ENZYMATIC DESIZING OF COTTON: A REVIEW

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Abstract:

For cotton made fabrics , the warp threads are coated wit an adhesive sizing agent to prevent the threads from breaking during weaving. Starch and its derivatives are the most commonsizing agents. After weaving, the size must be removed in order to prepare the fabric for dyeing and finishing. This process is called as desizing and it involves use of chemicals like acids, alkali and oxidising agents in a traditional protocol and also consumption of large amount of energy and water. Biotechnology also offers the potential for new industrial processes that require less energy and are based on renewable raw materials and environmentally healthy practices. Enzymatic desizing using amylase is a very old process for the complete remove sizing starches at milder temperatures with lesser use of caustic and with reduced energy & process water consumption without fiber damage. Nevertheless the effluents contain very low pollutants as the desizing process is very specific and release substances which are bio degradable making it extremely eco friendly. This work represents a review of α-amylase family and the major characteristics, microbial sources, production, properties and explores the potential of this enzyme.

Key words: Enzymatic Desizing, Starch, Microbial α-amylase, Industrial Applications.

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1. Introduction:

As textile industry is one of the largest industries in the world and different fibres such as cotton, silk, wool as well as synthetic fibres are all pre-treated, processed, coloured and after treated using large amounts of water and a variety of chemicals, there is a need to understand the chemistry of the textile effluents very well. Major pollutants in textile wastewaters are high suspended solids, chemical oxygen demand, heat, colour, acidity, and other soluble substances whose chemistry will be emphasised.

The application of biological organisms, systems and processes to manufacturing and processing industries is refered as biotechnology. Biotechnology as an ecological advantageous and moreover economical beneficial technology plays an increasingly important role in the industrial wet textile pretreatment and the finishing processes. This terms refers to the textiles that are based on enzymes. Especially in textile manufacturing the use of enzymes has a long tradition. The first microbial amylases were used in the 1950s for the removal of starch sizes, which today is routinely used by the industry [Ciechanska and Kazimierezak 2006; Marcher et al. 1993]. Amylases are enzymes which hydrolyse starch molecules to give diverse products, including dextrins and smaller polymers composed of glucose units [Gupta et al. 2003]. Sizing is carried out in the weaving mill to protect the warp yarn during the weaving process from damage or break. The size forms a protective film on the warp yarn, protruding fiber ends causing loom stops are minimized. About 75% of sizing agents used worldwide are starch and its derivatives [Cavaco-Paulo & Gübitz, 2003].

Desizing is a typical process in pretreatment of cotton woven fabrics and cotton blends but also necessary for all grey synthetic materials containing sizes. The sizing agents on the warp yarns, have to be removed before further processing in textile finishing [Cavaco-Paulo & Gübitz, 2003; Hashem, 2007]. In the past, hydrogen peroxide and sodium hydroxide were generally used as desizing agents. But this method was not economically and environmental-friendly. In conventional method of starch removing from a cotton article large amount of water, chemicals and energy have to be consumed. To decrease water and the chemicals consumption and in response to the environmental concerns, enzymatic desizing of cotton seems a practical alternative.

2. Literature Review

2.1. Cotton fibre and his structure

Cotton is the most important of the raw materials for the textile industry. Cotton grows as unicellular fibre on seeds. The cross section of a cotton fiber consists of a number of concentric layers. They can be broadly classified as belonging to either the outermost region called the primary wall or the inner region designated as the secondary wall. The surface properties of cotton fibers are largely the result of cellulosic structure plus a waxy material covering and impregnating this cellulosic structure.

The cuticle exists as the separable outer boundary and consists of a layer of wax and pectin material. This layer plays an important role in providing lubrication to cotton during spinning operation in the textile industry. Below this layer is the primary wall, which consists primarily of a network of cellulose fibrils.

Cellulose is the major component of cotton. Apart from cellulose, cotton is also associated with other external substances. The mature cotton fibre forms a highly convoluted flat ribbon, varying in width between 12 and 20 µm. Cotton fibres have a fibrillar structure. A mature cotton fibre is composed of several concentric layers and a central area called lumen. A cuticle, a primary cell wall, intermediary wall as well as secondary cell wall follow each other from the outer to the inner part of the fibre. The whole cotton fibre contains 88 to 96.5% of cellulose, the rest are uncellulosic substances, called incrusts.

