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Review

A review on influential behaviour of biopolishing on dyeability and certain physico-mechanical properties of cotton fabrics

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ABSTRACT

Biopolishing treatment, given to the cotton fabrics using cellulases, often influences dyebility and certain physical properties of the fabrics after treatments, besides improving appearance and handle values. Cellulase treatments prior to dyeing facilitate the dyeing process subsequently, while reactions of cellulases are retarded by the dyestuff present in the fabrics to different extents. Removal of protruding fibres imparts smooth appearance and defibrillation of cotton fibres alters the moisture absorption properties of the fabrics. Reduction in fabric strength, increase in elongation at break are also realized in biopolishing in addition to improved handle values. An attempt has been made to review the influential behaviour of cellulase treatment on dyeability and physical properties of cotton fabrics.

1. Introduction

Cellulase enzymes are complex mixtures of three major types of enzymes namely, endo-1,4-β-D-glucanases (EG) (EC 3.2.1.4), which randomly cleave internal glucosidic bonds within an unbroken glucan chain in the most accessible parts of cellulose polymers and newly created non-reducing chain ends then, become the substrate for 1,4-β-D-glucan cellobiohydrolases (CBH) (EC 3.2.1.91), which cleave them into cellobioses. Hydrolysis of cellobioses into the glucose end product is completed by β-glucosidases (BG) or cellobiases (EC 3.2.1.21), which splits cellobiose units into soluble glucose monomers (Fig. 1). Complete hydrolysis of native celluloses, largely, depends on the combined actions of these three component enzymes. However, in total crude cellulases, endoglucanases (EG), cellobiohydrolases (CBH) and cellobiases are present in non-uniform compositions (Table 1).

2. Biopolishing and dyeability

Biopolishing of cotton fabrics carried out, either before or after the dyeing process, has an influential role on dyeability of the fabrics. Bulky dye molecules used in cotton fabrics react only in the accessible regions of fibres, which are, also major parts of the substrates for enzyme hydrolysis during biopolishing. Extent of cellulase attack on dyed fabrics depends on molecular size of dyes (Arja, Londerborough, Joutsjoki, Rajia, & Jari, 2004; Choe, Park, Cha, & Jeon, 1997; Diller, Walsh, & Radhakrishnaiah, 1999; Gusakov, Sinitsyn, Berlin, & Markov, 2007; Ibrahim, Allam, Morsy, Zairy, & Hassan, 2000; Ibrahim, El Zairy, Allam, Morsy, & Hassan, 1997; Mori, Haga, & Takagishi, 1995, 1996), dye/fibre interactions (Choe et al., 1997; Ibrahim et al., 1997; Mori et al., 1996; Rendle, Crabtree, Wiggins, & Salter, 1994; Snyder, 1996; Diller & Traore, 1998; Blanchard, Graves, & Batiste, 2000; Azevedo, Bishop, & Paulo, 2002a; Azevedo, Bishop, & Paulo, 2002b; Betcheva, Stamenova, Boutris, & Tzanko, 2003; Prabhu & Arputharaj, 2003; Tzanov, Andreaus, & Gue, 2003; Yamade, Amano, Horikawa, Nozaki, & Kanda, 2005) reactive groups present in the dyes (Choe et al., 1997; Mori et al., 1996; Dille et al., 1998; Betcheva et al., 2003; Blanchard et al., 2000; Prabhu & Arputharaj, 2003; Zhou, Yeung, & Yuen, 2001; Rendle et al., 1994; Tzanov et al., 2003; Yamade et al., 2005; Yang, Zhou, Lickfield, & Parachura, 2003) and aggregation of dye molecules, besides the process conditions. Presence of dye molecules prevents hydrolysis depending on size of dye molecules present in the fabrics, however, irrespective of size of the dye molecules similar weight loss values are reached as that of undyed samples, on extended hydrolysis.

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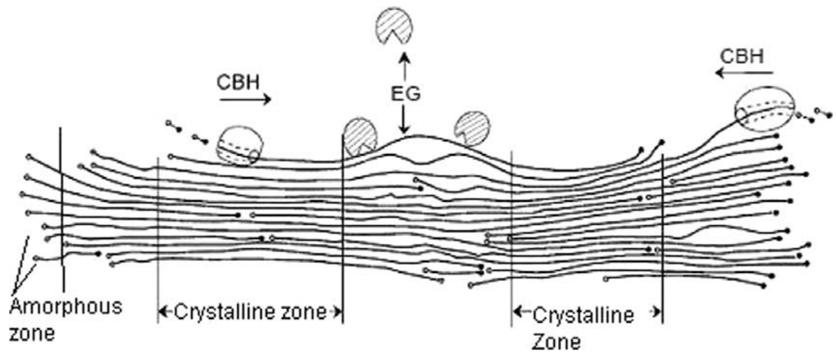

Fig. 1. Action of cellulases on cotton.

3. Biopolishing of dyed and finished fabrics

3.1. Fabrics dyed with direct dyes

In the case of fabrics dyed with direct dyes, the efficiency of biopolishing is highly influenced by size, substantivity, molecular weight and concentration of dyes in the fabrics (Choe et al., 1997; Diller et al., 1999; Mori et al., 1995; Mori et al., 1996; Prabhu & Arputharaj, 2003; Snyder, 1996). Planar Congo Red molecules, which align themselves in a preferential linear configurations, hinder penetration of the relatively bigger enzyme molecules. Cotton fibres dyed with direct dyes have been reported to be more difficult to digest by cellulase and, substantivity of the dyes, hydrogen bonds formed between dyes and fibres appears to block cellulase hydrolysis, however, weight loss has been reported to be independent of dye uptake at higher cellulase concentrations.

3.2. Fabrics dyed with reactive dyes

Fabrics dyed with reactive dyes of different reactive groups exhibit surface roughness after processing with crude cellulases, purified EG and CBH, due to poor biopolishing effects compared to the undyed fabrics (Rendle et al., 1994; Mori et al., 1996; Choe et al., 1997; Dille et al., 1998; Blanchard et al., 2000; Betcheva et al., 2003; Prabhu & Arputharaj, 2003; Yamade et al., 2005). Compared to mono-functional reactive dyes, weight loss values are less in the case of bifunctional reactive dyes. Dichlorotriazine dyes extensively retard enzyme hydrolysis compared to vinyl sulphone dyes, perhaps due to cross link effects of dichlorotriazine dyes between two cellulose molecules, which cause steric hindrance for enzyme hydrolysis. Hetero-bifunctional reactive dyes have higher substantivity than dichloro-dyes, and offer resistance to enzyme hydrolysis.

