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A new approach for biofinishing of cellulose-containing fabrics using acid cellulases

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ABSTRACT

The main objective of this study is to develop a new approach for biofinishing of cellulose-containing fabrics using cellulases under pad-wet batch conditions followed by washing cycle with a high level of mechanical agitation to terminate the enzyme and to remove the weakened fuzz fibers and surface pills, i.e. biopolishing of the fiber's surface. The effect of enzyme dosage, wet-pickup, batching time and temperature as well as type of substrate on the efficiency of enzymatic treatment as well as on the performance and dyeing properties is discussed. Experimental results revealed that padding the used substrates in a bath containing acid-cellulases (20 g/L) and nonionic wetting agent (2 g/L) to a wet-pickup 80% followed by batching at 50 °C for 18 h, and after washing under mechanical action (28 rpm, pH 9, temperature 75 °C, LR 1/20, for 30 min) could upgrade the final properties of the treated substrates especially fabric handle, drapability as well as dyeability with minimal loss in strength. The extent of improvement in the abovementioned properties is determined by the nature of the cellulose-containing fabric. SEM picture clearly shows that the surface of cellulases-treated cotton fabric appear smoother and softer than the untreated one.

1. Introduction

Enzymes are biological catalysts that accelerate the rate of chemical reaction without themselves undergoing any permanent chemical change. Enzymes have far greater reaction specificity than chemically catalyzed reactions (Jenkins, 2003; Vasconcelos & Paulo, 2006). Enzymatic catalysis takes place at atmospheric pressure, moderate temperature and mild pH conditions, thereby resulting in a reduction in production costs, improving quality and functionality of the textile products as well as increasing the environmental friendliness (Hebeish & Ibrahim, 2007; Jenkins, 2003; Vasconcelos & Paulo, 2006). Enzymes are principally classified and named according to the chemical reaction they catalyze. There are six classes of enzymes namely: oxidoreductases, transeferases, hydrolyases, lyases, isomerases and ligases (Vasconcelos & Paulo, 2006).

Cellulases are the most successful enzymes used in textile wet processing, especially finishing of cellulose-based textiles, with the goal of improved hand and appearance (Diller, Fanter, & Loth, 1999; Hebeish & Ibrahim, 2007). The efficiency of enzymatic hydrolysis of cellulose using cellulase enzymes is governed by: synergism among different type of cellulases, i.e. endoglucanases that hydrolyze cellulose chains randomly, cellobiohydrolyases that hydrolyze cellobiose from the cellulose chain ends and β-glucosidases that convert cellobiose into glucose, as well as the accessibility of the fiber surface to the enzyme (Tarhan & Sarllslk, 2009). Depilling/cleaning and/or ageing effects are the result of the synergistic action of cellulases and mechanical action simultaneously or sequentially (Paulo & Gubitz, 2003). Improving the dimensional stability of cellulosic fabrics using cellulases under pad-batch conditions had been made before (Cortz, Ellis, & Bishop, 2002).

Several attempts have been made to explore the effect of degree and sequence of mechanical agitation on the efficiency of cellulase treatment (Paulo, 1998; Paulo, Cortez, & Almeida, 1997). Our new investigation is concerned with the technical feasibility of conducting cellulases-treatment of cotton-containing fabrics using the pad-wet batch followed by washing at high level of mechanical action. Physico-mechanical properties, dyeability of cotton with reactive and cotton/polyester blend with reactive/disperse dyes as well as surface morphology were compared.

2. Experimental

2.1. Materials

The specifications of the used substrates are given in Table 1.

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Table 1
Description of experimental fabrics.

Fabric	Weave	Weight (g/m^2)	Warp tensile strength (kg)	Wrinkle recovery angle $(w+f)^{\circ}$	Flexural rigidity (mg/cm^2)	Rough (μm)	Wettability sec.
Bleached cotton	Plain	125	51	140	45	15.65	7
Mercerized cotton	Plain	120	53	152	50	16.42	6
Bleached cotton/polyester blend (50/50)	Plain	225	59	165	48	17.70	15