The primary wall in mature fibres is only 0.5-1 µm thick and contains about 50% of cellulose. Noncellulosic constituents consist of pectins, fats and waxes, proteins and natural colorants. The secondary wall, containing about 92-95% cellulose, is built of concentric layers with alternatic shaped twists. The layers consist of densely packed elementary fibrils, organized into microfibrils and macrofibrils. They are held together by strong hydrogen bonds. The lumen forms the centre of the fibres. Cotton is composed almost entirely of the polysaccharide cellulose.

Chemical composition of cellulose is a linear (1→4)-linked polymer of β-D-glucopyranose. The degree of polymerization of cellulose varies with its source and the processing stage of the cellulosic material.

The primary wall is about 1 µm thick and comprises only about 1 % of the total thickness of cotton fibre. The major portion of the noncellulosic constituents of cotton fibre is present in or near the primary wall.

Row cotton fibres have to go through several chemical processes to obtain properties suitable for use. With scouring, non-cellulose substances (wax, pectin, proteins, hemicelluloses…) that surround the fibre cellulose core are removed, and as a result, fibres become hydrophilic and suitable for bleaching, dyeing and other processing.

2.2. Enzymes

Enzyme is a naturally occurring biological product produced by all living organism. It is composed of a complex 3 dimensional globular protein, comprising about 200 to 250 amino-acids having molecular weight as high as 10^4 - 10^5 and which are capable of catalysing specific chemical reactions. Many enzymes also contain a non-protein component called "cofactor" for improved catalytic activity. Being catalysts of all reactions in the living system, the enzymes are also called as 'bio-catalysts'. However, the enzyme catalysts differ from chemical catalysts in following important ways:

- Enzyme-catalysed reactions are much faster than chemically-catalysed reactions;
- Enzymes have greater reaction specificity;
- Enzymes work under comparatively mild reaction conditions;
- Very small amounts of enzymes are required to carry out chemical reactions;
- Enzymes use significantly less water, energy and time for effective specific action.

The commercially available enzymes are manufactured from the micro-organisms by fermentation. Further purification steps involve precipitation, extraction, centrifugation and filtration.

The speed of the chemical reactions depends on the energy barrier between the substrate and the product. This barrier is known as the 'activation energy' and for molecules to react, they must possess the energy to overcome the barrier. However, enzymes do not increase the energy levels of substrate molecules, but provide an alternative low-energy route for the reaction to proceed. They achieve this by forming an intermediate enzyme-substrate complex, which alters the energy of the substrate such that it can be quite readily converted to the product. The enzyme itself is released unaltered at the end of the reaction, thus acting as a catalyst. Enzymes being highly specific catalysts, the substrate must fit precisely into the active site of the enzyme just like a key fitting into lock. The formation of enzyme substrate complex also requires very little energy. Consequently, enzymes are very effective catalysts, enhancing reactions up to several thousand-fold more than the most effective chemical catalysts. The substrate & reaction specificity is determined by the structure of enzyme. The primary structure is determined by the amino acid sequence, the secondary structure by the specific conformation of protein chain and the tertiary structure by the arrangement of chain segments.

Enzymes are sensitive to the outside environment during their storage. Even a long storage period can affect the activity of an enzyme. With the change in activity level, the effectiveness of the enzyme will also change.

Most of the industrial enzymes are produced by a relatively few microbial hosts like *Aspergillus* and *Trichoderma* fungi, *Streptomyces* fungi imperfecti and *Bacillus* bacteria. Yeasts are not good produces of extracellular enzymes and are rarely used for this purpose. There is a large number of microorganisms which produce a variety of enzymes [Boyer 1971; Fersht 2007].

2.3. Enzymes in textile processing

Modern wet processing industries are followed the enzymes in the preparatory process instead of using harmful chemical because enzyme are more convenient, effective and environment friendly. The application of enzymes has many advantages compared to conventional, non-enzymatic processes. Especially in textile manufacturing the use of enzymes has a long tradition. Enzymes for cellulosic textiles and their effects are shown in Table 1. The principal enzymes applied in textile industry are hydrolases and oxidoreductases. Moreover, cellulases, pectinases, hemicellulases, lipases and catalases are used in different cotton pre-treatment and finishing processes [Meyer-Stork, 2002].The group of hydrolases includes amylases, cellulases, proteases, pectinases and lipases/esterases, but their innovative applications are increasing and spreading rapidly into all areas of textile processing.

