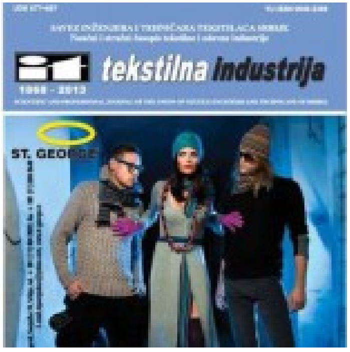

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SADRŽAJ

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ENZYMATIC TREATMENT OF WOOL: A REVIEW

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Review Article

Abstract: *The tendency of wool to felt and shrink is mainly due to its scaly structure. The enzymatic treatment of textiles significantly improves some of their properties as well as increases their aesthetic values and comfort of use. The application of enzymes in the wool modification process was studied, and it was proven that the application of enzymes has an important influence on changes in the surface structure. However, although proteases are large molecules, their attack is not only limited to the scales, they penetrate inside the fibre causing unacceptable weight and strength loss. It is believed that if the proteases are chemically modified in order to increase their molecular weight, then they will act just on the surface of the fibres, thus providing wool with anti-shrinking behaviour. The free enzyme penetrated into wool fibre cortex while the modified enzyme, with a bigger size, was retained at the surface, in the cuticle layer. Modified proteases can be a promising alternative for wool bio-finishing processes at an industrial level, since it is an effective way of removing wool scales.*

Keywords: enzymes, wool fibers, fiber properties, electrical surface resistance, electrical volume resistance, shrinking degree, dye absorption ability.

ENZIMSKI TRETMAN VUNE: PREGLED

Apstrakt: *Tendencija da se vune filca i skuplja je uglavnom zbog svoje ljuspičaste strukture. Enzimski tretman tekstila značajno poboljšava neke od svojih osobina, kao i povećava njihove estetske vrednosti i udobnost korišćenja. Primena enzima u procesu modifikacije vune je proučavano, i je dokazano da ima važan uticaj na promene u strukturi površine. Međutim, iako su proteaze veliki molekuli, njihov napad nije ograničen samo na krljušti, nego prodru unutar vlakana izazivajući neprihvatljivu težinu i gubitak jačine. Ako su proteaze hemijski modifikovani u cilju povećanja njihove molekulske težine, onda će delovati samo na površini vlakana, čime se obezbeđuje vuna sa anti-skupljanjem. Obični enzim prodire u korteksa vlakana vuna, dok modifikovani enzim, sa većim veličinom, je zadržan na površini, u sloju kutikule.*

Modifikovani proteaze može biti obećavajuća alternativa za vuna bio-dorade na industrijskom nivou, jer je to efikasan način uklanjanja krljušti vune.

Ključne reči: enzimi, vunene vlakna, svojstva vlakana, električni otpor površine, električni otpor volumena, stepen skupljanja, sposobnost absorpcije boja.

1. INTRODUCTION

Enzymes are biocatalysts with selective and specific activity, accelerating distinct reactions and remaining unchanged after the reaction.

The tendency of wool to felt and shrink is mainly due to its scaly structure. The use of chlorine as fibre-modifying agent is the most widespread process used to modify the scales of wool fibres with the purpose of providing resistance to felting and shrinkage. This agent produces environmentally unfriendly absorbable organic halogen by products. There have been many attempts to replace this

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chlorine process by an environmental friendly enzymatic process that would similarly degrade the scales. However, although proteases are large molecules, their attack is not only limited to the scales, they penetrate inside the fibre causing unacceptable weight and strength loss. It is believed that if the proteases are chemically modified in order to increase their molecular weight, then they will act just on the surface of the fibres.

Biotechnology provides enzymes in large enough quantities to make them economically viable. Advances in the field of genetic engineering allow enzyme manufacturers to design specific enzymes for specific processes. This paper surveys recent developments in the field of enzymatic processing of wool. Some techniques of increasing the proteases molecular weight were attempted. A more successful technique was attained by covalently coupling the enzyme to a soluble-insoluble polymer of high molecular weight. An enzyme conjugated to such a carrier may be used as a catalyst in its soluble form and then be recovered via the insoluble state.

When comparing to the native enzyme, the immobilized form presented a lower specific activity towards high molecular weight substrates but a higher thermal stability at all temperatures tested. It also exhibited a good storage stability and reusability, which makes this enzyme conjugate quite interesting from an industrial point of view. Wool fabrics were treated with the immobilized serine protease using harsh conditions and subjected subsequently to several machine washings, after which they presented a significant lower weight loss than wool treated with the native enzyme, in the same conditions [1]. Using a moderate enzymatic treatment, a reduction to about half of the initial area shrinkage was attained, both for free and immobilized enzymes.