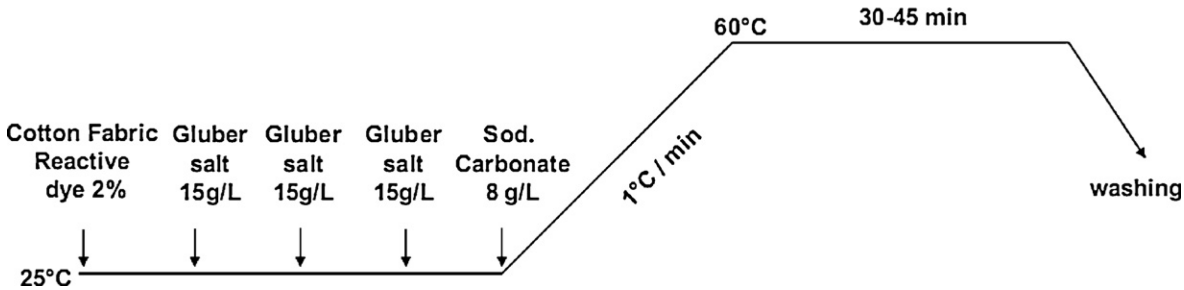

Fig. 1. Dyeing of cotton with reactive dye.

Multifunctional acid-cellulase enzyme formulations namely Cellusoft® L (activity 750 EGU/g, Novo Nordisk), and Hostapal® CV-ET (nonionic wetting agent based on alkaryl polyglycol ether-Clariant) were of commercial grade.

Commercial dyestuffs used namely (C.I. Reactive Yellow 25, C.I. Reactive Red 239, C.I. Reactive Blue 220, C.I. Reactive Red 195, C.I. Reactive Yellow 176, C.I. Disperse Red 239) were kindly supplied by DyStar. Other chemicals were of laboratory grade.

2.2. Methods

2.2.1. Enzymatic treatment

Fabric samples were padded twice with an aqueous formulations containing: acid cellulases (0–20 g/L), and nonionic agent (2 g/L) at pH 5, to 80% wet-pickup followed by batching for different periods (0–24 h) at different temperatures (20–60 °C) in nylon bags. The treated fabric samples were then washed at pH 9, temperature 75 °C for 30 min, fabric-to-liquor ratio (LR 1:20) using a Fim® stone wash rotary drum machine (28 rpm – Italian), to terminate the enzyme reaction as well as to remove the weakened fuzz fibers or fibrillar materials at the surface. The samples were then rinsed with hot and cold water, and dried at room temperature.

Typical formulations as well as treatment conditions of the aforementioned substrates are given in the text.

2.2.2. Post-dyeing

Reactive dyeing profile of bleached and mercerized cotton fabric samples as well as reactive/disperse dyeing of the blend fabric samples are given in Figs. 1 and 2, respectively.

2.2.3. Fabric evaluation

- Loss in weight calculated according to the following equation:

$$\mathrm{WL}(\%) = \frac{W_{\text{before treatment}} - W_{\text{after treatment}}}{W_{\text{before treatment}}} \times 100$$

- Flexural rigidity (FR) was assessed according ASTM: D50335-90.
- Dry wrinkle recovery angle, WRA $(w+f)^{o}$, of the treated samples was measured using the crease recovery apparatus type FF-07 (Metrimpex).
- Warp tensile strength was determined by the strip method according to ASTM Procedure D2256-66T.

