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Effects of Cellulase Enzyme Treatment on the Properties of Cotton Terry Fabrics

Abstract
Terry fabrics are exposed to frequent and intensive washing and must therefore be resistant to water, alkali, washing agents and rubbing. Washing agents frequently contain cellulase enzymes. The influence of two kinds of cellulase enzymes on the properties of a 100% cotton terry fabric was investigated. The whole cellulase mixture and an endoglucanase-rich cellulase product were used. Fabric strength, resistance to rubbing, wettability, hand feeling, whiteness and other properties were observed. Moreover the influence of different pretreatment processes on the properties of the terry fabric was investigated. The fabric was scoured with alkali or with pectinase enzymes, and bleached with hydrogen peroxide or peracetic acid. It was established that enzymatic scouring and peracetic acid bleaching consume less energy and water but provide fabrics with lower whiteness and wettability, suitable only for further dyeing in dark or medium shades. Cellulases deteriorate the properties of terry fabrics; however, worse are the whole cellulase mixtures.

Key words: *terry cloth, scouring, bleaching, cellulase, pectinase.*

Introduction

Terry fabric is a soft, usually cotton fabric composed of ground warp and weft yarns, as well as an additional warp system (pile) which forms loops [1]. Terry fabric is very popular due to its voluminosity, exceptional water absorbency and heat retentiveness. It is used for making bathrobes, towels, sheets as well as wellness and free-time apparels. Due to their nature, terry cloth products are exposed to frequent and intensive washing. They must be resistant to water, alkali, surfactants and rubbing. Various washing agents are used for washing terry fabric. Washing agents, which frequently contain oxidants and enzymes, can lead to the bleeding of colours. The addition of softening agents is not recommended as they deteriorate the absorbency of the terry fabric [1 – 4].

Raw cotton fibres have to go through several chemical processes to obtain properties suitable for use. With scouring, non-cellulose substances (wax, pectin, proteins, hemicelluloses etc) that surround the fibre cellulose core are removed, and as a result fibres become hydrophilic. Conventional scouring processes of cotton are conducted at temperatures of up to 100 °C in a very alkaline medium (pH 10 – 12) with sodium hydroxide. Since a non-specific reagent is used in the treatment, it attacks impurities; however, it also damages the cellulose portion of fibres. Several auxiliary agents, e.g. wetting agents, emulsifiers and sequestrants, which improve the efficiency of scouring and reduce damage to fibres, are also added to the scouring bath.

Scouring is regularly followed by the bleaching process, which removes the natural pigments of cotton fibres. Cellulose fibres are most frequently bleached with hydrogen peroxide (HP). Hydrogen peroxide is not ecologically disputable by itself, whereas the large amount of water used to rinse and neutralise the pretreated textiles is. Namely the bleaching process is conducted in an alkaline bath at pH 10 – 12 and at temperatures of up to 100 °C. Due to the high working temperature, a large amount of energy is consumed. Upon neutralisation of highly alkaline waste baths, large amounts of salts are produced [5].

To comply with more and more rigorous environmental regulations, as well as to save water and energy, biotechnology and several types of enzymes are used in the textile industry. Many papers describe the use of different enzymes for textile finishing [6 – 9]. Pectinases are an efficient alternative to sodium hydroxide in the removal of non-cellulose substances from the cotton fibre surface. This process occurs at moderate temperatures in a slightly acidic or alkaline medium. Since enzymes act selectively, no damage to fibres occurs during the treatment [8 – 10].

Bleaching with peracetic acid (PAA) is an alternative to that with hydrogen peroxide [11 – 13]. It is efficient at low concentrations and temperatures and in a neutral to slightly alkaline medium. Its products of decomposition are biologically degradable. Several commercial products are available as balanced mixtures of PAA, acetic acid and hydrogen peroxide (cf. ***Figure 1***). Today PAA products available on the market are safe, simple to use and price-effective. ***Figure 1*** shows the reaction that occurs when PAA is used for bleaching.

Cellulases are well established in textile wet processing as agents for fibre and fabric surface modification. The best known applications are bio-stoning for denim and bio-polishing for cleaning fabric surfaces by removing microfibrils, fuzz and lost fibres [14]. They are also used in laundry agents to remove fuzzy fibres from the surfaces of fabrics dyed for colour revival [15].