All these results prove that modified proteases attained by this immobilization method, using a soluble-insoluble polymer of high molecular weight, can be a promising alternative for wool bio-finishing processes at an industrial level, since it is an effective way of removing wool scales and can be an environmental friendly option to the conventional chlorine treatments.

2. LITERATURE REVIEW

2.1. PROPERTIES OF WOOL FIBRE

In the late 18th Century, the Industrial Revolution began a movement which took the textile industry from the home into the factory. The machines and factories developed an insatiable demand for fibres, and an international trade in textile fabrics began to develop.

All textile fabrics manufactured prior to 1884 were made of the natural fibres: wool, silk, cotton and linen. The most recent evolution in the textile industry has been the introduction of man-made fibres [2]. The first group of man-made fibres which are still widely in use were "regenerated" from naturally occurring products.

The next evolutionary step was to completely synthesize the fibrous material. The oil industry yielded the base products for the synthesis of nylons, acrylic and polyester fibres. Wool, one of the oldest textile fibres known, has survived the test of time because of its unique natural properties (Table 1.).

Hence, wool is a remarkable renewable resource with exceptional properties - cool in summer, warm in winter and in a variety of weights suitable for both apparel and interior fibre applications. Wool has excellent flame-resistant properties. This factor is of importance in industrial safety garments and in institutions [3].

2.2. MORFOLOGY OF WOOL

The most important breed for producing premium fine wools is the merino, which originated in Spain during the Middle Ages. A merino wool fibre, viewed under the scanning electron microscope is shown in Figure 1.

Wool is a complex natural fibre composed mainly of proteins (97%) and lipids (1%). Wool fibre consists of two major morphological parts: the cuticle and the cortex. The cuticle is subdivided into two main layers, exocuticle and endocuticle, and has an outermost is membrane called the epicuticle [1]. The cortex comprises spindle-shaped cortex cells that are separated from each other by a cell membrane complex. The former is composed of overlapping cells (scales) that surround the latter.

This scaly structure of wool is responsible, to a great extent, for the tendency of wool to felt and shrink [1, 4].

The main substance of wool is a keratin. Keratin macromolecules are crosslinked with cystine residues and contain a variety of side chains, some basic and some acidic [5]. The morphology of the wool fiber surface plays an important role in textile finishing processes. Chlorination is a commonly used process to modify the scales of wool fibres with the purpose of providing resistance to felting and shrinkage. There have been many attempts to replace this chlorine process by an environmental friendly enzymatic process that would similarly degrade the scales [1, 6, 7, 8]. However, despite proteases are large molecules, their attack is not only limited to the scales, causing unacceptable weight and strength loss to the fibres. It is believed that if the proteases are chemically modified in order to increase their molecular weight, their attack would be restricted only to the surface of the fibres.

Table 1. - *Brief description of wool's natural properties*

Health	Because wool has the ability to insulate against heat and cold, it protects against sudden changes of temperature, and it lets your body breathe.
Comfort	Wool is comfortable to wear because its elasticity makes garments fit well and yield to body movement. It absorbs moisture, allows your body to breathe, and yet never feels damp and clammy.
Fire Resistance	Wool is naturally safe. It does not have to be specially treated to become non-flammable. Wool does not melt when burned, and so will not stick to the skin and cause serious burns.
Water Repellence	While wool can absorb moisture, it repels liquids.
Static Resistance	Because wool naturally absorbs moisture from the air, its tendency to collect static electricity is reduced.
Dyeing	Wool dyes very easily and the range of colours is limitless. The scales on the surface of the wool fibre tend to diffuse light giving less reflection and a softer colour. Because proteins in the core of the fibre are reactive, they can absorb and combine with a wide variety of dyes. This means that the wool holds its colour well as the dye becomes part of the fibre.
Health	Because wool has the ability to insulate against heat and cold, it protects against sudden changes of temperature, and it lets your body breathe.