Table 1
Various components of total crude cellulases (Gama, 1998; Jones, 2001; Azevedo, 2002).

Component	%	Molecular weight (kDa)	Isoelectric point (pI)
CBH I	60	63	3.5–4.2
CBH II	20	58	5.1–6.3
EG I	10	46	4.6–5.0
EG II	1	48	5.5–6.1
EG III	Not determined		7.4
EG V	Not determined		2.8–3.0
β-Glucosidase	Not determined		8.7

3.3. Fabrics dyed with vat and sulphur dyes

Presence of vat dyes does not influence the weight loss during cellulase treatment in many cases; however, planar anthraquinone dyes obstruct cellulase access efficiently than indigo dyes (Arja et al., 2004; Choe et al., 1997; Gusakov et al., 2007). In the case of sulphur dyes, colour strengths are not altered with lower dye pick-up, however, presence of acidic groups in sulphur black, often, inhibits enzyme actions and results in lower weight losses than vat dyed samples (Ibrahim et al., 2000).

3.4. Acid and neutral cellulases in denim washing

In denim washing, acid cellulases are used in stonewashing, stoneless washing processes to impart various effects to the fabrics in terms of contrast, shade and smoothness (Schmitt & Prasad, 1998). Besides cellulose binding domain, certain hydrophobic sites and other non polar surfaces available in the cellulases interact, bind indigo dye molecules and act as an emulsifier, helping the dyes to float out of the cellulose fibers during hydrolysis (Fig. 2) (Ali, 1999; Andreaus, Campos, Gubitz, & Paulo, 2000; Andreaus, Campos, & Paulo, 2001; Chattopadhyay, Chatterjee, Bhadra, & Gumber, 1997; Gusakov et al, 2000a; Gusakov et al, 2001; Heikinheimo, Buchert, Oinonen, & Suominen, 2000; Kochavi, Videback, & Cedroni, 2000; Lantto, Oinonen, & Suominen, 1996; Park, Cha, & Choe, 1995; Paul & Naik, 1997; Tyndall, 1992; Oinonen & Suominen, 2002; Arja et al., 2004; Hebeish & Ibrahim, 2007). Binding of indigo also involves formation of hydrogen bond interactions between amino acid residues of enzymes and —NH and C=O groups of dye molecules (Gusakov et al., 2000a).

Low molecular weight 20 kDa EG performs well in washing of denim fabrics, while addition of high molecular weight EG of 50 kDa or CBH of 50 kDa decreases washing effects. EG I and CBH II from *Trichoderma reesei* provides moderate abrasive activity on denim fabrics while the performance of CBH I appears to be very poor (Rendle et al., 1994). Among various purified single component cellulases, EG II, EG III and EG V exhibit the higher adsorption ability on indigo particles with better performance mainly due to the exposure of higher aromatic residues (Tyr + Phe + Trp) and non-polar residues (Tyr + Phe + Trp + Val + Leu + Ileu + Pro + Met) at the interface in high proportions, than CBHI, II and EGI. Elimination of cellulose binding domain from CBH I not only results in loss of ability to bind to cellulose but also the indigo binding to a significant degree due to removal of tyrosine residues (Pedersen & Schmidt, 1994). Enzymes with poor, moderate abrasive activity have only about 1.4–1.7% of aromatic residues exposed to solvents, while cellulases with high washing performance have up to 2.5–5.7% of (Tyr + Phe) and (Tyr + Phe + Trp) residues and their combinations available for biopolishing.

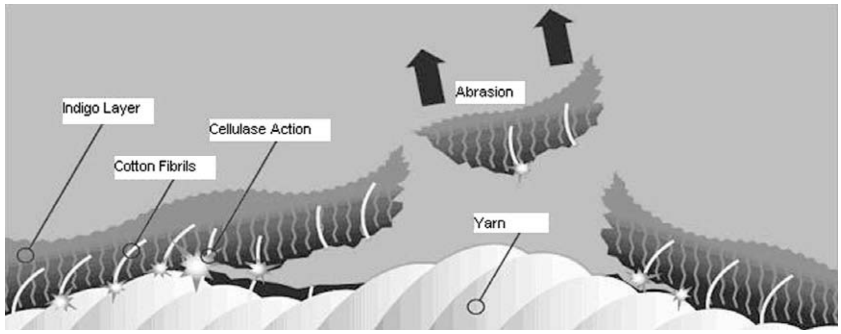

Fig. 2. Action cellulases on denim fabrics.

3.5. Backstaining of denims and neutral cellulases

Indigo dye particles released during cellulase washing turns the wash liquor dark blue and subsequently the indigo particles redeposit on undyed weft yarns and white pocket materials, giving a lighter blue shade back that results in dull look with less contrast on the fabrics, a phenomenon known as backstaining (Klahorst, Kumar, & Mullins, 1994; Lantto et al., 1996; Park et al., 1995; Chattopadhyay et al., 1997; Paulo, Cortez, & Almeida, 1997; Dille et al., 1998; Pedersen & Schmidt, 1994; Ali, 1999; Andreaus et al., 2000; Andreaus et al., 2001; Gusakov et al., 2001; Heikinheimo et al., 2000; Kochavi et al., 2000; Oinonen & Suominen, 2002; Schmitt & Prasad, 1998; Arja et al., 2004; Sariisik, 2004; Chinedu et al, 2007). Amino groups of dye molecules get protonated in acidic medium, generate a positive charge while the cellulose maintains negative charge in acidic medium used in the acid cellulase washing, which causes mutual attraction. However, as the pH of treatment increases from 5 to 7, whiteness retention value also increases for acid cellulase too, mainly because of lower activities of acid cellulases at pH 7.0. In the case of neutral cellulases, maximum colour removal takes place at pH 6.0 and retains about 90% of colour removing activity at pH 7.0–7.5, while the acid cellulases have maximum colour removing activity at pH 5.0 and less than 40% of that at pH 6.0. Crude neutral cellulases from *Humicola insolens* appear to agglomerate the dye particles and reduce backstaining with visible increase in contrast between white and blue threads, while acid cellulases from *Trichoderma reesei* disperse the dye particles and reduce the size of indigo particles that facilitate re-adsorption and backstaining on fabrics (Anon, 2003; Menezes, 2003).