Different wood consuming fungi and bacteria produce cellulases in nature. Cellulase is a multicomponent mixture of cellulose degrading enzymes [16]. There are at least three major groups of

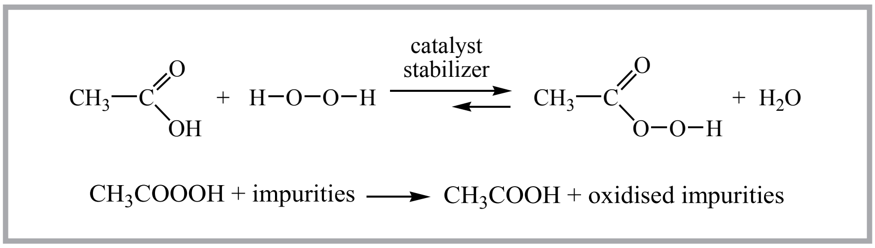

Figure 1. *Balanced mixture of peracetic acid, hydrogen peroxide and acetic acid (above) and the reaction of bleaching with peracetic acid (below).*

cellulases involved in the hydrolysis of cellulose:
- Endoglucanase (endo-1,4-β-D-glucanohydrolase), which hydrolyses cellulose chains randomly, preferably in the amorphous regions of the fibre;
- Exoglucanase or cellobiohydrolase (1,4-β-D-glucan cellobiohydrolase), which splits cellobiose from cellulose ends. It is active also in the crystalline parts of the fibre;
- β-glucosidase (β-1,4-glucosidase), which hydrolyses cellobiose to glucose.

All these enzymes act in a synergism during the degradation of cellulose. At first, endoglucanase randomly attacks the cellulose chain, generating new chain ends. The exotype cellulase acts in a progressive way on the chain ends, forming glucose or cellobiose as the main reaction products. Cellobiose is also decomposed to glucose by β-glucosidases [15].

Optimal working conditions for cellulases are pH 4 – 5.5 and temperature 50 – 55 °C. A temperature rising above 60 °C and pH above 9 is recommended to deactivate their activity after the treatment.

The major drawback associated with the use of cellulase is the loss of mass and a reduction in the fabric tensile strength. One way to reduce the strength loss is to choose a less aggressive cellulase mixture or monocomponent solution [15]. It was established that the reduction in breaking strength was smaller for cotton fabrics treated with endoglucanases than with total cellulase [14, 15].

The goal of our work was to establish if existing pretreatment processes of raw cotton terry fabric can be replaced by a new, environmentally friendlier process. Therefore the terry fabric was scoured with alkali or with pectinases, and further bleached with hydrogen peroxide or peracetic acid. Furthermore another goal of the research was to characterise the cellulase activity on differently scoured and bleached cotton fabrics. After the scouring and bleaching, the samples were exposed to a cellulase treatment with a complex mixture of cellulase and with endoglucanase-rich cellulase solutions.

Table 1. *Recipes and conditions of scouring.*

	Alkaline scouring	Bioscouring
		4% Beisol PRO
	2 g/l Na_2CO_3 calc.	1 ml/l Na_2CO_3 10%
	1 ml/l Invatex MD	
pH	11.5	7.7
T, t	95 °C, 60 min	55 °C, 60 min
Rinsing	80 °C, 15 min	

Table 2. *Recipes and conditions of bleaching.*

	HP bleaching	PAA bleaching
	0.5 g/l Invatex MD 0.5 g/l Stabilizator SIFA 3.75 ml/l NaOH 48°Bé 7.5 ml/l H_2O_2 35%	15 ml/l Persan S 15 0.5 g/l Invatex MD 45 ml/l 1 N NaOH
pH	12.2	7.5
T, t	95 °C, 60 min	60 °C, 60 min
Rinsing	80 °C, 15 min	

Table 3. *Recipes and conditions of cellulase treatments.*

	Endoglucanase-rich cellulase	Complex mixed cellulase
	8.2 g/l CH_3COONa	
	6 ml/l CH_3COOH	
	3% Indiage RFW	3% Indiage 44L
pH	4.5	
T, t	55 °C, 30 min	
Rinsing	80 °C, 10 min	

Experimental

Materials

A desized cotton terry fabric, 400 g/m^2, was obtained from Svilanit, Slovenia. Pectinase Beisol Pro was supplied by Bezema, Switzerland. Hydrogen peroxide, 35%, and peracetic acid as a 15% equilibrium solution in commercial bleaching agent Persan S15 were obtained from Belinka, Slovenia.