Enzymes are widely used in the textile industry owing to their eco friendliness and suitability of application on different substrates under varying application conditions. The enzymes are now considered to be an integral part of almost every wet processing step of natural fibres, ranging from fabric preparation to the garment finishing. Enzymes are part of "White Biotechnology", which is aimed at practicing environment-friendly applications and using renewable resources. During the last decade many new applications have been developed and commercialised, which has also expanded the market size considerably.

Table 1. Enzymes for cellulosic textiles

Type	Effect
Amylases	Desizing (to decompose starches applied in sizing).
Protease, lipases and pectinase	When combined, act on proteins, pectins and natural waxes to effect scouring.
Catalases	Act on H_2O_2 to decompose it into water & oxygen
Cellulases	Break down cellulosic chains to remove protruding fibres by degrading and create wash-down effect by surface etching on denims etc.
Laccases	Decomposes indigo molecules for wash-down effect on denim

Enzymes have found wide application in the textile industry from fabric to garment finishing for improving efficiency of processing and enhancing aesthetic appeal. Enzymes are used in the textile industry because they:

- Act only on specific substrates;
- Can replace harsh chemicals;
- Operate under mild conditions;
- Accelerate reactions;
- Are safe and easy to control;
- Are biodegradable;

The major usage of enzymes in textile processing is in the areas of:

- Desizing - of cotton woven fabrics, terry towels and denims;
- Bioscouring - of cotton yarn & knits;
- Biocleaning - degumming of silk, flax retting, decolourisation of dye house waste water.;

- Biobleaching - of Wool;
- Bleach clean-up - post bleaching peroxide neutralization;
- Biopolishing - loose fibre, surface fuzz removal from knits/towels for anti-pilling;
- Biosoftening - soft finish on knits & garment, fading of denims.

As the enzymes are very specific in action, as each type can affect only one chemical bond, more control over final effects is easily achieved. In terms of effluent, enzymes are quite clean and affect effluent only mildly, if at all.

Depending on substrate specificity, the commonly used enzymes during textile processing are:

- Amylases - for Starch;
- Cellulases - for Cellulose;
- Catalases - for Hydrogen Peroxide;
- Pectinases - for Pectins;
- Proteases - for Proteins.

2.4. Desizing of cotton

Cotton is the most widely used natural cellulosic substrate. One of the processing steps involves sizing of yarn (coating of the warp threads by starch) in order to prevent their breakage during subsequent weaving. Generally, the sizing agents are selected depending on the quality of yarn and the fabric construction. The typical sizing agents used are natural starch and modified starch derivatives, polyvinyl alcohol (PVA), carboxy methyl cellulose (CMC), etc.

Starch comprises a mixture of a linear polymer and a branched polymer. Amylose is a flexible linear polymer of glucose residues joined by alpha-1,4 glycosidic bond, which may be formed from several thousand glucose molecules. Amylopectin, however, is a branched molecule of glucose residues joined by either the alpha-1,4 or alpha-1,6 glycosidic bond. The proportion of the two polymers, amylose and amylopectin, depends upon the source of starch. Starch from wheat, for example, contains approximately 25% amylose and 75% amylopectin.

However, during the subsequent process this applied size (surface coating on yarn) has to be removed from woven fabric for further wet processing comprising bleaching, dyeing, printing and finishing. The removal of starch from yarn surface is termed as **"desizing"**. The purpose of desizing is to adequately remove enough of the size film to allow further wet processing steps to occur at optimum efficiency. Thus, desizing is considered to be a key parameter, which determines performance of further processing.

Desizing process involves impregnation of fabric with the desizing agents allowing it to degrade or solublise the size and finally to wash off the degraded products. Traditionally, desizing was carried out by treating the fabric with water or by chemicals such as acids and oxidising agents. Amylases are used to remove starch. Enzyme desizing is the most widely practiced method of desizing starch. Amylase is a hydrolytic enzyme which catalyses the breakdown of dietary starch to short chain sugars, dextrin and maltose. The advantage of these enzymes is that they are specific for starch, removing it without damaging to the support fabric [Ahlawat et al. 2009; Feitkenhauer, 2003; Gupta 2003]. Although the specific action of amylases for starch splitting was known earlier, the industrial scale enzymatic desizing was commercialised in the late 1960s. An amylase enzyme can be used for desizing processes at low-temperature (30-60 ºC) and optimum pH is 5,5-6,5 [Cavaco-Paulo and Gübitz, 2003].