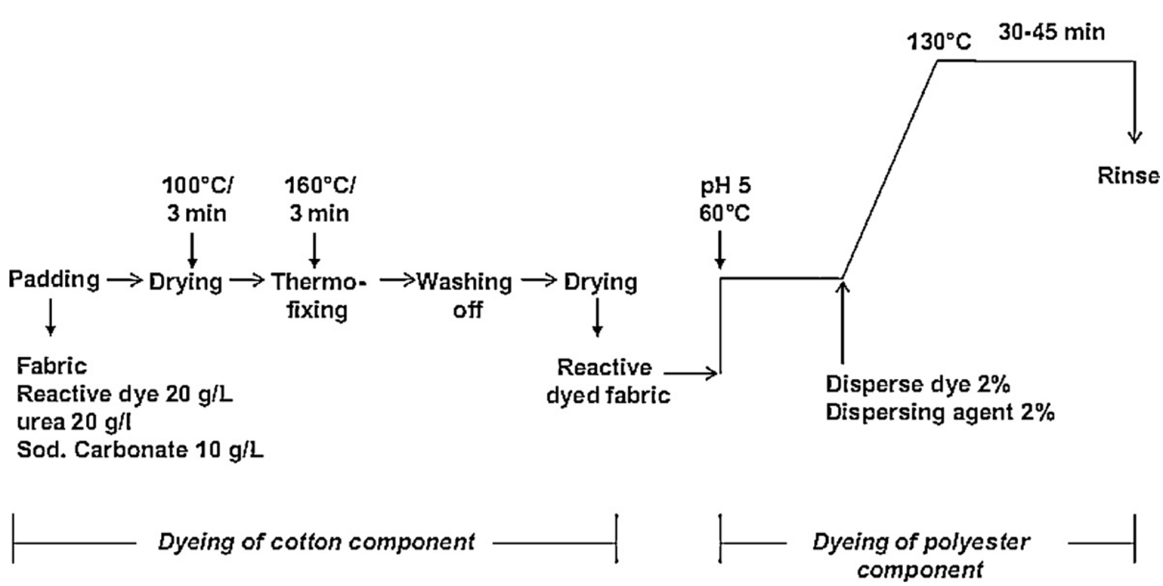

Fig. 2. Dyeing of cotton/polyester bend.

- Wettability was evaluated according AATCC Standard Test (79-1968).
- Roughness was measured according to JIS 94 Standard using SE 1700α instrument, Japan.
- The color strength, expressed as K/S value, of the obtained dyeings was measured at the wavelength of maximum absorbance using an automatic filter Spectrophotometer, and calculated by the Kubelka Munk equation (Duff & Sinclair, 1989): $K/S = (1 - R)^2/2R$, where K is the absorption coefficient, S is the scattering coefficient, and R is the reflectance of the dyed samples.
- Fastness properties to washing (WF) and rubbing (RF) were assessed according to AATCC Test Methods: (91-1972) and (8-1972), respectively.
- A scanning electron microscope (SEM) examination was carried out by mounting the untreated and treated fabric samples on sub with double stick adhesive tape and coated with gold in S150 A Sputter Coater Unit (Edwards, UK), the gold film thickness was 150 Å, then viewed in a JEAOL-840 A electron probe micro-analysis. All the determinations in this study were performed in triplicate.

3. Results and discussion

3.1. Enzyme dosage

The impact of enzymatic treatment using Cellusoft® L, a multi-functional acid-cellulase formulation with specific catalytic action on 1–4 β-glucosidic bonds of cellulose, at different dosages (0–20 g/L) using the pad-wet batch technique followed by subsequent washing with mechanical agitation, on the % loss in weight, stiffness (FR) as well as resiliency, expressed as WRA, of the treated fabric samples are demonstrated in Fig. 3a–c respectively. For a given set enzymatic treatment conditions, the obtained results signify that:

(i) Increasing the enzyme dosage – results in an increase in the weight loss (Fig. 3a), a decrease in fabric stiffness (Fig. 3b) along with an improve in the fabric resiliency (Fig. 3c) regardless of the used substrate, (ii) the change in the a aforementioned properties is attributed to highly aggressive attack on the surface and accessible amorphous areas of the cellulose thereby: yielding soluble products such as short-chain oligomers and glucose, i.e. increase in weight loss, polishing of the fiber's surface, i.e. decrease in fabric stiffness, as well as imparting a smooth surface and soft-handle, i.e. improved resiliency (Ibrahim, Fahmy, Hassan, & Mohamed, 2005; Paulo et al., 1997; Vasconcelos & Paulo, 2006); (iii) the extent of increase or decrease in the aforementioned properties reflects the differences among the treated substrates in: surface morphology, cellulose-component, amount of surface fibers, fabric weight, thickness and construction, pretreatment history, as well as number, availability and accessibility of sites for cellulase attack, (iv) the lower weight loss obtained in the cotton/polyester blend is attributed to the reduction in the surface area of the exposed cotton fibers to enzyme attack as well as adsorption of the used enzyme formulation on the polyester component in a competitive manner in the presence of cellulose component (Vasconcelos & Paulo, 2006), and (v) pre-mercerization of bleached cotton fabric enhances the extent of hydrolysis, i.e. higher weight loss, due to the larger surface area of the more cylindrical mercerized fibers in comparison with the bleached ones (Paulo et al., 1997).