Endoglucanase-rich cellulase Indiage RFW (CE) and complex mixed cellulase Indiage 44L (CM) were obtained from Genencor, Denmark.

Sodium hydroxide was supplied by Šampionka, Slovenia, and acetic acetate, acetic acid and sodium carbonate were obtained from Riedel-de Haen, Germany. Wetting agent Invatex MD and peroxide stabiliser Stabilizer SIFA were obtained from Clariant.

Treatment methods

The cotton terry fabric underwent alkaline and enzymatic scouring. The scoured fabrics were bleached with two bleaching agents, i.e. hydrogen peroxide and Persan S15. After the bleaching, the samples were treated with cellulases. The recipes and conditions of scouring, bleaching and cellulase treatments are shown in ***Tables 1 – 3***. Demineralised water was used in all processes. The treatments were performed on a dyeing apparatus, Starlet-2, DaeLim, Korea. Dyeing pots of 500 ml were loaded with 50 g of fabric at liquor ratio 1:10. Sample abbreviations and their finishing steps are presented in ***Table 4***.

Analytical methods

Prior to measurements, fabrics were conditioned for 24 hours at 20 °C and 65% relative humidity.

The samples of the residual bleaching and scouring solutions were collected after all treatments. The total organic carbon (TOC) was measured on a Shimadzu TOC-5000A according to ISO 8245 and the pH was measured using an ISKRA

Table 4. *Abbreviations used in the paper*

Abbreviations	Treatment step
Alkali	alkaline scouring
Bio	bioscouring
HP	peroxide bleaching
PAA	peracetic acid bleaching
NO	no bleaching
CE	endoglucanase-rich celullase treatment
CM	complex cellulase treatment
no	no cellulase treatment

MA5740 pH meter, calibrated attwo points.

The quantity of dry substances was determined by weighing an empty beaker, and a beaker after evaporating and drying 50 ml of the treatment solution, expressed as a percentage.

The degree of whiteness was measured on a Spectraflash SF600 Plus (Datacolor, Switzerland) using the CIE method according to the EN ISO 105-J02:1997(E) and EN ISO 105-J01:1997(E) standards.

Water absorbency was estimated by measuring the sinking time of 1 g of a sample which was dropped from 1 cm to 10 cm height into a beaker filled with warm distilled water at 20 °C. The time taken for the sample to sink below the water surface was measured with a stopwatch. The average result of four tests was calculated.

Measurements of tenacity at a maximum load were performed on an Instron Tensile Tester Model 5567 (Instron, UK). The mean degree of polymerisation (DP) was determined with the viscosimetric method in cuoxam and expressed in Eisenhut's tenderity factors.

The fabric stiffness was measured according to the ASTM D1388-96 standard.

The resistance to abrasion was tested on a Martindale SDL 253 (Atlas, USA) universal wear tester with a 12 N load according to the SIST EN ISO 12947-3:2000 standard. The towels were subjected to 2500 abrasion cycles with F 180s and paper. The weight loss due to abrasion was determined by weighing the samples before and after abrasion, expressed as a percentage.

The fabric hand feeling was evaluated by a panel of 8 evaluators who touched the samples and marked them on a scale of 1 to 5, where 1 meant a hard, desolate and empty feeling, and 5 a soft, pleasant, comfortable feeling. Average values were calculated from individual marks.

Results and discussion

Cotton terry fabrics for hygienic products are subjected to alkaline scouring and hydrogen peroxide bleaching. The goal of our research was to establish if these processes can be replaced by modern bioscouring with enzymes and bleaching with peracetic acid. Since terry products are often washed with washing agents with integrated cellulases, we also wanted to investigate their influence on differently pretreated terry fabrics.

Tables 5 – 7 comprise the parameters of treatment baths before and after the treatment, and of the first washing bath: pH, amount of dry substances and TOC.

Alkaline scouring and peroxide bleaching proceed at a very high pH, which remains high even after the washing. Further washing or neutralisation is necessary, resulting in high water consumption. Bioscouring and PAA bleaching proceed close to a neutral pH. Short rinsing without neutralisation suffices to obtain a neutral material. The consumption of water is therefore much lower. The pH of cellulase solutions is slightly acidic and is easily neutralised in the first washings.