3.6. Biopolishing as pretreatment

Pretreatment of cotton fabrics with cellulases reduce the problems related to immature fibre neps, which do not pick up same amount of dye as that of matured cotton fibres (Diller et al., 1999; Klahorst et al., 1994). Cellulase pretreatment enhances penetration of alkali during scouring and increases the alkaline degradation of seed fragments in the subsequent process (Ravichandran, 2000; Li & Jin, 2003). Disaggregating cellulose molecules and development of newer regions leads to improvement in dyeability though in some cases dyeability decreases with hydrolysis initially, due to decrease in already available accessible regions by the endo component. Affinity of the dyes increases then decreases in the biopolished fabrics during extended hydrolysis, indicating the reduction of additionally developed accessible regions also (Mori et al., 1995; Kanchagar, 2001). K/S values of fabrics dyed after cellulase treatment improves by 16–19% in the case of reactive dyes, perhaps due to the removal of protruding fibres that otherwise would decrease the scattering coefficient, which depends on degree of polymerisation, ratio of amorphous to crystalline regions, swellability, accessibility, chemical reactivity, surface morphology and affinity for dyes.

4. Physical properties of biopolished fabrics

4.1. Surface morphology

Presence of various components in the total cellulases plays a dominating role in altering surface morphology of the fibres (Fig. 3) (Tripp, Moore, & Rollins, 1957; Porter, Carra, Tripp, & Rollins, 1960; Rowland, Wade, & Robats, 1973; Betrabet, Paralikar, & Patil, 1980; Traore & Diller, 1999; White, Brown, & Jr., 1981; Takai, Hayashi, Nisizawa, & Kanda, 1983; Focher, 1981; Hemmpel, 1991; Tyndall, 1992; Lee, Evans, Lane, & Woodward, 1996; Dourado, Mota, Pala, & Cama, 1999; Traore & Diller, 1999; Lee, Evans, & Woodward, 2000; Pinto, Moreira, Mota, & Gama, 2004; Obturk & Bechtold, 2008), further influenced by the bilateral structure of native cotton fibres (Porter et al., 1960; Kassenback, 1970; Roberts, Bose, & Rowland, 1972; White & Brown, 1981; Gama & Mota, 1997). Adsorption of cellulases on the surface of substrates takes place immediately after the introduction and remains even after washing, indicating strong binding of various components to the cellulose (White & Brown, 1981; Paulo & Almeida, 1994; Azevedo et al., 2002a; Azevedo et al., 2002b). Combination of biopolishing with shearing, singeing, considerably reduces the surface defects (Zadhoush, Khoddami, & Aghakhani, 2001).

Native cotton fibres possess highly curved surface with high density of fibrillar packing and low accessibility while the convex part that shows concentric layers has higher accessibility to reactivity in the peripheral regions (Fig. 3). Cellulase hydrolysis results in systematic removal of primary and secondary walls, progressively. On extended hydrolysis, the most accessible zone (zone N) completely disappears while zone C, the collapsed concave part of the fibres, partly or completely disappears (Kassenback, 1970). Elimination of primary wall of cotton fibre in the initial step of enzyme hydrolysis results in the reduction in the fineness of fibres and subsequently hydrolysis continues in a sub layer manner (Porter et al., 1960; Mori, Haga, & Takashishi, 1999; Zadhoush et al., 2001; Wang et al., 2006). After initial hydrolysis, microfibrillar structure becomes so weakened that the enzyme penetration within microfibrils, causes scissioning and rupture of fibrils (Paralikar & Bhatawdekar, 1984). General pattern of cellulose degradation begins with splaying and splitting of ribbons into bundles of microfibrils along its long axis into bundle of microfibrils, followed by a thinning of bundles until they are dissolved (Fig. 4) (White & Brown, 1981). Fibrillation increases with increase in crystalline orientation factor (Obturk & Bechtold, 2008). Cellulase treatments remove the corrugated spiral structures, causing erosion and longitudinal fissures (Betrabet et al., 1980; Traore & Diller, 1999). Spiral fissures that appear in the degraded fibres extend up to lumen on prolonged treatment, which results in helical cleavages, while the transverse fissures

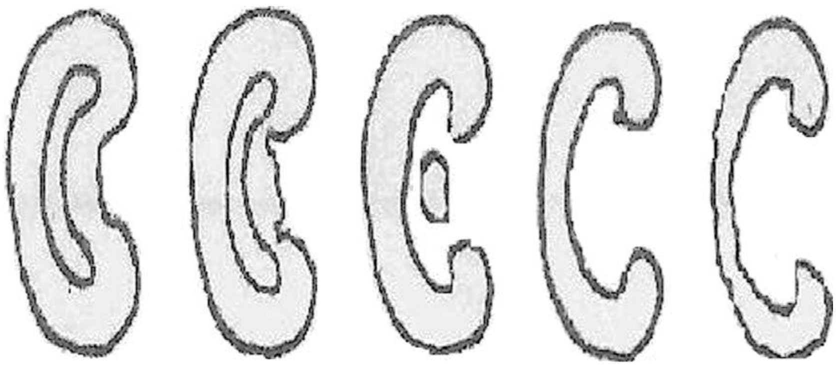

Fig. 3. Changes in morphology of cotton fibre during cellulase treatment (Kassenback, 1970).

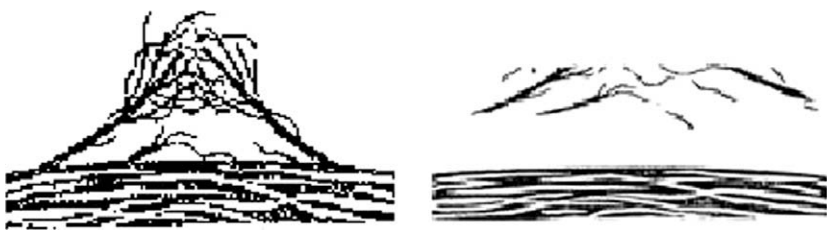

Fig. 4. Surface morphology.

result in the complete transverse breakage or fragmentation (Blum & Stahl, 1952; Paralikar & Bhatawdekar, 1984).

