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Short communication

Influence of pretreatment of cotton yarns prior to biopolishing

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ABSTRACT

Cellulase is one of the enzymes most commonly used in the textile industry for the biopolishing process. The appropriate choice of pretreatment is a possible route to promoting enzymatic attack in situations in which this is not favored due to the effects of packing. In order to evaluate the influence of pretreatment the yarn was maintained in water for 24 h before biopolishing to promote greater spacing between the chains. In the tensile testing the pretreated Combed 13/1 yarn showed a greater percentage reduction in the maximum breaking force following biopolishing, evidencing a stronger enzymatic attack. Also, the Combed 13/1 and OE 14/1 yarns without pretreatment had an approximately 22% reduction in the shrinkage and after pretreatment the Carded 13/1 yarn had the best shrinkage reduction values (18%). These data demonstrate that the introduction of the pretreatment promotes a change in the access of the enzyme to the fiber.

1. Introduction

The focus of this study was to investigate the pretreatment processes which are commonly applied to textile substrates at industrial plants. These processes influence the performance of the enzymatic processes. In particular, the parameters associated with the packing of the fibers in processed products were investigated. These parameters were yarn count, arrangement of yarns on packing according to the type of manufacturing process used (ring spinning or open-end twisting of the strands), and packing density of the yarns in bobbins and in the form of fabric.

The industrial importance of this study lies in the verification of the influence of some parameters related to the biopolishing on the mechanical properties of the yarns. The most notable parameters related to the biopolishing identified in this study were the process used to obtain the cotton yarn (ring spinning or open-end (OE)), fiber packing (reflected in the yarn count) and the pretreatment processes. Based on these results specific adjustments to the biopolishing process can be recommended considering the relevant parameters identified (Saravanan, Vasanthi, & Ramachandran, 2009; Zadhoush, Khoddami, & Aghakhani, 2001).

The state of Santa Catarina hosts the second largest textile industry pole in Brazil. This is considered one of the most advanced poles in Latin America, one of the largest textile poles in the world and the main pole in terms of the exportation of woven fabric articles and bed/table/bath linen in Brazil (ABIT, 2012).

The fabric production process can be divided into the stages of spinning, weaving and finishing (Freitas, 2002). In the finishing stage the fabrics are treated in order to obtain characteristics such as better touch, hydrophilicity or hydrophobicity and dimensional stability (Araújo & Castro, 1986). In this stage, besides the textile substrate, several substances are used including water, resins, dyes, tensoactive agents, enzymes, etc. (Abrahão & Silva, 2002).

Cotton is the purest form of cellulose found in nature and is a fiber which originates from plants of the *Gossypium* species (Shore, 1995). It is the most important cellulosic fiber and is also currently the most used of all textile fibers (Vasconcelos, 2005) due to its availability and low price (Kavkler & Demšar, 2011).

In the textile industry the treatment of fibers, yarns and fabrics is traditionally carried out under very harsh conditions resulting in effluents with characteristics which are very damaging to the environment. Enzymatic treatments have been introduced into several of the textile processing stages in order to satisfy the needs for textile material quality, reducing the pollutant load of the textile effluents (Basto, 2007).

In nature cellulose is degraded by fungi and bacteria. These produce enzymes (cellulases) which specifically degrade the polymeric chain of the cellulose, giving rise to polymers with shorter chains. The diffusion of the enzyme to the interior of the fabric is possibly the greatest operational limitation associated with enzymatic treatments. Thus, enzymatic treatments in which the action of the enzyme is aimed at the surface of the textile material, as in the use of cellulases for the superficial treatment of cellulosic fiber fabrics, have received greater acceptance in industrial applications (Basto, 2007).

Cellulases are among the enzymes most used in the textile industry (Cavaco-Paulo, 1998). They are extensively employed to

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produce the stone-washed appearance of denims, to reduce the hairiness of woven cotton fabric and to control special touch characteristics of certain regenerated cellulose fabrics, such as Tencel (Cortez, Ellis, & Bishop, 2002). They are also commonly used in products for clothes washing, where their function is to aid the detergent action and to clean the fiber surfaces, improving the appearance in terms of brightness and color (Cavaco-Paulo, 1998).