As expected, more substances are removed from the cotton material in alkaline scouring and peroxide bleaching than in bioscouring and PAA bleaching, which can be seen from ***Table 6***. The quantity of substances removed is quite high in cellulase treatments, higher in the whole cellulase mixture than in the endoglucanase-rich sample. In no case is the quantity of dry substances problematic from the point of view of ecological parameters.

The TOC values represent the amount of organic substances in water solutions. It is an ecological parameter; however, it can also serve as a measure of substances removed from fibres. In ***Table 7***, we can see again that the amount of organic substances removed is higher in alkaline scouring than in bioscouring and that peroxide bleaching removes more substances than PAA bleaching. On the contrary, in the solutions before the treatments, bioscouring has higher TOC than alkaline scouring and PAA bleaching has higher TOC than peroxide bleaching. Both agents, enzymes and peracetic acid, are organic compounds and contribute to high TOC on their own. The TOC values of all first wastewaters are too high to be released into waters or the sewage system [16].

The cellulase treatment baths also have very high initial TOC values, which even increase after the treatment due to the split cellulose chains that dissolve in water. The portion of organic substances removed is higher in whole cellulases than in endoglucanase-rich cellulases.

Table 5. *pH values of scouring, bleaching and cellulase treatment baths before and after the treatment and that of first washing bath.*

Treatment	pH		
	before	after	washing
Alkali	11.6	9.7	9.6
Bio	7.7	6.8	7.5
HP	12.2	11.7	11.6
PAA	7.4	5.4	5.6
CE	4.5	4.3	4.4
CM	4.2	4.3	4.4

Table 6. *Dry substances in the scouring, bleaching and cellulase treatment baths before and after the treatment and in the first washing bath.*

Treatment	Dry substances, %			
	before	after	washing	removed
Alkali	0.25	0.70	0.19	0.66
Bio	0.17	0.53	0.14	0.49
HP	0.38	0.55	0.21	0.36
PAA	0.45	0.47	0.11	0.12
CE	0.99	1.10	0.23	0.34
CM	0.99	1.18	0.25	0.44

Table 7. *TOC of scouring, bleaching and cellulase treatment baths before and after the treatment, and that of the first washing bath.*

	TOC			
	before	after	washing	removed
Alkali	378	1676	798	2096
Bio	537	1533	720	1715
HP	219	1247	583	1611
PAA	1878	1975	556	653
CE	289	4304	1230	2643
CM	2858	4434	1327	2903

Bleaching with HP gives higher whiteness values than that with PAA in all cases (cf. ***Figure 2***). Moreover the alkaline scoured samples are in all cases whiter than the bioscoured samples, which was expected since alkaline scouring is more intensive and removes more non-cellulosic substances than enzymatic scouring. Other studies confirmed that alkaline scoured cotton is lighter and whiter than bioscoured cotton [10]. Treatment with cellulases decreased the whiteness values of all scoured and bleached samples.

The sinking time is used for measuring wettability. Scouring, alkaline or enzymatic, alone does not give adequate water absorbency. The sinking times are longer than 2 seconds (cf. ***Figure 3***). All alkaline scoured samples have shorter sinking times than the bioscoured ones, which means that they are more wettable. The same holds true for HP v. PAA bleached ones; the peroxide bleached samples are more wettable. Treatment with cellulases improves the wettability of only scoured samples but decreases the wettability of scoured and bleached samples, which is a consequence of the differences in the primary wall of the pretreated cotton fibres. Only scoured fibres preserve some non-cellulosic substances in the primary wall, which keeps the fibre slightly hydrophobic and protects it from cellulase attack. Cellulases partly degrade the short cellulose chains in the primary wall and contribute to the improvement in hydrophilicity. Various other investigations also led to the conclusion that cellulases improve the wettability of cotton fibres [17 – 19]. However, the influence of cellulases on clean unprotected cellulose fibres after bleaching is different, as they can enter into the amorphous phase of the fibre and degrade the cellulose chains to a remarkable extent. Water can only enter the amorphous phase of the fibre, and when the ratio of the amorphous phase decreases, the fibres become less water absorbent [19].

In the research, it was confirmed that alkaline scouring and peroxide bleaching give higher whiteness and better wettability; however, when the damage caused to the fibres is compared, it can be seen that the PAA bleached samples have an impressively higher mean degree of polymerisation (cf. ***Figure 4***). The way of scouring did not influence the DP of fibres.

