Enzymatic process for machine washable wool

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Abstract

The target of this work was to design a combined process for machine washable wool using transglutaminase and protease enzymes exploiting the benefits provided by each of these enzymes. Proteolytic removal of the cuticle scales of the fibres would bring about shrink-resistance, but would also allow for penetration of the transglutaminase and improved dimensional stability and mechanical characteristics of the fibres due to (glutamyl)lysine crosslinking of wool proteins. In contrast to previously described protease-based processes for shrink resistant wool, the anti-felting properties achieved in the simultaneous enzymatic treatment are combined with insignificant fibre damage, confirmed also by scanning electron images of the fabrics.

Introduction

Wool, a natural biopolymer fibre, is one of the most important textile materials.Because of the presence of overlapping scales on the wool fibre surface, an interlocking effect of scales on adjacent fibres can occur during washing and friction, causing the fibres to migrate until they are completely entangled and thus producing permanent shrinkage, which is the most important disadvantage of woollen fabrics.

The elimination of felting shrinkage by chemical modification with a polymer has been extensively investigated. The typical commercial shrink-resist finishing used for decades is the chlorine-Hercosett process [1]. This effective process, consisting in a strong acid chlorine treatment followed by polymer resin application has the disadvantage of disposal of absorbable organic chlorides (AOX) in addition to the specific “synthetic” handle of the resin-coated fabrics. Hence, there is aneed for development of efficient and environmentally friendly processes for shrink-resistant wool. The enzymatic processes using proteases to hydrolyse the cuticle cells of the fibres and to reduce the inter-fibre friction thereby eliminating the cause for the shrinkage are difficult to control, and are not sufficiently predictable and reproducible in industrial scale. Such treatment, besides of removal of the cuticle layer, can cause excessive proteolytic damage to the fibre with consequent high levels of weight and tensile strength loss due to penetration of the protease into the bulk of the fibres. The application of proteases alone for shrink-proof wool could therefore not find any industrial application so far [2]

To overcome this limitation in the protease processing of wool two alternative approaches have been proposed. One is to limit the action of the proteases only to the surface of the fibres by increasing their molecular size grafting soluble polymers adducts, e.g. PVA or PEG on the enzyme proteins [4]. Normally increased molecular size of the enzymes is translated in lower activity, and thus longer process time to achieve the desired shrink-resist effect. Besides of this the process for enzyme modification is rather complicated and not easily reproducible, requiring expensive crosslinking agents and purification thereafter.

The other recently developed approach is to apply transglutaminases (TG) as a pre- or post-treatment to prevent or compensate the reduction of tensile strength and degradation of wool in proteases treatment [2, 3, 5,]. Transglutaminase is an enzyme able to cross-link proteins as well as peptides and various primary amines through acyl transfer reactions [6]. The strength improvement was attributed to the formation of TG-mediated intra- and inter-isopeptide crosslinks (ε-(γ-Glu)Lys), grafting the ε-amino group of a lysine to the γ-carboxyl group of a glutamic acid residue. Though this two step process appears to be efficient, its major drawback is the increased time and energy consumption.

Taking in account the above considerations the main target of this work was to design a simultaneous process using transglutaminase and protease exploiting the benefits provided by each of these enzymes. Partial proteolysis of the cuticle

scales of the fibres would provide shrink-resistance, while but would also allow for penetration of the transglutaminase-catalysed (glutamyl)lysine crosslinking would improve the dimensional stability and mechanical characteristics of the fabrics.

Materials and Methods

Textile material and enzymes

Woven 100 % wool fabric supplied by Lokateks (Slovenia) was washed previous to the enzymatic treatment with 1 g l^{-1} non-ionic surfactant Cotemol NI (Color Center, Spain) in liquor to good ratio 20:1 in a laboratory winch machine (0.1 M Na_2CO_3, $NaHCO_3$ buffer pH 9.0) at 40 ºC for 30 min. Thereafter the fabric was bleached at the same bath ratio with 0.1 ml l^{-1} of 30 % H_2O_2 (0.1 M Na_2CO_3, $NaHCO_3$ buffer pH 9.0) at 55 ºC for 1 h [7]. The bleached textile material was further treated with commercial protease Esperase 6.0T (EC 3.4.21.14) 1.01 mg prot. ml^{-1} from Novozymes A/S, Denmark, and microbial transglutaminase (EC 2.3.2.13) 4.86 mg prot. ml^{-1} from BDf, Spain.