The enzymatic activity of the cellulase produced by *Trichoderma reseei* rapidly reduces (by approximately 40%) with an increase in pH and to maintain the optimum pH during the whole treatment an appropriate buffer system needs to be used (Cavaco-Paulo, Almeida, & Bishop, 1998; Saravanan et al., 2009).

The enzymatic pretreatment affects the surface properties of the fiber, either through its functionalization when treated, for instance, with peroxidase enzymes or by way of an attack on the polymeric cellulose chain, modifying the roughness of the fiber surface and consequently the shear stress of the fibers (Ribitsch, Stana-Kleinsschek, & Jeler, 1996; Tyndall, 1992a, 1992b).

Cellulase is an enzymatic complex in which the enzymes act synergistically and they can be subdivided into three classes: (i) endo-1,4-β-D-glucanases or endoglucanases, which break the glycoside bonds of the cellulose chains creating new terminals; (ii) exo-1,4-β-D-glucanases or cellobiohydrolases, responsible for the action at the terminals leading to cellobiose; and (iii) 1,4-β-D-glucosidases which hydrolyze cellobiose to glucose.

The endo-1,4-β-glucanases or 1,4-β-D-glucana-4-glucanohydrolases (EC 3.2.1.4) act randomly in the amorphous regions of cellulose and its derivatives, hydrolyzing glycosidic β-(1,4) bonds. Their catalytic activity can be measured through the reduction in the viscosity of the medium, due to a decrease in the average molar mass of cellulose or its derivatives. The cellobiohydrolases (exo-1,4-β-D-glucanases, EC 3.2.1.91) act at the reducer terminals of the cellulose chains, releasing D-cellobiose. The "β-D-glucosidases" or β-D-glucoside glucohydrolases (EC 3.2.1.21) catalyze the release of monomeric units of D-glucose from cellobiose and soluble cellodextrins.

Biofinishing or biopolishing are terms used to describe the removal of fibrils or microfibrils from cotton using cellulases. The presence of fibrils leads to problems with the final articles related to the formation of pilling and a faded appearance due to an apparent loss of color. The enzymatic removal of fibrils results in softer and 'cleaner' articles, which retain the original color (Arja, 2007; Tyndall, 1992b).

Several studies have been carried out to minimize the negative aspects of biopolishing (such as the excessive loss of weight and reduction in strength) and in this regard a better understanding of the cotton hydrolysis mechanisms is required (Lin & Hsieh, 2001; Pere, Puolakka, Nousiainen, & Buchert, 2001).

The objective of this study was to determine the influence of cellulose packing conditions on the enzymatic action of cellulase on textile cotton yarn.

2. Materials and methods

2.1. Samples and materials

The samples were comprised of bobbins of pre-bleached 100% cotton yarn of 3000 m length produced by different types of spinning with different counts (OE 12/1, 14/1 and 16/1; Carded 13/1 and Combed 13/1).

The cellulase used in this study was Quimilase BP produced by the company Quimisa.

Acetic acid and sodium acetate were used to prepare the buffer solution.

2.2. Methods and instrumentation

2.2.1. Biopolishing

The biopolishing of the bobbins was carried out in a Thies series 8788 dyeing machine, manufactured in 1974, with a capacity of 4290 L.

Initially, washing of the substrates was carried out with distilled water. The bath content was then discarded and 0.5 M acetate buffer (pH 4.8) and the commercial *Trichoderma reesei* cellulase enzyme in a concentration of approximately 17 U/g_{yarn} (6%) were added. The system was heated to 50 °C and this temperature was maintained for 60 min. After this time heating at a rate of 3 °C min^{-1} was applied for 10 min up to a temperature of 80 °C, which was maintained for 10 min for the deactivation of the enzyme to occur. Finally, the bath content was discarded and a further washing with distilled water was carried out at 25 °C for 5 min.