The treatment with cellulases decreased the DP values of all samples, more for the HP bleached than for the PAA bleached samples. Again we can ascribe this to the easier entrance of cellulases into the clean unprotected HP bleached fibre than into a more protected PAA bleached fibre. The DP values of samples treated with endoglucanase-rich cellulase are lower than those in the whole cellulase mixture. Namely endoglucanase splits the cellulose chains randomly into long oligosaharides and DP, thus decreasing faster than with whole cellulases that contain quite a high proportion of cellobiohydrolases, which split only cellobiose from the cellulose chain ends.

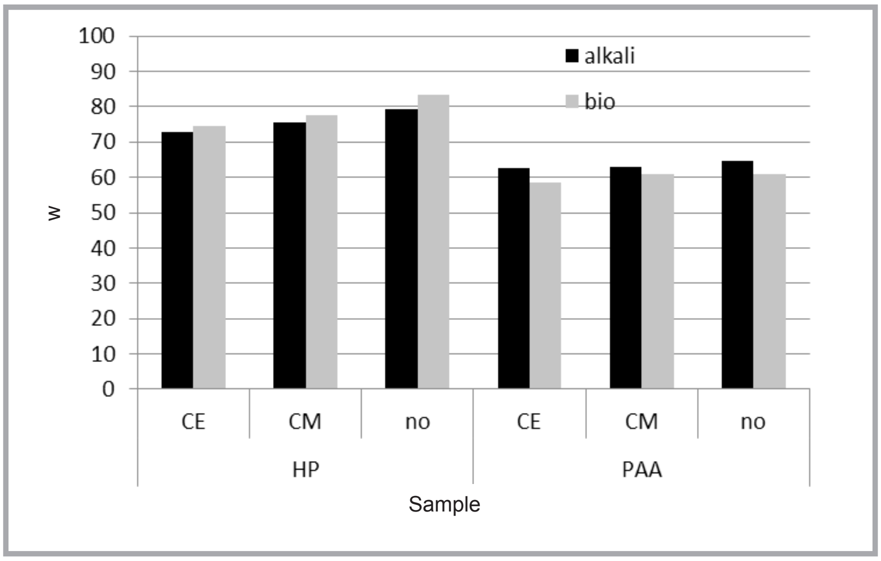

Figure 2. *Whiteness values of scoured, bleached and cellulase treated samples. (for abbreviations cf.* ***Table 4****).*

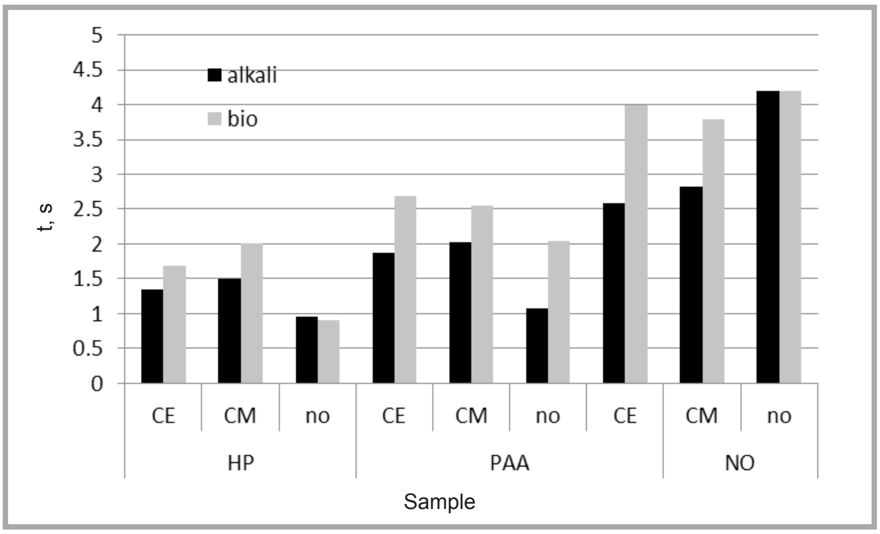

Figure 3. *Sinking time (t) of scoured, bleached and cellulase treated samples. (for abbreviations cf.* ***Table 4****).*

