by the dyeing/finishing formulation constituents and their concentrations as well as thermofixation temperature. Surface modification of the treated blend was confirmed by SEM.

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