3.2. Batching time

The effect of batching time on the % weight loss, stiffness (FR) and fabric resiliency is shown in (Fig. 4a–c) respectively. From the graphs, it is clear that: (i) prolonging the batching time up to 18 h at 50 °C is accompanied by a gradual increase in the weight loss, a slight decrease in the stiffness along with a reasonable improve in fabric resiliency, regardless of the treated substrate, (ii) proper batching time is needed to adsorption of cellulases at the fabric surface, diffusion from the fabric surface into the fabric interior (especially cellulose component), formation of a transition state ES in which the substrate S is bonded to the enzyme E, i.e. $E + S \leftrightarrow ES$, and catalyzation of the degradation and breakdown of protruding cellulosic fibers to short chain fragments (P), i.e. $ES \rightarrow E + P$ (Ibrahim, El.Hosamy, Morsy, & Eid, 2004; Ibrahim et al., 2005; Paulo & Gubitz, 2003), (iii) a longer batching time, i.e. beyond 18 h, has practically a marginal or no effect on the abovementioned properties, and (iv) the higher loss in weight of mercerized cotton fabric samples is due to its larger surface area as well as availability and accessibility of its surface regions for the active sites of cellulases where only certain molecules can stereo-fit in, thereby intensifying the extent

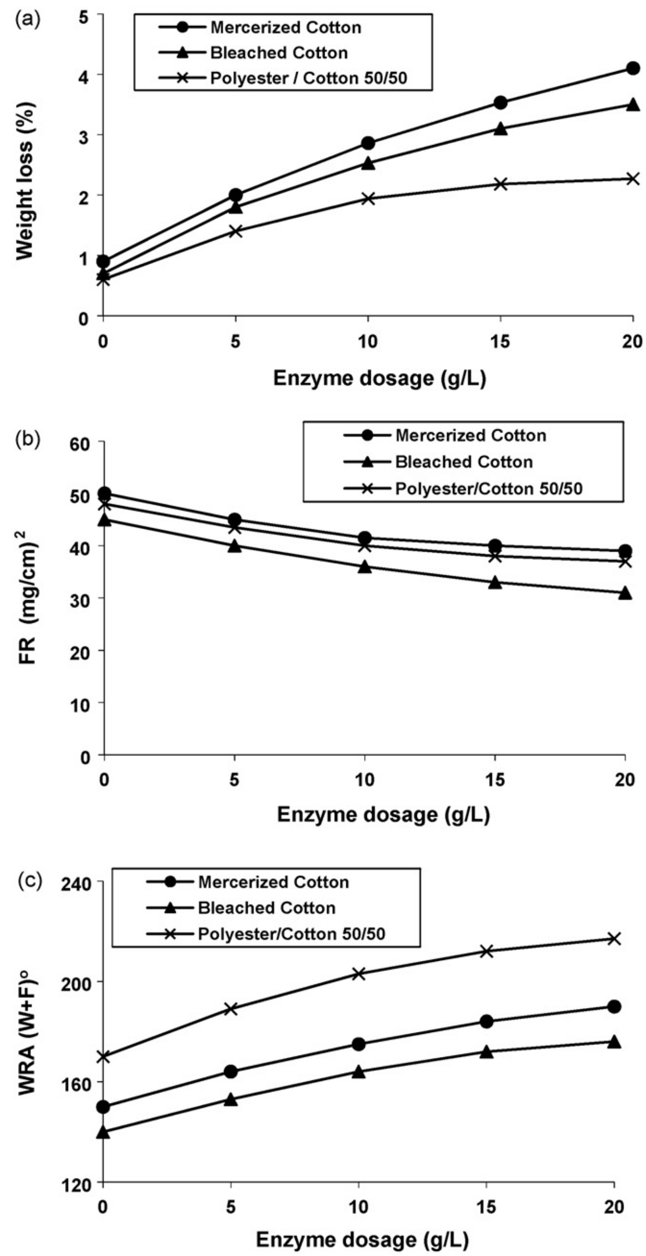

Fig. 3. Effect of enzyme dosage. Padder pressure (1 bar); pH 5; temp 50 °C; batching time 24 h.