Cellulase monocomponents like EG I, EG II, CBH I, CBH II, neither destroy nor create large or small pores that are found in the native fibres though process results in loss of cellulose microfibrils (Gama, Vilanova, & Mota, 1998; Rouselle, Bertoniere, & Howley, 2003). Irreversibly bound enzymes are likely to form the non-effective complexes, which severely reduces the enzyme efficiency, unless they move laterally on the fibre surface (Kassenback, 1970). EG or EG rich preparations are the best for ageing and defibrillation of fibre surfaces while complete cellulase systems are recommended for cleaning and depilling effects (Takai et al., 1983; Paulo et al., 1997; Schulein, Henriksen, Lassen, & Kauppinen, 2005; Schulein et al., 2007). Inactivated CBH enzymes cause hole like defects along the fibre axis to an extent of 23–75 nm, after washing that represents the images of CBH I and movement along the cellulose chain length (Lee et al., 1996). Action of CBHs on cotton causes a number of longitudinal and transverse cracks and many erosions and between CBH I and CBH II, CBH II causes more surface cracks than CBH I (Traore & Diller, 1999; Yamade et al., 2005).

4.2. Moisture properties

Water absorbency and water retention properties of fabrics are modified after biopolishing, further influenced by the fabric construction parameters and extent of hydrolysis (Ogiwara & Arai, 1968; Takai et al., 1983; Almeida & Paulo, 1993; Diller, Zeronian, Pan, & Yoon, 1994; Gulrajani, Roy, Agarwal, & Chand, 1998b; Radhakrishnaiah, Meng, Huang, Diller, & Walsh, 1999; Prabhu & Arputharaj, 2003; Mahmood, Weijun, Nazir, Iqbal, & Abdullah, 2006; Cuissinat & Navard, 2008). Cellulase treated fabrics show higher energy dissipation under wet condition, implying that they might offer slightly superior thermal comfort performance under hot, humid conditions (Radhakrishnaiah et al., 1999). Wettability of the fabrics after biopolishing improves by 35–85% depending upon construction of the fabrics, which further improves with softener treatment (Takai et al., 1983; Raje, Gurjar, & Kawlekar, 2001). As the enzyme hydrolyses and removes certain accessible amorphous portions during hydrolysis, the absorption of moisture decreases with treatment time. In the case of unmercerised fabrics, moisture regain reduces from 7.3% to 6.7% and 7.8 to 7.4% for unmercerised fabrics and marginal increase in the moisture regain from 6.0% to 6.10% under high agitation levels have also been reported mainly due to defibrillation effects (Focher, Marzetti, Cattaneo, Beltrame, & Carniti, 1981; Almeida & Paulo, 1993; Rouselle & Howley 1998; Rousselle, Bertoniere, Howley, & Goynes, 2002).

Changes in the relative proportions of amorphous and crystalline regions alters the accessible regions, in turn, affects swelling actions in the fibres due to the actions of endo and exo components present in the total cellulase, termed as "S" factor in the reaction (Marsh, Bollenbacher, Butler, & Guthrie, 1953; Youatt, 1962; Ogiwara & Arai, 1968; Ueda, Koo, Wakida, & Yoshimura, 1994; Gusakov et al., 2007). Enzyme treatment of cotton fabrics increases transverse swelling of fibres by 14%. Water retention capacity of cotton and cotton/linen fabrics increases by 24–28%, due to splitting of microfibrils (Diller et al., 1994; Radhakrishnaiah et al., 1999). Water imbibition of fibres is not significantly affected after the treatment with any of the components and remains at 29–31% for the fabrics constructed from various spun yarns (Rouselle et al., 2003).

4.3. Tensile properties

Changes in the degree of polymerization, degree of crystallinity and weight loss of fabrics significantly influence tensile properties in terms of tensile elongation, tensile and compressive resilience, shear rigidity, hysteresis and surface friction are influenced as high as 50% and better drapeability reduced air permeability are also observed in cellulase biopolished samples (Almeida & Paulo, 1993; Diller et al., 1994; Paulo & Almeida, 1996a; Paulo & Almeida, 1996b; Saraf, 1997; Gulrajani et al., 1998b; Mori et al., 1999; Radhakrishnaiah et al., 1999; Wakida, Moriya, Lee, Yoshikora, & Yanai, 2000; Raje et al., 2001; Radhakrishnaiah, He, Cook, & Diller, 2005; Hebeish & Ibrahim, 2007). Though surface roughness decreases remarkably, due to reduction in surface hairs and neps, the coefficient of friction does not change with respect to the treatment time, perhaps due to rifts in the longitudinal sections (Almeida & Paulo, 1993; Chong, 1994; Ramkumar & Abdalah, 2001).

Gradual degradation of fibres along the spiral plane contributes to the initial tensile strength loss and once the fissures reach the lumen, further degradation in strength occurs rapidly (Blum & Stahl, 1952; Almeida & Paulo, 1993; Koo, Ueda, Wakida, Yoshimura, & Igarashi, 1994; Paulo et al., 1997). Treatment time that has a maximum effect on strength loss, followed by enzyme concentrations and pretreatments with endoglucanases can accelerate strength loss of the fabrics at low agitation levels itself. Ratio of breaking load over weight loss is high for preparations with higher EG activities and, combinations of high agitations with EG activities synergistically tear away fiber surfaces, exposing fresh surfaces for further attack and leading to loss in breaking strength up to 35% (Paulo & Almeida, 1996a; Paulo et al., 1997). At low agitation levels, breaking load decreases to a very low extent at 4%, while the percent strength increases up to 70% in similar duration with higher concentration enzymes (Tyndall, 1992; Rouselle & Howley, 1998) and, at 10% strength loss elongation at break increases significantly from 7.0% to 11–12.0%. Strength of dyed fabrics appears to be better (less strength loss) than that of fabrics treated with enzymes and then dyed, though the differences are not significant. Fabrics made of ramie and linen retains higher strength than cotton and viscose rayon fabrics (Diller et al., 1994; Park et al., 1995; Blanchard et al., 2000).

Retention of tearing strength after cellulase treatment is higher in the case of mercerized fabrics, demonstrating the effects of mercerization in relieving strength loss problems. Tearing strength does not change with CBH I, CBH II and EG I, while EG II at higher dosage shows marginal decrease. Due to the fact that more numbers of adsorption sites are available in the case of rotor spun yarn fabrics because of open construction of the yarns, the tear strength losses are high in such fabrics compared to ring yarn fabrics (Cortez, Ellis, & Bishop, 2001). In the case of bursting strength, higher losses are observed with EG-rich cellulases compared to CBH-rich enzyme, and the highest losses are observed in the case of total crude cellulases at 13.0%, 11.2% and 15.2%, respectively. Abrasion resistance increases due to smoothness of the fabric surface after biopolishing depending of the yarn structures; while carded yarn fabrics show significant improvements due to inherent rough surfaces, combed yarn fabrics do not show improvements to similar extents (Chong, 1994; Gulrajani, Dayal, & Chakraborty, 1998a).