2.2.2. Tensile strength

The tensile strength and elongation of the yarns were evaluated according to ASTM D2256 – 97 (Standard test method for tensile properties of yarns by the single-strand method).

2.2.3. Hairiness

The hairiness of the cotton yarns in the bobbins was evaluated according to ASTM D 1425 – 81 (Standard test method for unevenness of textile strands using capacitance testing equipment).

2.2.4. Shrinkage

The shrinkage of the cotton yarns was evaluated according to the Brazilian norm NBR 13215 – 94 (Determination of Yarn Shrinkage).

2.2.5. Pretreatment

For the pretreatment the yarns were maintained immersed in water for 24 h in order to increase the spacing between the chains and promote the swelling of the fibers.

3. Results and discussion

The types of yarn selected were open-end (OE), which originally has a lower degree of packing due to the way in which it is produced, and Carded and Combed, which are produced by ring spinning and generally have a greater degree of fiber packing.

In order to evaluate the effect of this packing on the enzymatic action OE yarns of three different counts were used (12/1, 14/1 and 16/1), the 12/1 yarns having the largest diameter, that is, less packing and 16/1 being the thinnest yarn with the greatest degree of packing. Thus, the increasing order of packing for the OE type yarns is 12/1 < 14/1 < 16/1.

The five different yarns (in bobbins) were biopolished on a dyeing machine and for each sample the respective blank (in the absence of enzyme) was tested in order to eliminate the interference of buffer in the analysis.

After the biopolishing of the bobbins the yarns were analyzed in order to evaluate their physical properties. Tests were performed on all samples, including those with the absence of enzyme (blanks). The data for the maximum breaking force, elongation and hairiness are presented. The data for the maximum breaking force are presented in Fig. 1.

On evaluating the maximum breaking force it was observed that of the blank samples the OE 12/1 was the strongest (greater maximum breaking force values).

In all of the tests it could be observed that the yarn was more fragile after the biopolishing, as was expected considering that this enzymatic treatment acts by degrading the cellulose of the cotton fiber. However, in general, the greatest reduction in strength was

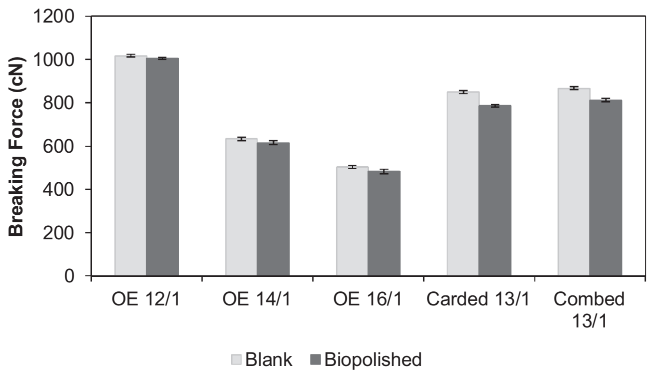

Fig. 1. Data for the maximum breaking force of different yarns.

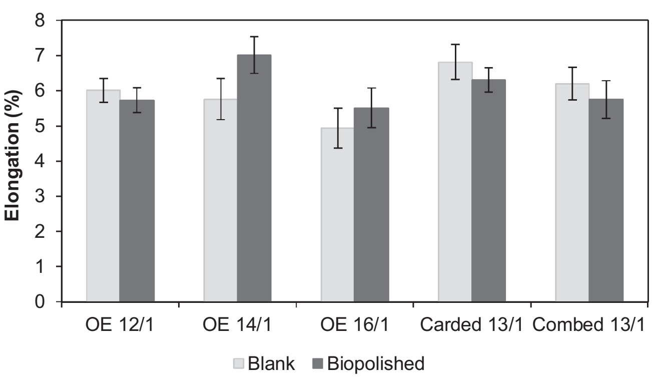

Fig. 2. Data for the elongation of different yarns.