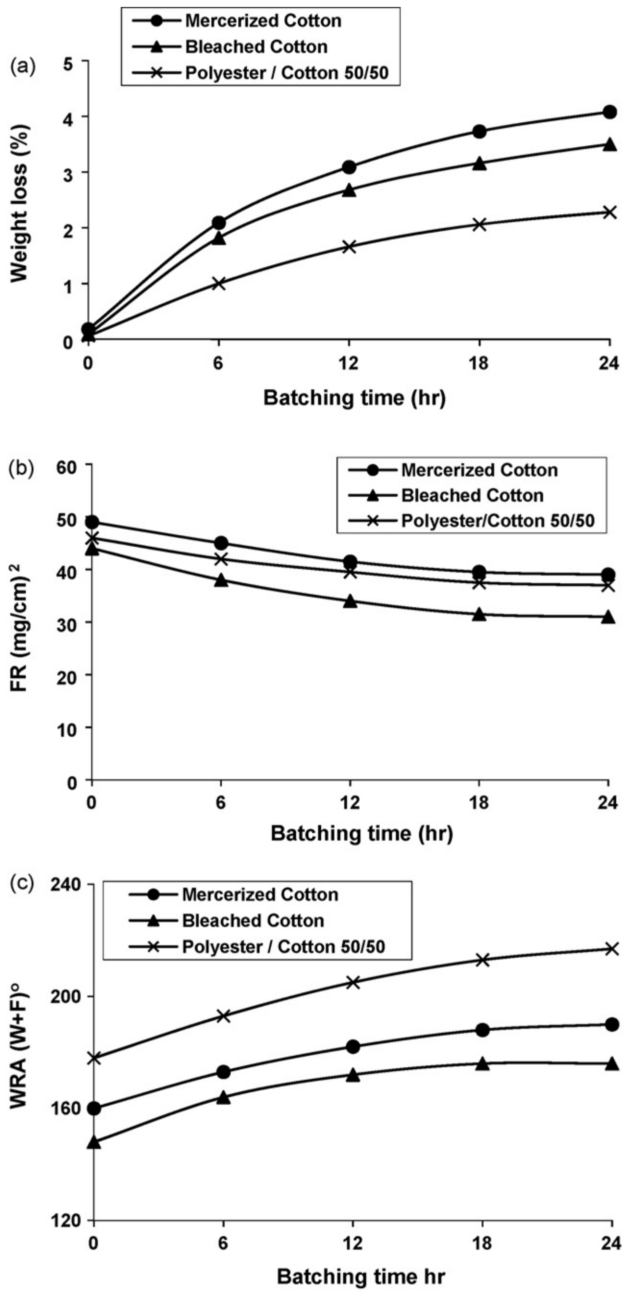

Fig. 4. Effect of batching time. Padder pressure (1 bar); enzyme dose 20g/L; pH 5; batching temperature 50 °C.

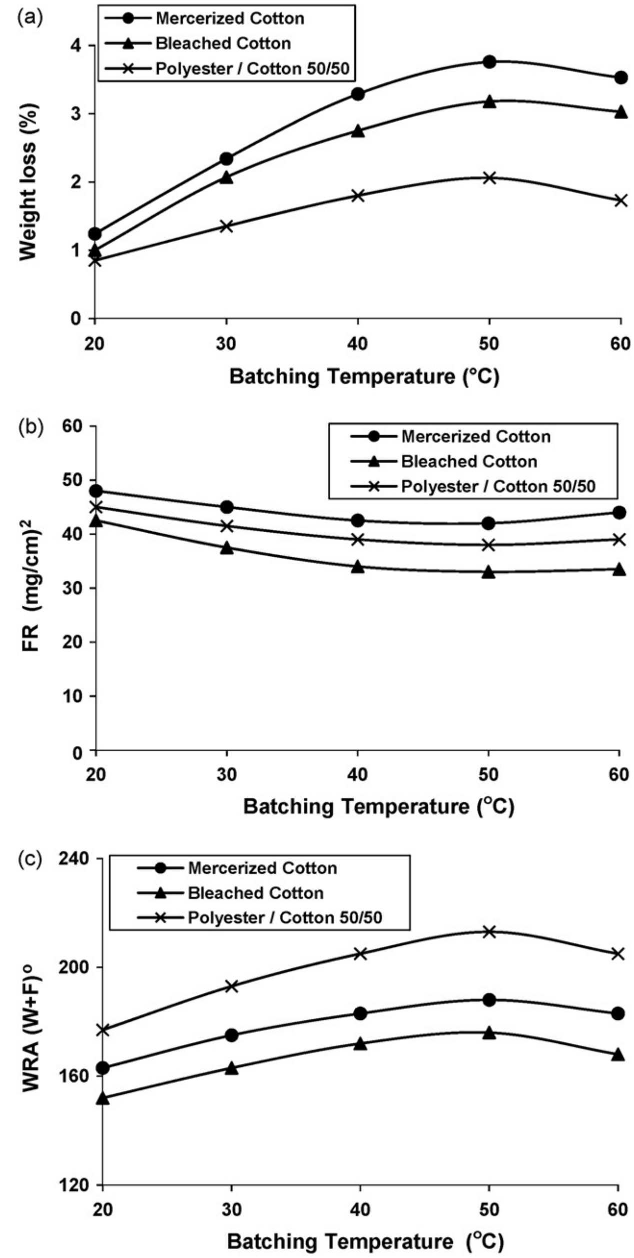

Fig. 5. Effect of batching temperature. Padder pressure (1 bar); enzyme dose 20 g/L; pH 5; batching time 18 h.

of attack (Ibrahim et al., 2004; Ibrahim et al., 2005; Paulo & Gubitz, 2003).