Increase in time, temperature and concentration of cellulases decrease bending length and bending modulus significantly and reduction in bending hysteresis is greater with higher weight losses (Paulo et al., 1997; Gulrajani et al., 1998b). Initially, bending stiffness increases due to consolidation of fabric structure, reduction in interstices and as the treatment proceeds, effect of enzymes become prominent enough to reduce stiffness, which can, further, be reduced with softener treatment, on account of decrease in inter-fibre, inter-yarn frictions (Raje et al., 2001). Bending hysteresis decreases after treating the fabrics with CBH-rich cellulases due to cleaner surface without fibrillations, while it increases for EG-rich enzyme treatment. The compressional energy decreases with increasing concentrations of enzymes and resilience of compression is relatively lower for cellulase treated fabrics than softener treated fabrics at lower concentrations, however, as the concentration of enzyme increases, the value improves for enzyme treated fabrics.

4.4. Pilling and handle

A linear relationship exists between depilling and weight losses for total cellulase and endo-rich cellulase (Pedersen, Screw, & Cedroni, 1993; Koo et al., 1994; Chiweshe & Crews, 2000; Liu et al., 2000; Gusakov, Sinitsyn, Berlin, Markov, & Ankudimova, 2000b; Raje et al., 2001; Ramos, Pinto, Sampaio, Mota, & Gama, 2005). EG and EG-rich cellulases exhibit better pilling rating at lower weight losses compared to other components of cellulases. For knitted fabrics, a weight loss of about 1–2% appears to be enough to realise a remarkable reduction in pilling tendency while woven fabrics shows no significant pilling reduction till 8–9% weight loss, however, improvements are also evident under high mechanical actions and for various combinations of process parameters, i.e. pH and temperatures.

Slow kinetics of enzymatic degradation of crystalline cotton celluloses allows handle of the fabrics to be improved without excessively damaging the fabrics (Tyndall, 1992; Almeida & Paulo, 1993; Pedersen et al., 1993; Chong, 1994; Gulrajani et al., 1998a; Paulo, 1998; Radhakrishnaiah et al., 2005). Harshness produced by the alkaline mercerization can be counteracted by cellulase treatment, while soft handle of liquid ammonia treated samples can further be enhanced by the cellulase treatment. Composition containing EG III and CBH I are capable of enhancing feel, appearance, softness, colour and appearance of the cotton fabrics, after the treatment (White & Brown, 1981; Rouselle et al., 2003). Actual thickness of fabrics reduces with biopolishing, while the apparent thickness appears to increase with mechanical actions that lead to fibrillations (Almeida & Paulo, 1993; Pedersen et al., 1993; Paulo & Almeida, 1994). Decrease in the flexural rigidity and drapeability is observed with reference to concentration and time, which could possibly improve handle of the fabrics (Chong, 1994). Cellulase treatment lowers the tensile and compressional energy, which essentially means improved handle, also confirmed by decreased bending rigidity and shear rigidity, i.e. improvement in the softness (Gulrajani et al., 1998a). Enzyme treated fabrics show the total crease recovery angle of 169°, significantly higher than untreated samples (130°), and the drape coefficient reduces from 0.925 to 0.760 (Chattopadhyay, 1997). Effects of agitation, during biopolishing, on primary hand qualities such as stiffness, smoothness, fullness, stiffness and thermal performance have been widely studied, in the past (Focher et al., 1981; Paulo & Almeida, 1996a; Paulo & Almeida, 1996b; Hes, Pinheiro, Mc Goncalves, & Paulo, 1997; Saraf, 1997; Radhakrishnaiah et al., 1999; Ramkumar & Abdalah, 2001) and total hand value increases from 3.3 to 3.5, after cellulase treatment, which further increases up to 3.75, with softener treatments. Hydrolysis of cellulose molecules in different regions of the cotton fibres also alters the dimensional stability of the fabrics (Cortez, Ellis, & Bishop, 2002). While untreated samples show about 3% shrinkage, cellulase treatments reduce the shrinkage to 0.5–1.0% levels which further improves with EG-rich enzymes.

5. Conclusion

Biopolishing of cotton fabrics offers unmatched results that can otherwise be achieved using chemical finishes. By suitably optimizing the process conditions, the strength loss during the process can be aimed to a required level, without compromising other handle related properties. Reasonably good results obtained in the fabrics dyed with various dye classes, show the flexibility and versatility of the treatment in the manufacturing process.

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References

Ali, S. I. (1999). Development of cellulase enzymes and evaluation of stonewash effect. *International Journal of Clothing Science and Technology, 11*, 19–20.

Almeida, L., & Paulo, A. C. (1993). Softening of cotton by enzymatic hydrolysis. *Melliand English, 74*, 404–407.

Andreaus, J., Campos, R., Gubitz, G., & Paulo, A. C. (2000). Influence of cellulases on indigo back staining. *Textile Research Journal, 70*, 628–632.

Andreaus, J., Campos, R., & Paulo, A. C. (2001). Reduction of indigo back staining by post washing. *Melliand International, 7*, 318–320.

Anon (2003). Bio-flexible finishes. *Textile Month,* 2, 20–21.

Arja, M. O., Londerborough, J., Joutsjoki, V., Rajia, L., & Jari, V. (2004). Three cellulases from *Melanocarpus albomyces* for textile treatment at neutral pH. *Enzyme and Microbial Technology, 34*, 332–341.

Azevedo, H., Bishop, D., & Paulo, A. C. (2002a). Possibilities for recycling cellulases after use in cotton processing. *Applied Biochemistry and Biotechnology, 101*, 61–75.

Azevedo, H., Bishop, D., & Paulo, A. C. (2002b). Possibilities of recycling cellulases after use in cotton processing, part II. *Applied Biochemistry and Biotechnology, 101*, 77–91.

Betcheva, R., Stamenova, M., Boutris, C., & Tzanko, T. (2003). Objective evaluation of the efficiency of cellulase finishing of cotton fabrics dyed with reactive dyes. *Macromolecular Materials and Engineering, 288*, 957–963.

Betrabet, S. M., Paralikar, K. M., & Patil, N. B. (1980). Effect of cellulase on the morphology and fine structure of cellulosic substrates. *Cellulose Chemistry and Technology, 14*, 811–820.