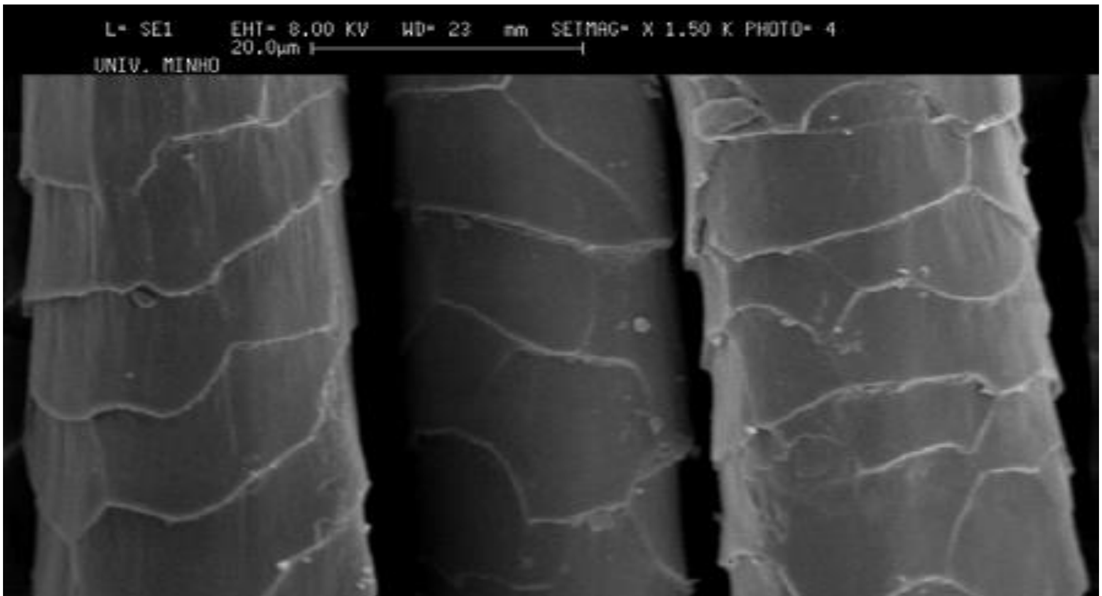

Figure 1. - *Scanning electron micrograph of clean merino wool fibres.*

2.3. FELTING AND SHRINKAGE

One of the intrinsic properties of wool, that is peculiar to wool only, is its tendency to felting and shrinkage. Under certain conditions, such as moisture, heat and mechanical agitation, wool shrinks, basically due to its morphological and scale structure. There are two kinds of shrinkage: relaxation shrinkage and felting shrinkage.

Relaxation shrinkage describes the shrinkage which appears during production when fabrics are subjected to more or less strong mechanical tensions in warp or in weft direction.

Felting shrinkage describes the shrinkage of garments due to the felting of wool fibres.

Only keratin fibres, grown on animals from their skin, can be induced to felt. This is because a directional surface structure is provided by the scales which occur on all animal fibres [9].

2.4. PROTEOLYTIC ENZYMES

Proteolytic enzymes catalyse the hydrolysis of certain peptide bonds in protein molecules, as already mentioned in the previous section (Figure 2.)

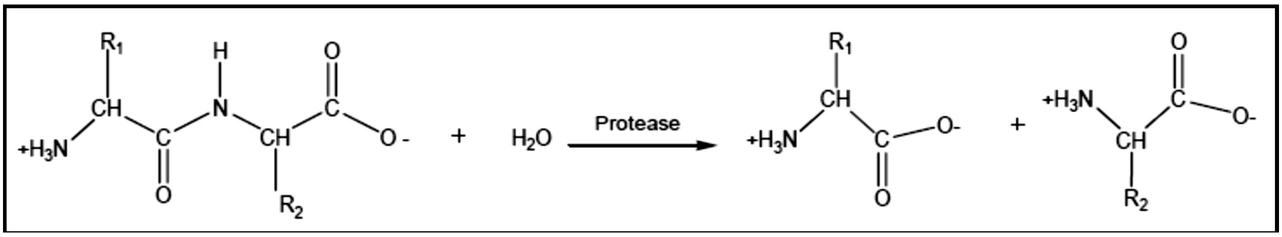

Figure 2. - *Schematic representation of the cleavage of a peptide bond by a protease*

Microbial proteases are among the most important hydrolytic enzymes and have been studied extensively since the advent of enzymology [10].

Protease treatments can modify the surface of wool and silk fibres to provide new and unique finishes. Research has been carried out on the application of proteases to prevent wool felting [1, 7, 8, 11]. The bio-industrial viewpoints of microbial alkaline proteases have been reviewed [10, 12].

A more rational system is now based on a comparison of active sites, mechanism of action and threedimensional structure [13, 14]. The serine peptidases are the most thoroughly studied class of enzymes in the protease field, and perhaps in all of enzymology [15], being characterized by the presence of a serine group in their active site [16].