3.3. Batching temperature

As far as the changes in the extent of enzymatic attack on the treated substrates under investigations as a function of batching temperature, the obtained results clearly demonstrate that (i) raising the batching temperature from 20 °C to 50 °C for 18 h results in a significant increase in the weight loss (Fig. 5a), a decrease in the stiffness (Fig. 5b) along with an improve in treated fabric resiliency (Fig. 5c), irrespective of the used substrate, (ii) the change of the abovementioned properties reflects the positive impact of proper batching temperature on enhancing the extent of swellability and accessibility of the treated substrate-surface and amorphous regions as well as upgrading the activity of the used enzyme thereby increasing the extent of enzymatic attack and consequently the cellulose hydrolysis (Ibrahim, El-Zairy, Allam, & Hassan, 1999), i.e. higher loss in weight, lower fabric stiffness along with better fabric resiliency, (iii) further increase in batching temperature, i.e. beyond 50 °C for 18 h, has practically a marginal negative impact on the aforementioned properties, and (iv) the negative impact of raising the temperature up to 60 °C could be discussed in terms of its adverse effect on the stability and enzyme proteins to maintain their folded native state to operate (Ibrahim et al., 1999; Novo Nordisk A/S, 2000; Paulo & Gubitz, 2003), i.e. inactivation.

3.4. Padder pressure

The results in Fig. 6a–c illustrate the weight loss, stiffness and resiliency results respectively obtained for a pad-wet batch

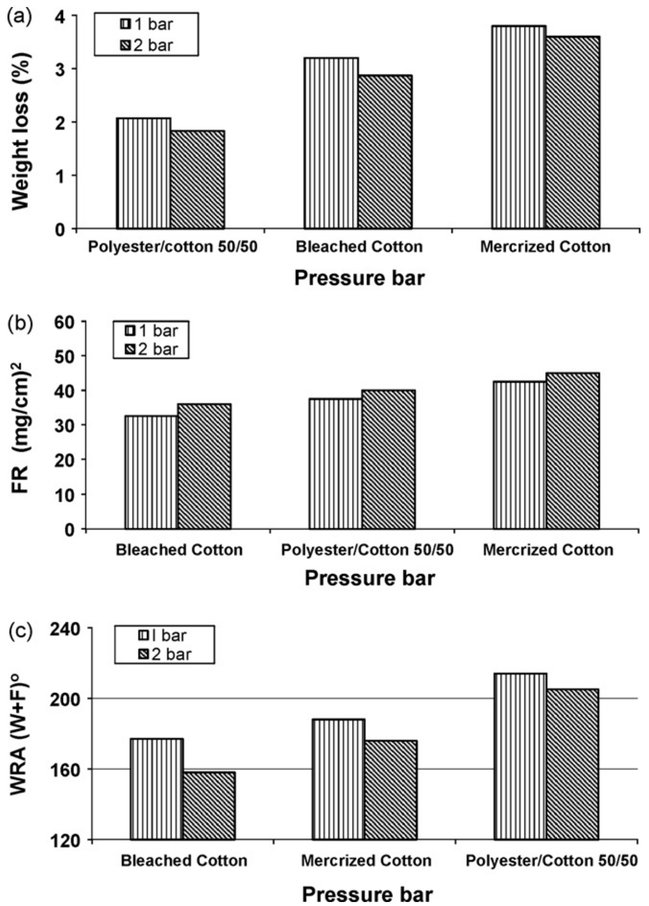

Fig. 6. Effect of padding pressure. Enzyme dose 20 g/L; pH 5;batching temperature 50 °C; batching time 18 h. 1 bar (80% wet-pickup); 2 bar (65% wet-pickup).