Blanchard, E. J., Graves, E. E., & Batiste, S. L. (2000). Enzymatic hydrolysis of modified cotton. *Textile Chemists and Colorists & American Dyestuff Reporter, 32*, 37–41.

Blum, R., & Stahl, W. H. (1952). Enzymatic degradation of cellulose fibers. *Textile Research Journal, 22*, 178–192.

Chattopadhyay, D. P., Chatterjee, K. N., Bhadra, I., & Gumber, R. (1997). Studies on the enzymatic fading of denim. *Man Made Textiles in India, 40*, 452–454.

Chinedu, S. N., Okochi, V. I., Smith, H. A., Okafor, U. A., Okerenta, O. B. M., & Omidiji, O. (2007). Effect of carbon sources on cellulase (EC 3.2.1.4) production by penicillium chrysogenum PCL 501. *African Journal of Biochemistry Research, 1*, 6–10.

Chiweshe, A., & Crews, P. C. (2000). Influence of household fabric softeners and laundry enzymes on pilling and breaking strength. *Textile Chemists and Colorists & American Dyestuff Reporter, 32*, 41–47.

Choe, E. K., Park, S. Y., Cha, H. C., & Jeon, B. D. (1997). Effect of pre-existing dyes and fabric type on cellulase treatment of cotton fabrics. *Textile Research Journal, 67*, 155–162.

Chong, C. L. (1994). Biostoning of Cotton Knits. *American Dyestuff Reporter*(3), 54–58. 64.

Cortez, J. M., Ellis, J., & Bishop, D. P. (2001). Cellulase finishing of woven cotton fabrics. *Journal of Biotechnology, 89*, 239–245.

Cortez, J. M., Ellis, J., & Bishop, D. P. (2002). Using cellulases to improve the dimensional stability of cellulosic fabrics. *Textile Research Journal, 72*, 673–680.

Cuissinat, C., & Navard, P. (2008). Swelling and dissolution of cellulose – part III plant fibres in aqueous system. *Cellulose, 15*, 67–74.

Diller, G. B., Zeronian, S. H., Pan, N., & Yoon, M. Y. (1994). Enzymatic hydrolysis of cotton, linen, ramie and viscose rayon fabrics. *Textile Research Journal, 64*, 270–279.

Diller, G. B., & Traore, M. K. (1998). Influence of direct and reactive dyes on the enzymatic hydrolysis of cotton. *Textile Research Journal, 68*, 185–192.

Diller, G. B., Walsh, W. K., & Radhakrishnaiah, P. (1999). Effect of enzymatic treatment on dyeing and finishing of cellulose fibres: A study of the basic mechanisms and optimization of the process. *National Textile Center Annual Report,* C96–A01, 1–9.

Dourado, F., Mota, M., Pala, H., & Cama, F. M. (1999). Effect of cellulase adsorption on the surface and interfacial properties of cellulose. *Cellulose, 6*, 265–282.

Focher, B., Marzetti, A., Cattaneo, M., Beltrame, P. L., & Carniti, P. (1981). Effects of structural features of cotton cellulose on enzymatic hydrolysis. *Journal of Applied Polymer Science, 26*, 1989–1999.

Gama, F. M., & Mota, M. (1997). Enzymatic hydrolysis of cellulose (II): X-ray photoelectron spectroscopy studies on cellulase adsorption, effect of the surfactant Tween-85. *Biocatalysis and Biotransformation, 15*, 237–250.

Gama, F. M., Vilanova, M., & Mota, M. (1998). Exo and endo-glucanolytic activity of cellulase purified from *Trichoderma reesei*. *Biotechnology Techniques, 12*, 677–681.

Gulrajani, M. L., Dayal, A., & Chakraborty, M. (1998a). Kawabata evaluation of enzyme treated cotton knitted fabrics. *Indian Journal of Fibre and Textile Research, 23*, 160–164.

Gulrajani, M. L., Roy, P., Agarwal, R., & Chand, S. (1998b). Enzymatic treatment of cotton knits. *Indian Journal of Fibre and Textile Research, 23*, 242–249.

Gusakov, A. V., Sinitsyn, A. P., Markov, A. V., Skomarovsky, A. A., Sinitsyna, O. A., Berlin, A. G., et al. (2000a). Indigo binding domains in cellulase molecules, biocatalysis – 2000. *Fundamentals and Applications, 41*, 77–80.

Gusakov, A. V., Sinitsyn, A. P., Berlin, A. G., Markov, A. V., & Ankudimova, N. V. (2000b). Surface hydrophobic amino acid residues in cellulase molecules as a structural factor responsible for their high denim washing. *Enzyme and Microbial Technology, 27*, 664–671.

Gusakov, A. V., Sinitsyn, A. P., Markov, A. V., Sinitsyn, O. A., Ankudimova, N. V., & Berlin, A. G. (2001). Study of protein adsorption on indigo particles confirms the existence of enzyme – indigo interaction sites in cellulases molecules. *Journal of Biotechnology, 87*, 83–90.

Gusakov, A. V., Sinitsyn, A. P., Berlin, A. G., & Markov, A. V. (2007). Surface hydrophobic amino acid residues in cellulase molecules as a structural factor responsible for their high denim washing performance. *Enzyme and Microbial Technology, 27*, 664–671.

Hebeish, A., & Ibrahim, N. A. (2007). The impact of frontier sciences on textile industry. *Colourage, 54*, 41–55.

Heikinheimo, L., Buchert, J., Oinonen, A. M., & Suominen, P. (2000). Treating denim fabrics with *Trichoderma reesei* cellulases. *Textile Research Journal, 70*, 969–973.

Hemmpel, W. H. (1991). The surface modification of woven and knitted cellulosic fibre fabrics by enzymatic degradation. *International Textile Bulletin – Dyeing/Printing/Finishing, 3*, 5–14.

Hes, L., Pinheiro, L. H., Mc Goncalves, M., & Paulo, A. C. (1997). The effect of selected mechanical properties acquired by the KES-F instruments on the level of puckering of cotton fabrics after washing. *International Journal of Clothing Science and Technology, 9*, 188–192.

Ibrahim, N. A., El Zairy, M. R., Allam, E., Morsy, M. S., & Hassan, T. M. (1997). Dyeability of biofinished cellulosic fabrics. *Colourage Annual, 44*, 47–54.

Ibrahim, N. A., Allam, E., Morsy, M. S., Zairy, M. R. E., & Hassan, T. M. (2000). Biofinishing of Pre-dyed Cotton Fabrics. *Colourage*(4), 29–35.