Enzymatic treatment of wool

The bleached wool fabric was treated simultaneously with 2.5 U ml^{-1} protease and 0.01 to 0.1 U ml^{-1} TG in 50 mM Tris-HCl buffer pH 8 at 50 ºC for 60 min, in an Ahiba (Datacolor) laboratory dyeing machine at 30 rpm. After the bio-treatment the samples were washed extensively and dried in an oven for 2 h at 50 ºC.

Fabric shrinkage

Fabric shrinkage after washing was assessed according to ISO 6330 as described in IWS Test Method 31. The fabrics were washed in a Wascator washing machine (Wascator FOM71 special, Electrolux-wascator, Sweden) in one cycle of wash program 7A for relaxation and three cycles program 5A for felting shrinkage, both at 40 °C with a load (polyester fabric) and standard detergent. All samples were tumble-dried after washing and conditioned at room temperature before measuring the area shrinkage. The results were expressed as percentage of area shrinkage and are mean value of the shrinkage measured on three different samples.

Tensile strength and weight loss

The samples were conditioned at 23 ºC 60 % relative humidity for 24 h prior to evaluation. Tensile strength was determined using a tensile tester machine PT-

250 (Investigación Sistemas Papeleros, S.L. Spain) in a standard procedure with 2 Kgf maximum capacity load and 115 mm min^{-1} speed. The tensile resistance values are given as the mean of 9 samples tested.

The percentage of weight loss was calculated based on the weight of the fabric prior and after the enzymatic treatment as $((W_1-W_2)/W_1)$ x100, where W_1 is the weight of the sample before and W_2 after the enzymatic treatment. Three measurements were carried out for each sample.

Surface morphology

Microscopic photographs (magnification x1500 and x1500) of the surface of the bio-treated fabrics were obtained using JSM 5610 scanning electron microscope (JEOL Ltd, Japan).

Results and discussion

Tensile strength, weight loss and shrinkage of the enzymatic treated fabrics

Fabric samples were treated with protease and TG separately, and in a combined process with TG. Protease treatment alone was able to reduce fabric shrinkage after washing, but also caused strength decrease and weight loss in comparison to the untreated sample (Fig. 1, 2, 3, data shown at the optimum treatment conditions). TG alone did not influence significantly the shrinkage behaviour and the mechanical properties of the fabric. The results showed significant improvement in fabric strength as well as reduction of shrinkage and weight loss with the combined treatment with TG (P+TG) when compared to the untreated (C) and protease-treated fabrics (P).

In the one-bath bioprocess, however, interaction between the enzymes might be expected in terms of digesting of TG by protease or crosslinking of protease by TG. Indeed, a decrease of protease activity was observed with the increase of TG concentration (data not shown). This might be due to either crosslinking of protease by TG or acting of TG as a competing substrate in the protease enzymatic activity essay.

However, In the combined bio-process enhancement of wool properties was most probably due to proteolytic removal of the cuticle scale thereby creating conditions for penetration of TG beyond the cuticle layer into the cortex of the fibre [3], where the amount of glutamine residues is higher, catalyzing ε-(γ-Glu)Lys crosslinking.

Surface morphology of the bio-treated fabrics

Surface SEM images of the enzymaticaly treated fabrics in Fig. 4 (a) showed significant proteolytic damage of the fibres, however, not uniform due to the heterogeneity of the wool itself [8]. Some proteolytic damage and less defined cuticle scales can be observed also on the fibres treated in the combined bio-process in Fig. 4 (b).

Conclusion

The shrink resistance of woven wool fabrics achieved in this one step, mild conditions approach was superior to the shrink-resistance achieved in a single protease or transglutaminase treatment. Weight and tensile strength loss caused by the protease treatment of wool fabrics was nearly completely in the simultaneous treatment with transgllutaminase. Fibre damage due to the protease/TG treatment was not observed in the scanning electron micrographs of the fabric surface.