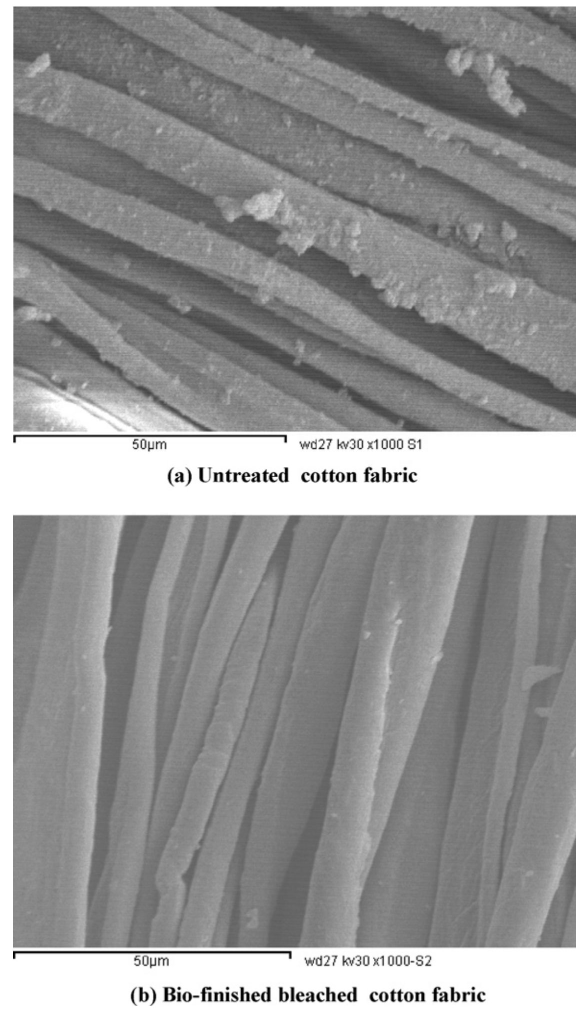

Fig. 7. SEM of untreated and bio-polished bleached cotton fabric.

treatment (enzyme dosage 20 g/L, nonionic wetting agent 2 g/L padder pressure: 1 bar (80% wet-pickup) or 2 bar (65% wet-pickup), batching for 18 h at 50 °C, followed by washing under mechanical agitation using Fim® stone wash rotary drum machine (28 rpm) on the treated cellulose-containing substrates. The obtained data bars indicate that: (i) increasing the padder pressure from 1 to 2 bar results in a decrease in weight loss, in the fabric resiliency as well as a slight increase in fabric stiffness (FR) regardless of the used substrate, (ii) the higher the pressure the lower is the uptake of the used enzyme formulations (Cortz et al., 2002), thereby decreasing the enzyme concentration and enzyme–substrate complex formation and therefore minimizing the extent of enzymatic attack on scission and degradation of accessible cellulose chains, (iii) the results of 1 bar pressure show slightly higher of weight losses with little improvement in fabric softness and resiliency, and (iv) variation in the obtained results value upon using different cellulose-containing fabrics, keeping other parameters constants, could be ascribed to differences in fabric structure, chemical composition, thickness, amorphous/crystalline cellulose, hydrophilic/hydrophobic property, extent of diffusion, penetration within the fabric structure, etc. (Ibrahim et al., 1999).

3.5. Performance and dyeing properties

A comparison between some performance and dyeing properties of the used three substrates before and after cellulases-treatment under the optimal conditions derived in earlier experiments would reveal that: (i) enzymatic treatment results in: a loss in weight, stiffness, roughness as well as in tensile strength along with increase in fabric resiliency, (ii) the extent of variation in the abovementioned performance properties is determined by the nature, surface morphology, fabric weight, thickness and construction as well as susceptibility to the enzymatic attack in addition to differences among them in inherent performance properties (Ibrahim et al., 1999, 2005; Vasconcelos & Paulo, 2006), (iii) the loss in weight and strength as well as the enhancement in fabric resiliency, smoothness and drapability are unequivocally owing to the action of cellulases (adsorption/hydrolysis) on easily accessible pills or fibrils at the surface of the treated substrate (Ibrahim et al., 2005; Paulo & Gubitz, 2003), i.e. depilling/cleaning as a confirmed by SEM micrographs of the untreated and bio-polished bleached cotton fabrics (Fig. 7), and (iv) the low weight loss and the high retained strength is a direct consequence of applying the less abrasive proposed method, i.e. enzymatic treatment under pad-wet batch conditions followed by subsequent washing with mechanical agitation, than the traditional simultaneous action of cellulases and mechanical action (Diller et al., 1999; Paulo et al., 1997; Vasconcelos & Paulo, 2006), thereby minimizing the extent of diffusion of enzyme into the fabric structure as well as creation of more sites for enzyme attack, i.e. lowest fabric strength loss.