Kanchagar, A. P. (2001). Effect of enzymatic treatment of cotton on colour yield in dyeing. *Colourage Annual, 48*, 29–32.

Kassenback, P. (1970). Bilateral structure of cotton fibers as revealed by enzymatic degradation. *Textile Research Journal, 40*, 330–334.

Klahorst, S., Kumar, A., & Mullins, M. M. (1994). Optimizing the use of cellulase enzymes. *Textile Chemists and Colorists, 26*, 13–18.

Kochavi, D., Videback, T., & Cedroni, D. (2000). Optimizing processing conditions in enzymatic stone washing. *American Dyestuff Reporter, 89*, 24–28.

Koo, H., Ueda, M., Wakida, T., Yoshimura, Y., & Igarashi, T. (1994). Cellulase treatment of cotton fabrics. *Textile Research Journal, 64*, 70–74.

Lantto, R., Oinonen, A. M., & Suominen, P. (1996). Back staining in denim wash with different cellulases. *American Dyestuff Reporter, 85*, 64–65. 72.

Lee, I., Evans, B. R., Lane, L. M., & Woodward, J. (1996). Substrate–enzyme interactions in cellulase systems. *Bioresource Technology, 58*, 163–169.

Lee, I., Evans, B. R., & Woodward, J. (2000). The mechanism of cellulase action on cotton fibres – evidence from atomic force microscopy. *Ultramicroscopy, 82*, 212–221.

Li, S., & Jin, D. J. (2003). Use of enzymes in dyeing and finishing. *Textile Asia, 34*, 52–55.

Liu, J., Otto, E., Lange, N., Husain, P., Condon, B., & Lund, H. (2000). Selecting cellulases for biopolishing based on enzymes selectivity and process condition. *Textile Chemist and Colourist & American Dyestuff Reporter, 32*, 30–36.

Mahmood, K., Weijun, Y., Nazir, K., Iqbal, R. Z., & Abdullah, G. A. (2006). Study of cellulolytic soil fungi and two nova species and new medium. *Journal of Zhejiang University Science B, 7*, 459–466.

Marsh, P. B., Bollenbacher, K., Butler, M. L., & Guthrie, L. R. (1953). "S Factor", a microbial enzyme which increases the swelling of cotton in alkali. *Textile Research Journal, 23*, 878–888.

Menezes, E. (2003). The Bioroute. *Textile Month, 3*, 43–46.

Mori, R., Haga, T., & Takagishi, T. (1995). Relationship between cellulase treatment and the dyeability with a direct dye for various kinds of cellulosic fibres. In *Proceedings of bilateral symposium on eco-friendly textile processing* (pp. 63–67). New Delhi: Indian Institute of Technology.

Mori, R., Haga, T., & Takagishi, T. (1996). Reactive dye dyeability of cellulose fibres with cellulase treatment. *Journal of Applied Polymer Science, 59*, 1263–1269.

Mori, R., Haga, R., & Takashishi, T. (1999). Bending and shear properties of cotton fabrics subjected to cellulase treatment. *Textile Research Journal, 69*, 742–746.

Obturk, H. B., & Bechtold, T. (2008). Splitting tendency of cellulosic fibres – part III tendency of viscose and modal fibres. *Cellulose, 15*, 101–109.

Ogiwara, Y., & Arai, K. (1968). Swelling degree of cellulose materials and hydrolysis rate with cellulase. *Textile Research Journal, 38*, 885–891.

Oinonen, A., & Suominen, P. (2002). Enhanced production of *Trichoderma reesei* endoglucanase and use of the new cellulase preparations in producing the stone washed effect on denim fabric. *Applied and Environmental Microbiology, 68*, 3956–3964.

Paralikar, K. M., & Bhatawdekar, S. P. (1984). Hydrolysis of cotton fibres by cellulase enzymes. *Journal of Applied Polymer Science, 29*, 2573–2580.

Park, S. Y., Cha, H. C., & Choe, E. K. (1995). Cellulase treatment of cotton fabrics: Part ii, the fabric type dependency and the remarkable pilling reduction. In *Proceedings of third Asian textile conference,* (Vol. II pp. 617–634). Hong Kong.

Paul, R., & Naik, S. R. (1997). Denim finishing – the Buzz Word of survival in international market. *Textile Dyer and Printer, 9*, 14–18.

Paulo, A. C., & Almeida, L. (1994). Cellulase hydrolysis of cotton cellulose: the effects of mechanical action, enzyme concentration and dyed substrates. *Biocatalysis, 10*, 353–360.

Paulo, A. C., & Almeida, L. (1996a). Effect of agitation and endoglucanase pretreatment on the hydrolysis of cotton fabrics by a total cellulase. *Textile Research Journal, 66*, 287–294.

Paulo, A. C., & Almeida, L. (1996b). Cellulase activities in finishing effects. *Textile Chemists and Colorists, 28*, 28–32.

Paulo, A. C., Cortez, J., & Almeida, L. (1997). The effect of cellulase treatment in textile washing process. *Journal of Society of Dyers and Colorists, 113*(7–8), 218–222.

Paulo, A. C. (1998). Mechanism of cellulase action in textile processes. *Carbohydrate Polymers, 37*, 273–277.

Pedersen, G. L., Screw, G. A., Jr., & Cedroni, D. M. (1993). Biopolishing of cellulosic fabrics. *Melliand English, 74*, E419–E420.

Pedersen, G., & Schmidt, M. (1994). Removal of excess dye from new textiles. US Patent Office, Pat. No. 5 356 437.

Pinto, R., Moreira, S., Mota, M., & Gama, M. (2004). Studies on the cellulose binding domains adsorption to cellulose. *Langmuir, 20*, 1409–1413.