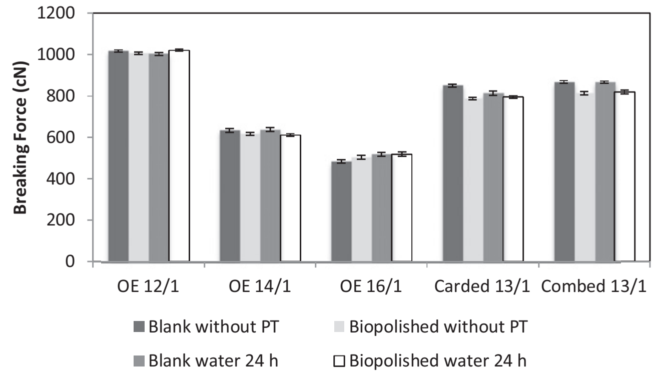

Fig. 4. Data for the maximum breaking force of different yarns, applying different biopolishing methods.

verified for the yarn Carded 13/1 (7.5%). This yarn showed the greatest enzymatic attack, which is highlighted by a greater reduction in the toughness value compared with the other samples and their respective blanks, indicating that this yarn was the most accessible to the enzyme.

Analysis of the tensile test results showed that the OE 16/1 and OE 14/1 yarns, besides showing a greater breaking strength also had a greater elongation after the biopolishing, which indicates the importance of action of the cellulase on the surface of these fibers, reducing the rugosity (since the OE 16/1 and OE 14/1 yarns are thinner and the fibers are more compressed) (Fig. 2).

The main function of the cellulase enzyme is to act in the removal of fibrils or micro-fibrils from the cellulose surface. This effect can be observed through the analysis of the hairiness of the cotton yarn (Fig. 3).

The biopolished yarns were found to have less hairiness; however, it was difficult to define which condition led to the greatest removal of fibrils. It can be observed that the OE 14/1 and 16/1 yarns showed a lower concentration of pilling which is due to greater twisting of these yarns which makes them more packed than the OE 12/1 yarns.

The tensile strength, elongation and hairiness tests showed that the Carded 13/1 yarn was more accessible to the cellulase enzyme in all situations.

Thus, a pretreatment of the yarns was carried out to verify whether there was any alternation in the accessibility of the enzyme to the fibers. The yarns were maintained in water for 24 h before biopolishing to promote larger spacing between the chains.

The profile for the maximum breaking force observed in Fig. 4 indicates that there was decrease in the strength after the biopolishing; however, in this case the greatest reduction occurred for the Combed 13/1 yarn, indicating that the enzyme had greater accessibility to this yarn when it was pretreated for 24 h with water.

On evaluating the elongation it was also observed that the greatest reduction occurred for the Combed 13/1 yarn pretreated for 24 h with water. These results are presented in Fig. 5.

In the hairiness test, after the pretreatment, the Carded 13/1 yarn again showed the greatest reduction in pilling, as expected since this test reveals only changes occurring on the surface of the cotton yarn and is not affected by internal alterations.

The thickness of the OE yarn reduces from a count of 12/1 to 16/1. Since yarns with a smaller diameter have less fiber in the cross sectional area, the breaking force is lower, as shown in Figs. 1 and 4, both for the yarns without pretreatment and for those which receiving biopolishing. The results given in Figs. 2 and 5 verify that for yarn OE12/1, thick yarn, the pretreatment did not have a significant influence, while for thinner yarns, OE14/1 and OE 16/1, the effect of pretreatment favored greater elongation when compared

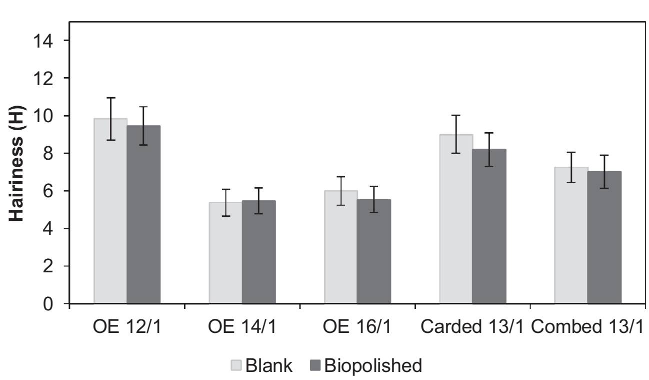

Fig. 3. Data for the hairiness of different yarns.