2.5. PROPERTIES OF ENZYMES

Enzymes also play a significant role in non-food applications. Industrial enzymes are used in laundry and dishwashing detergents, stonewashing jeans, pulp and paper manufacture, leather dehairing and tanning and desizing of textiles. Most of the enzymes are, however, produced by microorganisms in submerged cultures in fermentors.

The simplest way to use and apply enzymes to practical processes is to add them into a process stream where they catalyse the desired reaction and are gradually inactivated during the process. In these applications the price of the enzymes must be low to make their use economical.

The traditional chemical treatments are generally non-specific, not always easily controlled, and may create harsh conditions. Often they produce undesirable side effects and/or waste disposal problems. Biotechnology is gaining ground rapidly due to the various advantages that it offers over conventional technologies. Industrial enzymes represent the heart of biotechnology processes. Textile enzymes are the third most significant segment of the market of industrial enzymes.

2.6. ENZYMATIC FINISHING PROCESSES FOR WOOL

Textile processing requires the use of vast amounts of water, chemicals and energy, and therefore it has important effects on the quality of the environment in textile manufacturing regions [17].

One control strategy that has given proof of efficiency in replacing pollutant processes in textile industry is, as already mentioned, the use of enzymes to replace the conventional chemical processes. The textile industry has widely and generally accepted the use of enzymes in its processes, especially in fairly simple large-scale applications, such as stone-washing [18]. Enzymes can be applied potentially to all stages of textile production. The following step in the textile process comprises the removal of dirt and impurities from the fabrics (scourig). Pectinases have been used together with cellulases in the elimination of impurities in cotton and wool [12, 19, 20]. The use of proteases to reduce prickle and improve softness in wool has been investigated with encouraging results [12].

3. FUTURE PERSPECTIVES

Further studies will contribute to the understanding of the mechanism of the proteolytic attack and will completely elucidate the factors that affect this reaction, like the smallest proteases molecular weight needed to avoid their penetration inside the wool fibre.

The progress in biotechnology of proteases and related enzymes is truly remarkable

and attracting worldwide attention. These developments together with improved scientific knowledge are expected to pave the way for a remarkable success in the biotechnology of proteases and related enzymes in the 21st century.

The possibility of leveraging innovations over industries could lead to new opportunities for biobased textile processes. Enzymes can be used in order to develop environmentally friendly alternatives to chemical processes in almost all steps of textile fibre processing. New enzymes with high specific activity, increased reaction speed, and tolerance to more extreme temperatures and pH could result in development of continuous processes. Find the optimal process parameters for the anti-felting treatment of wool, where weight loss, shrinkage and tensile strength will be minimized. Produce new modified proteases with reduced diffusing ability in wool. Develop bio-scouring processes (using an enzymatic cocktail of cellulases, pectinases, lipases, xylanases, hemicellulases and this modified protease) to achieve significant improvements in scouring efficiency, whiteness and dyeability of wool, which would reduce the chemical use and costs of the conventional scouring method.

The use of enzymes not only make the process less toxic (by substituting enzymatic treatments for harmful chemical treatments) and eco-friendly, they reduce costs associated with the production process, and consumption of natural resources (water, electricity, fuels), while also improving the quality of the final textile product.

There is still considerable potential for new and improved enzyme applications in future textile processing. It seems that in the future it will be possible to do every process using enzymes.

4. CONCLUSION

The use of various enzymes is in the early stages of development but their innovative applications are increasing and spreading rapidly into all areas of textile processing. The textile industry can greatly benefit from the expanded use of these enzymes as non-toxic, environmentally friendly compounds.

Textile processing industry is characterized by high consumption of energy and resources and time consuming processes.

Enzymes are a sustainable alternative to the use of harsh chemicals in industry and reduce energy and water consumption, and chemical waste production during manufacturing processes. With modern biotechnology tools, especially in the area of microbial genetics, novel enzymes and new enzyme applications will become available for the various industries

Also, been developed the use of protease enzymes for a range of wool finishing treatments aimed at increased comfort (reduced prickle, greater softness) as well as improved surface appearance and pilling performance. The improved enzyme treatments will allow more selective removal of parts of the wool cuticle, without degradation or weakening of the wool fibre as a whole and without the need for environmentally damaging pre-chlorination treatment.

Modified proteases attained by the described immobilization method, using a soluble-insoluble polymer of high molecular weight, can be a promising alternative for wool bio-finishing processes at an industrial level, since it is an effective way of removing wool scales and can be an environmental friendly option to the conventional chlorine treatments. This process needs to be further characterized for its complete understanding and optimization.

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