Porter, B. R., Carra, J. H., Tripp, V. W., & Rollins, M. L. (1960). Effect of cellulases on cotton fiber microstructure–part i degradation by cellulase in fungal growth filtrates. *Textile Research Journal, 30*, 249–258.
Prabhu, H. G., & Arputharaj, A. (2003). Studies on cellulase treatment on cotton. *Colourage, 50*, 31–34.
Radhakrishnaiah, P., Meng, X., Huang, G., Diller, G. B., & Walsh, W. K. (1999). Mechanical agitation of cotton fabrics during enzyme treatment and its effect on tactile properties. *Textile Research Journal, 69*, 708–713.
Radhakrishnaiah, P., He, J., Cook, F. L., & Diller, G. B. (2005). Hand related mechanical behaviour of enzyme treated yarn, part I- role of spinning system. *Textile Research Journal, 75*, 265–273.
Raje, C. R., Gurjar, M., & Kawlekar, S. R. (2001). Finishing of cotton fabrics with cellulase enzymes. *Indian Textile Journal, 112*, 37–41.
Ramkumar, S. S., & Abdalah, G. (2001). Surface characterization of enzyme treated fabrics. *Colourage, 48*, 15–16. 24.
Ramos, R., Pinto, R., Sampaio, L., Mota, M., & Gama, F.M. (2005). Textile depilling: Use of enzymes and cellulose binding domains. In *Proceedings of the second Mercosur congress on chemical engineering – ENPROMER,* Rio de Janeiro.
Ravichandran, P. (2000). Biopolishing boosts cotton dyeability. *Indian Textile Journal*(8), 31–38.
Rendle, D. F., Crabtree, S. R., Wiggins, K. G., & Salter, M. T. (1994). Cellulase digestion of cotton dyed with reactive dyes and analysis of the products by thin layer chromatography. *Journal of Society of Dyers and Colourists, 110*(11), 338–341.
Roberts, E. J., Bose, J. L., & Rowland, S. P. (1972). Evidence for two types of accessible surfaces in fibrous cotton. *Textile Research Journal*(4), 217–221.
Rouselle, M. A., & Howley, P. S. (1998). Molecular weight of cotton cellulose: effect of treatment with a total cellulase. *Textile Research Journal, 68*(6), 606–610.
Rousselle, M. A., Bertoniere, N. R., Howley, P. S., & Goynes, W. R. Jr., (2002). Effect of whole cellulase on the supramolecular structure of cotton cellulase. *Textile Research Journal, 72*(11), 963–972.
Rouselle, M. A., Bertoniere, N. R., & Howley, P. S. (2003). Effect of Purified *T. reesei* cellulaes on the supramolecular structure of cotton cellulose. *Textile Research Journal, 73*(10), 921–928.
Rowland, S. P., Wade, C. P., & Robats, E. J. (1973). Enzymatic hydrolysis as a source of structural information on cellulose. *Textile Research Journal, 2*(6), 351–356.
Saraf, N. M. (1997). Further handle modification of biopolished fabrics. *International Dyer*(1), 24–25.
Sariisik, M. (2004). Uses of cellulases and their effects on denim fabrics. *AATCCReview*(1), 24–29.
Schmitt, B., & Prasad, A. K. (1998). Update of indigo denim washing. *Colourage*(10), 20–24.
Schulein, M., Henriksen, T., Lassen, S.F., & Kauppinen, M.S. (2005). Endoglucanases. US Patent Office, Pat. No. 6, 855, 531.
Schulein, M., Henriksen, T., Andersen, L. N., Lassen, S. F., Kauppinen, M. S., Lange, L., Nielsen, R. I., Takagi, S., & Ihara, M. (2007). Endoglucanases. US Patent Office, Pat. No. 7, 226,773.
Snyder, L. G. (1996). Improving the quality of 100% cotton knits fabrics by defuzzing with singeing and cellulase enzymes. *AATCC Review, 29*(6), 218–229.
Takai, M., Hayashi, J., Nisizawa, K., & Kanda, T. (1983). Morphologic observation of cellulose microfibrils degraded by exo and endo cellulases. *Journal of Applied Polymer Science-Applied Polymer Symposium, 37*, 345–361.
Traore, M. K., & Diller, G. B. (1999). Influence of wetting agent and agitation on enzymatic hydrolysis of cotton. *Textile Chemist and Colorists & American Dyestuff Reporter, 1*(4), 21–56.
Tripp, V. W., Moore, A. T., & Rollins, M. L. (1957). The surface of cotton fibers. *Textile Research Journal, 27*(6), 419–426.
Tyndall, R. M. (1992). Improving the softness and surface appearance of cotton fabrics and garments by treatment with cellulase enzymes. *Textile Chemists and Colorists, 24*(6), 23–26.
Tzanov, T., Andreaus, J., & Gue, G. (2003). Protein interactions in enzymatic processes in textiles. *Electronic Journal of Biotechnology,* 6(3) Available from http://www.ejbiotechnology.info/content/vol6/issue3/full/8/bip/index.html.
Ueda, M., Koo, H., Wakida, T., & Yoshimura, Y. (1994). Cellulase treatment of cotton fabrics – part II inhibitory effect of surfactants on cellulase catalytic reactions. *Textile Research Journal, 64*(10), 615–618.
Wakida, T., Moriya, T., Lee, M., Yoshikora, H., & Yanai, Y. (2000). Effect of liquid ammonia, NaOH/liquid ammonia and subsequent cellulase treatment on mechanical properties of cotton fabrics. *Textile Research Journal, 70*(2), 161–165.
Wang, L., Zhang, Y., Gao, P., Shi, D., Lu, H., & Gao, H. (2006). Changes in the Structural Properties and Rate of Hydrolysis of Cotton during Extended Enzyme Hydrolysis. *Biotechnology and Bioengineering, 93*(3), 443–456.
White, A. R., & Brown, R. M., Jr. (1981). Enzymatic hydrolysis of cellulose – visual characterisation of the process. In *Proceedings of national academy of science* (pp. 1047–1051). Pennsylvania, USA.
Yamade, M., Amano, Y., Horikawa, E., Nozaki, K., & Kanda, T. (2005). Mode of action of cellulase on dyed cotton with a reactive dye. *Bioscience Biotechnology and Biochemistry, 69*(1), 45–50.
Yang, C. Q., Zhou, G. C., Lickfield, G. C., & Parachura, K. (2003). Cellulase treatment of durable press finished cotton fabric: effects of fabric strength, abrasion resistance and handle. *Textile Research Journal, 73*(12), 1057–1062.
Youatt, G. (1962). The S Factor in the enzymatic hydrolysis of cellulose. *Textile Research Journal*(2), 158–160.
Zadhoush, A., Khoddami, A., & Aghakhani, M. (2001). The influence of enzymatic hydrolysis of cellulosic substrates on the final quality of coated fabrics. *Journal of Industrial Textiles, 30*(3), 211–221.
Zhou, L. M., Yeung, K. W., & Yuen, C. W. M. (2001). Combined cellulase and wrinkle-free treatment on cotton fabrics. *Journal of Donghua University, 18*(1), 11–15.