The enzymatic desizing of cotton with α-amylases is state-of-the-art since many decades [Marcher et al. 1993]. The amylose is bioconverted to 100% by the α-amylase into glucose whereas the amylopectin is converted to 50% into glucose and maltose. Bio desizing is preferred due to their high efficiency and specific action. Amylases bring about complete removal of the size without any harmful effects on the fabric besides eco friendly behavior. These enzymes degrade starch to shorter polymeric fragments, known as dextrins and maltose, a disaccharide, which contain two glucose residues. Alpha-amylases are found in microorganisms, plants and animals.

Depending on the type of substrate (woven fabric, terry towel, denim/garment) and the machinery in use (jigger, soft flow/winch, drum washer, pad-batch, pad-steam), desizing operation is performed by exhaust, semi continuous or continuous application methods.

Desizing on pad rolls is continuous in terms of the passage of the fabric. However, a holding time of 2 - 16 hours at 20 - 60°C is required using low-temperature α-amylases before the size is removed in washing chambers. With high-temperature amylases, desizing reactions can be performed in steam chambers at 95 - 100°C or even higher temperatures to allow a fully continuous process.

After desizing, the fabric should be systematically analysed to determine the uniformity, effectiveness and thoroughness of the treatment. The commonly used test methods are:

- Assessment of weight loss;
- Water, colour solution absorbency;
- Hand feel;
- Bending length;
- Effect on tensile and tear strength.

3. Future Directions:

The continued development of new enzymes through modern biotechnology may, for example, lead to enzyme products with improved cleaning effects at low temperatures. This could allow wash temperatures to be reduced, saving energy in countries where hot washes are still used. Today, white biotechnology is geared towards creating new materials and biobased fuels from agricultural waste and providing alternative biobased routes to chemical processes. These efforts could lead to the development of improved enzymes such as amylases, hemicellulases or cellulases that could be used in the textile industry. The use of various enzymes in the early stages of development but their innovative applications are increasing and spreading rapidly into all areas of textile processing. Enzyme producing companies constantly improve their products for more flexible application conditions and a more wide-spread use. The textile industry can gratly benefit from the expanded use of these enzymes as non-toxic, environmentally friendly compounds if their effects on the textile substrate and the basic mechanisms involved are better understood. New and exciting enzyme applications are likely to bring benefits in other areas: less harm to the environment; greater efficiency; lower costs; lower energy consumption; and the enhancement of a product's properties.

4. Conclusion:

Biotechnology finds finds wide application in textiles. Enzymes are not only beneficial from ecological point of view but they are also saving lot of money by reducing water and energy consumption which ultimately reduce the cost of production. It seems that in the future it will be possible to do every process using enzymes.

In textile processing the enzyme can be successfully used for preparatory process like desizing, scouring and bleaching. These enzymatic processes are gives the similar results as that of conventional methods. Though this enzymatic processes we can reduce the water consumption, power energy, pollution, time, and increasing quality.

Sizing is necessary to ensure that yarns are adequately protected during weaving as the modern looms operate at very high speeds, causing excessively high abrasion to the yarn. Starch is the preferred sizing agent for cotton and blends. To ensure that fabric is well prepared for dyeing and further processing, all size must be removed adequately and uniformly.

Amylases are used to remove starch. Amylase is a hydrolytic enzyme which catalyses the breakdown of dietary starch to short chain sugars, dextrin and maltose. Enzyme desizing is the most widely practiced method of desizing starch. The advantage of these enzymes is that they are specific for starch, removing it without damaging to the support fabric.

This is just one application of Biotechnology, however many such potentials are yet to be explored. The textile industry was identified as a key sector where opportunities available from adapting biotechnology are high but current awareness of biotechnology is low.

Enzymes are emerging in a big way in the field of textile wet processing. If their cost can be managed, enzymes can be put to use in a much bigger way for textile processing applications.

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