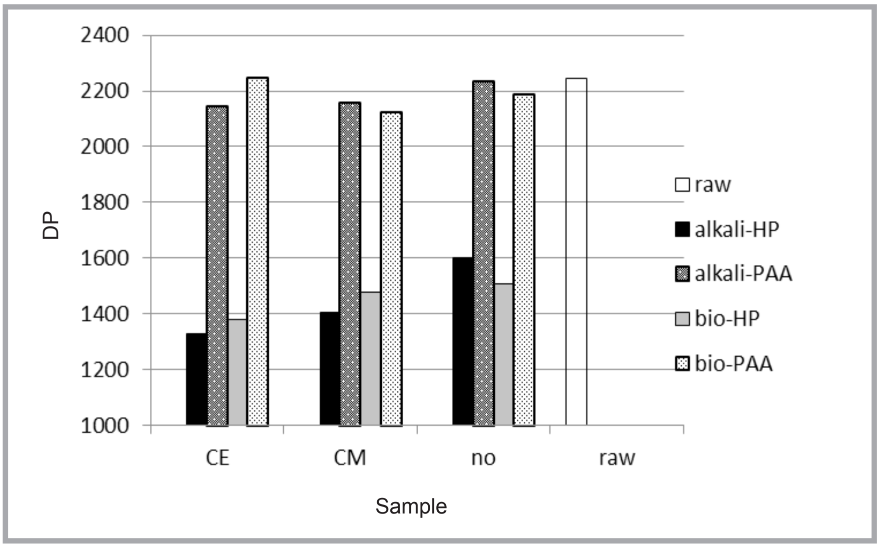

Figure 4. *Polymerisation degree, DP, of differently scoured, bleached and cellulase treated samples. (for abbreviations cf.* ***Table 4****).*

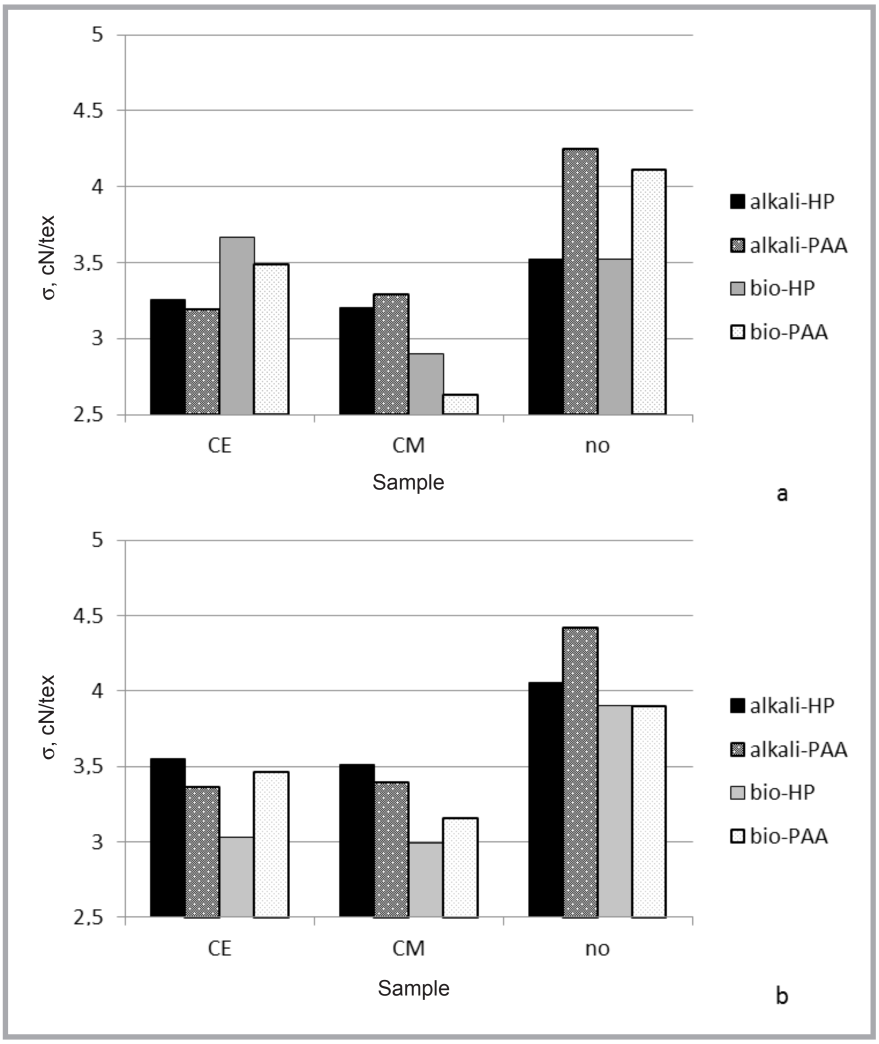

Figure 5. *Tenacity, δ, of a) warp and b) weft of differently scoured, bleached and cellulase treated samples. (for abbreviations cf.* ***Table 4****).*