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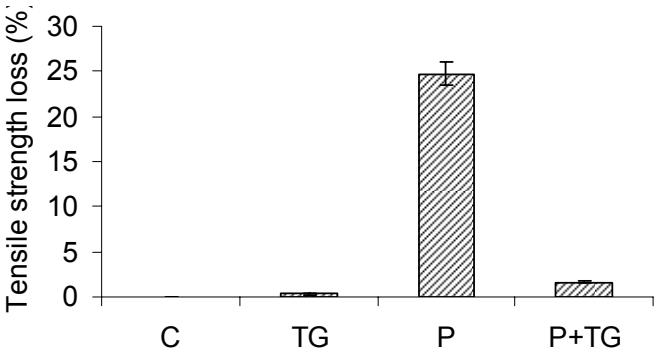


Figure 1. Tensile strength loss of wool fabrics after bio-treatment in 50 mM Tris-HCl buffer, pH 8, 50 ºC for 60 min of samples C: Control sample treated only with buffer; TG0: 0.1 U ml^{-1} TG; P: 2.5 U ml^{-1} protease; P+TG: 2.5 U ml^{-1} protease and 0.1 U ml^{-1} TG

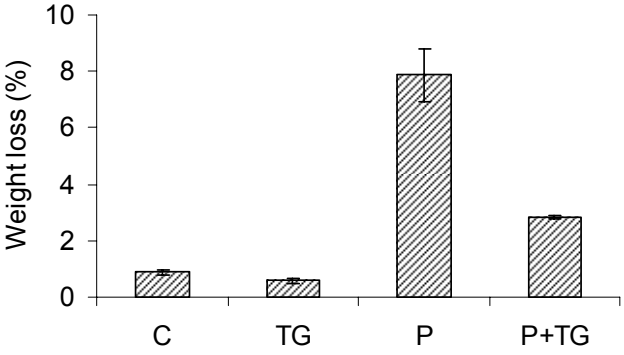


Figure 2. Weight loss of wool fabrics after bio-treatment in 50 mM Tris-HCl buffer, pH 8, 50 ºC for 60 min; sample description as in Fig. 1

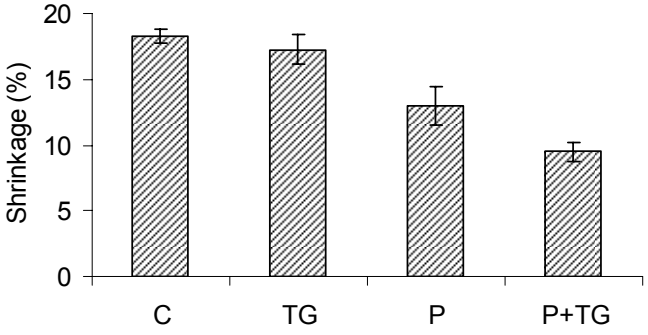
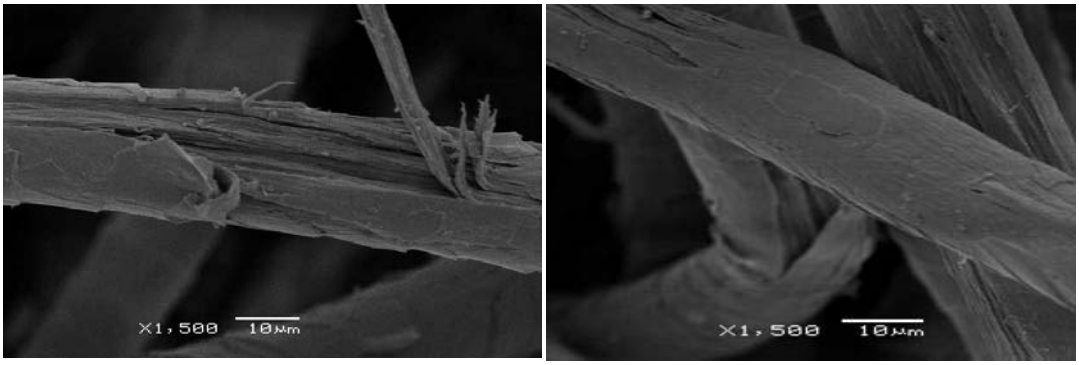


Figure 3. Shrinkage of wool fabrics after bio-treatment in 50 mM Tris-HCl buffer, pH 8, 50 ºC for 60 min; sample description as in Fig. 1



a) b)

Figure 4. SEM images [magnification x1500 and x1500] of wool fabrics after bio-treatment in 50 mM Tris-HCl buffer, pH 8, 50 ºC for 60 min with: a) 2.5 U ml^{-1} protease, b) 2.5 U ml^{-1} protease and 0.1 U ml^{-1} TG