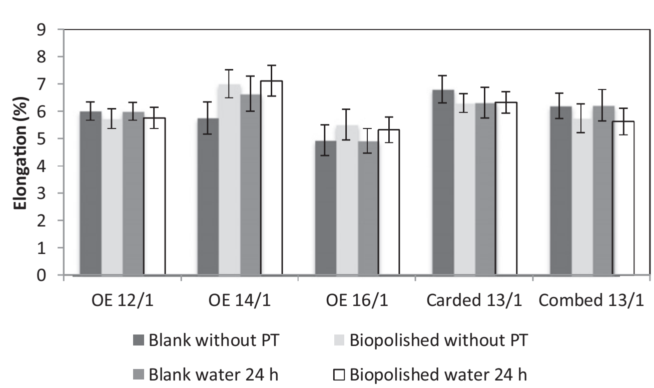

Fig. 5. Data for the elongation of different yarns, applying different biopolishing methods.

Table 1
Shrinkage values for the pretreated and biopolished yarns in bobbins.

	OE 12/1	OE 14/1	OE 16/1	Carded 13/1	Combed 13/1
Blank without PT	−2.4	−3.6	−1.8	−3.0	−3.6
Biopolished without PT	−2.0	−2.8	−1.8	−2.8	−2.8
Blank water 24 h	−2.6	−2.8	−2.6	−3.4	−3.8
Biopolished water 24 h	−2.4	−2.8	−2.4	−2.8	−3.6

with those without treatment. This effect can be explained by the action of the enzyme on the surface of the fiber, modifying its roughness and favoring shearing between the fibers. This effect is only observed when the fiber packing is greater and the shearing effect becomes determinant. In the case of yarn OE 12/1 the tension of the fibers on packing is lower making the yarn more voluminous and the fibers have greater mobility and consequently greater elongation (see blank in Fig. 1). In contrast to the OE yarns, the carded and combed yarns are ring spun and have greater tensile strength due to the parallelization of the fibers and to the greater tension of the fibers. In this case the enzymatic action results in the yarn losing its tensile strength and consequently its elongation is reduced.

The results for the shrinkage test carried out on the samples of the textile yarns biopolished in bobbins are given in Table 1.

The negative values obtained in the tests indicate that shrinkage of the yarns tested occurred. The greatest shrinkage was observed for the blank sample of the Combed 13/1 yarn pretreated with water for 24 h, followed by the untreated (blank) sample of this yarn and of OE14/1. In general, after the biopolishing the samples showed less shrinkage and the Combed 13/1 and OE 14/1 yarn samples gave the best results, that is, the greatest reduction in shrinkage. These data show that the enzymatic treatment can aid in minimizing the effect of dimensional variation, which is one of the most significant problems in the textile industry (Ulson de Souza et al., 2010). Enzymatic hydrolysis can be employed in this treatment, since it promotes breaking of the cellulosic chains reducing the packing of the fibers and thus improves the dimensional stability.

4. Conclusions

In this study the influence of the introduction of a pretreatment on the accessibility of the yarn to the enzyme during biopolishing was determined. The pretreatment was shown to be an important tool for inducing the enzymatic attack in situations which are not favorable in this regard due to packing effects. The pretreatment with water for 24 h promoted an effect similar to a swelling of the cotton fibers relaxing the tensions between the chains and thus favoring the accessibility to the enzyme.

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