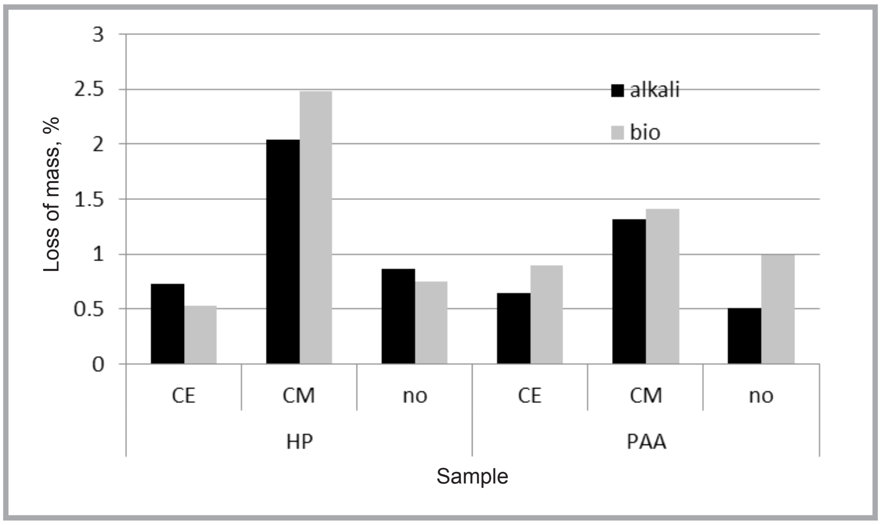

Figure 6. *Loss of mass after 2500 abrasion cycles of scoured, bleached and cellulase treated samples (for abbreviations cf.* ***Table 4****).*

Different parameters influence the strength of treated fabrics. After alkaline scouring, the fabric shrinks and becomes denser and stronger. Therefore all alkaline scoured samples have higher tenacity at a maximum load than the bioscoured samples (cf. ***Figure 5***). Bleaching does not decrease it. On the other hand, treatment with cellulases decreases the fibre strength substantially, complex cellulase even more than endoglucanases. Endoglucanases are active only in the amorphous parts of the fibre, while cellobiases in a complex mixture also degrade the crystalline parts of the fibre. These particular parts are responsible for the fibre strength.

The loss of mass of fibres during abrasion was also the highest in the whole cellulase mixture (cf. ***Figure 6***), meaning that different cellulases in the whole cellulase mixture in a synergistic action damage the terry fabric and shorten its lifecycle. Less damage is caused to the fabric with endoglucanase-rich cellulase, which cannot damage the crystalline part of the fibre. The way of scouring and bleaching has no influence on the loss of mass during abrasion.

Figure 7 shows that the PAA bleached samples are less stiff than the peroxide bleached ones. It also shows that the alkaline scoured samples are less stiff than the bioscoured ones. Cellulases increase the stiffness of the peroxide bleached samples, while they do not change the stiffness of the PAA bleached samples.

A subjective evaluation of the hand feeling shows that the samples bleached with PAA have in general a more pleasant feeling than those bleached with hydrogen peroxide (cf. ***Figure 8***). The influence of different scouring is not visible, which is probably a consequence of the fact that further bleaching and cellulase treatment covers the differences in fibres arising from different scourings. ***Figure 8*** also shows that cellulase treatment deteriorates the feeling of the terry fabric. The most pleasant feeling is characterised by the bioscoured and PAA bleached sample, not treated with cellulases. This sample lost the lowest mass and preserved the highest quantity of waxes and pectins, which give softness and voluminosity to the fabric.