Table 2 demonstrates also that: (i) enzymatic treatment of the nominated substrates has a positive impact on the extent of dyeing regardless of the used dyestuffs, expressed as *K*/*S* values, (ii) the extent of improvement in dyeability, expressed as % increase in *K*/*S*,

Table 2
Effect of enzymatic treatment on some performance and dyeing properties of treated substrates.

Substrate	Performance properties					Dyeing properties				RF	
	Wt. loss (%)	DFR (%)	DR (%)	Incr. WRA (%)	RTS (%)	Dyestuff	K/S	Incr. K/S (%)	WF	Dry	Wet
Bleached cotton fabric	3.2	28.9	3.25	25.71	97.7	C.I. Reactive Yellow 25	2.46 (3.14)	27.64	4–5 (4–5)	4 (4)	4 (4)
						C.I. Reactive Blue 220	1.89 (2.47)	30.69	4 (4–5)	4 (4)	3–4 (4)
						C.I. Reactive Yellow 176	3.89 (4.93)	26.73	4–5 (4–5)	4–5 (4)	4 (4)
						C.I. Reactive Red 195	5.20 (6.32)	21.45	4–5 (4–5)	4 (4)	3–4 (4)
Mercerized cotton fabric	3.8	16.0	8.28	23.68	94.8	C.I. Reactive Yellow 25	3.82 (4.99)	30.63	4–5 (5)	4–5 (4–5)	4 (4)
						C.I. Reactive Blue 220	2.05 (2.91)	41.95	4 (4–5)	4 (4)	3–4 (4)
						C.I. Reactive Yellow 176	4.05 (5.32)	31.36	4–5 (4–5)	4–5 (4–5)	4 (4)
						C.I. Reactive Red 195	5.50 (7.01)	27.45	4–5 (4–5)	4 (4–5)	4 (4)
Bleached cotton/polyester blend	2.1	20.8	2.20	35.15	96.3	C.I. Reactive Red 239/C.I. Disperse Red 60	5.37 (7.11)	32.40	4–5 (4–5)	4–5 (4–5)	4 (4)

Enzyme dosage (20 g/L); nonionic wetting agent (2 g/L); pH (5); wet-pickup (80%); batching at 50 °C for 18 h; followed by washing at pH (9), LR 1/20 at 75 °C for 30 min with mechanical agitation (28 rpm).
DFR: decrease in flexural rigidity; DR: decrease in roughness; Incr. WRA: increase in wrinkle recovery angle; RTS: retained tensile strength; Incr. K/S: increase in color strength; WF: wash fastness; RF: rubbing fastness.
Values in parenthesis represent color strength and fastness properties of treated substrates.

is governed by both the type of the substrate as discussed earlier as well as the nature of the dye, e.g. molecular size, functionality, mode of interaction, availability, accessibility of dyeing sites (Choudhury, 2006; Ibrahim et al., 1999), etc. (iii) compared to the bleached cotton fabric, mercerized cotton fabric exhibits increased in *K*/*S* values most probably due to difference between nominated substrates in reactivity, amorphous/crystalline ratio (Choudhury, 2006; Paulo & Gubitz, 2003), availability and accessibility of –OH groups as well as in extent of surface modification after enzymatic treatment, (iv) the increase in *K*/*S* of the bio-treated fabric could probably be explained by creation of new dye-absorbing surface, alteration of pore structure along with simultaneous removal of fibrillar matters thereby enhancing the extent of dye diffusion/penetration into the treated fabric structure as well as fixation of dye molecules along with decreasing the scattering coefficient, i.e. deeper shades (Ibrahim et al., 1999; Kanchagar, 2001; Paulo & Gubitz, 2003) and (v) enzymatic treatment has a marginal positive or no impact on the wash and rubbing fastness properties of the dyed fabric samples.

4. Conclusion

A new attempt has been made to upgrade the surface and dyeing properties of cellulose-containing fabrics, i.e. bleached cotton, mercerized cotton and cotton/polyester blend fabric (50/50) via cellulases-treatment, using the pad-wet batch technique, followed by subsequent washing under mechanical action. The optimum treatment condition was found to be cellulases dosage (20 g/L), wet-pickup (80%), batching time (18 h), batching temperature (50 °C), followed by immediate after-washing under mechanical agitation (28 rpm). The extent of loss in weight, improvement in surface properties, resiliency as well as dyeability with the nominated dyestuffs is determined by the type of substrate. The upgrading of surfaced morphology of the bio-polished cotton fabric was confirmed by SEM micrographs.

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