Conclusions

It can be concluded that bioscouring is a suitable process for terry fabric and can substitute alkaline scouring, especially when the material is subsequently bleached. Bleaching covers the differences arising from previous treatments; in consequence, the properties of differently scoured and bleached samples are similar. A comparison of bleaching with hydrogen peroxide and peracetic acid shows that the samples bleached with

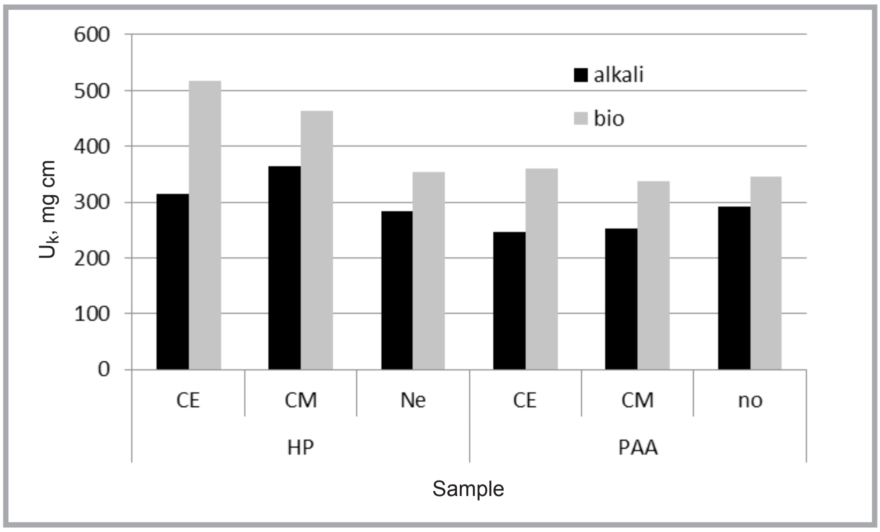

Figure 7. *Stiffness of scoured, bleached and cellulase treated samples. (for abbreviations cf.* ***Table 4****).*

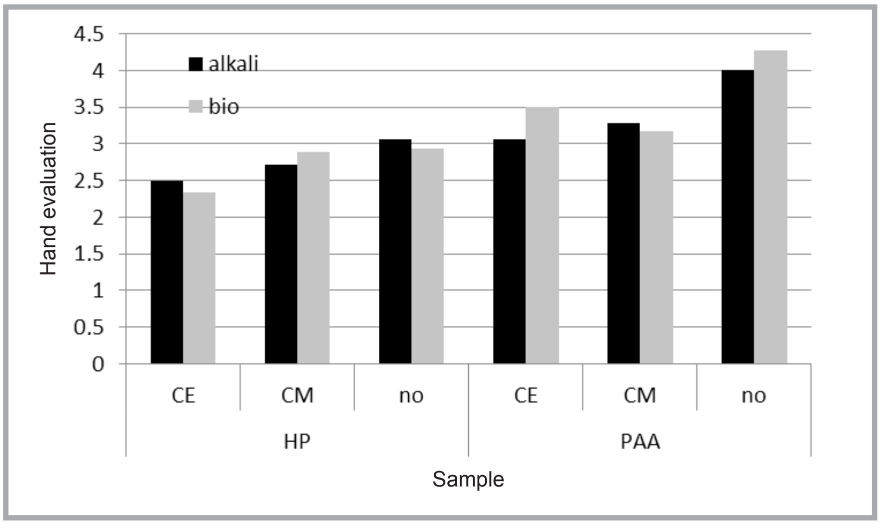

Figure 8. *Hand evaluation values of scoured, bleached and cellulase treated samples. (for abbreviations cf.* ***Table 4****).*

peracetic acid display lower whiteness and longer sinking times, but they do have a more pleasant feeling and lower stiffness, and are almost not damaged. Bleaching with PAA is, hence, appropriate for items which are further dyed in medium to dark shades.

Treatment with cellulase has no beneficial effect on cellulosic material whatsoever. The fabric loses a lot of mass, the sinking time increases, the feeling deteriorates, and the polymerisation degree and fabric strength decrease, while the wearing out during abrasion increases. The pronounced negative effect on terry fabric is caused by whole cellulase mixtures, while endoglucanase-rich cellulase deteriorates the material to a lower extent. We strongly dissuade from the use of cellulases during the finishing and washing of terry fabrics. We suggest the use of only endoglucanases as additives for the washing agents, or even better washing agents without integrated cellulases.

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Received 21.03.2012 Reviewed 05.04.2013