

Application of Enzyme on Woolen Products for Its Value Addition: An Overview

L. Ammayappan

National Institute of Research on Jute and
Allied Fiber Technology
India

lammayappan@yahoo.co.in

ABSTRACT

Enzyme plays an important role in textile processing. Wool being a hydrophobic fiber, tends to shrink during washing. To prevent shrinkage, enzyme pretreatment is preferred. This paper overviews the types of enzyme used for wool modification and their role on wool modification.

Keywords: Dyeing, Enzyme, Finishing, Handle, Pre-treatment, Protease, Wool

INTRODUCTION

Textile industries use various chemicals in different processes like from desizing to finishing of fabrics. After processing, these chemicals can increase the pollution load in the effluents; even some of them are corrosive, which cannot be easily regenerated or recycled. However, with the introduction of enzymes and enzymatic processes in textile industries the scenario has been changed in recent times, which are ensuring eco-friendly processing of textile products and are successfully used in textile processes like preparatory process, bleaching, dyeing, finishing and even in surface modification (Shukla 2001, Karmakar 1999). The stringent environmental and industrial safety conditions have ensured the environment friendly production and increased the potential use of enzymes in textile processing.

J
T
A
T
M

Enzymes, being an eco-friendly natural macromolecules used in the textile industry since 1960's, that ranged from desizing of cotton fabrics, polishing of wool cuticle surface, degumming of silk fabrics, activated peroxide bleaching, scouring aid in laundry of worsted garments and also in decolorization of dye house wastewaters. Due to climatic change and global warming, innovations in eco-friendly processing are rapidly intensifying. Enzyme based processing of cellulosic fibers is well established for the improvement of handle and properties, but for woolen products is still in the development stage. Enzymes being natural products are completely biodegradable and accomplish their work quietly and efficiently without leaving and pollutant behind (Pardeshi et.al, 2002). Initially, enzymatic processing of wool concerned with shrink-resistant process and present days it is focused on carbonizing, bleaching, dyeing and finishing of woolen products (Shenai 2002).

To enhance the eco-friendly process of wool using enzyme, it is right time to overview the research caps present in the application of enzymes on improvement in properties of wool. Based on the background, this objective of the paper is to review the types of enzymes applied for the improvement of properties of wool with future research scope.

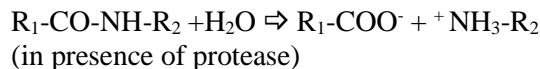
ENZYMES

Enzymes are organic proteinaceous catalysts produced by all living cells. They are specialized protein complex composed of 200-250 amino acids that function in the acceleration of bio-chemical reactions; therefore, it is also called as “Bio-catalyst”. They found in plants as well as animals and microorganisms where they play important role in the function of cells. The molecular weight of these is very high and is of the order 10^4 - 10^5 (Zubay et.al, 1995). Enzyme can bring about hydrolysis, oxidation, reduction, coagulation, and decomposition although the most common reaction is the hydrolysis. An enzyme is temporarily covalently bonded to a molecule (substrate) during intermediate stages of the reaction, but at the end of the reaction the enzymes will regain its original form as the product is released. Enzymes react specific in nature; catalyze efficiently; work at atmospheric pressure; active in mild conditions of temperature and pH in lower concentration. They obtained from three main sources i.e., plant, animal and microbial sources like bacterial, fungal and yeast (West and Todd, 1961).

Classification of enzymes

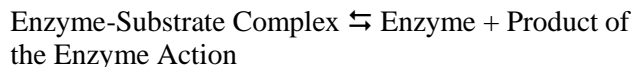
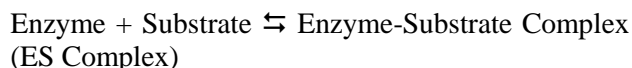
In 1956, the International Union of Molecular Biology (IUBMB) has established a system where all enzymes classified based on the type of reaction. They classified into six major classes (Devlin 1997) and each sub divided into sub-classes that are further subdivided. Each enzyme prefixed with the reaction type and suffixed with “-ase” (Table 2). For example, hydrolase involves in the hydrolytic cleavages of $>C=O$, $>C=N$ and $>C=S$ bonds (West and Todd, 1967; Cavaco-

Paulo, 1998 Cavaco-Paulo and Gübitz, 2003) by enzyme. The cleavage of a polypeptide bond by a protease enzyme is a good example.



Mode of enzyme action

Michaelis and Menton postulate the basic mechanism of the enzyme action on any substrate and that postulation is known as enzyme-substrate complex theory. The following equations set forth the two phases of enzyme action according to the hypothesis.



J
T
A
T
M
An enzyme-catalyzed reaction occurs within the confined pocket of the enzyme called the active site (Kirk Othmer 1971). The number of active sites per molecule is very small, generally only one. The molecule that is bounded by the active site and acted upon by the enzyme is called the substrate. The active site contains a functional group, particularly amino acid side chains which involved in catalyzing the reaction. The active site of an enzyme may become temporarily bound to a substrate in “lock-key fashion” through a number of weak bonds including hydrogen bonding / Vander Waals’ interaction etc., with small release of free energy known as binding energy. The binding energy is a major source of free energy used by enzymes to lower the activation energy of the chemical reaction, so that the reaction proceeds at a faster rate. It is noted that no enzymes alter the equilibrium constant of any catalyzed reaction, while it provides a lower-energy reaction path so that the rate of reaction is accelerated (Devlin 1997).

Finally, the enzyme-substrate complex disintegrated and released the products with the original enzyme, which can be reused once again. The process will

continue, until the enzyme is terminated by change in either temperature, pH or by other negative conditions in the processing environment. The enzyme-catalyzed reaction is the first order reaction since the rate of reaction is directly proportional to the concentration of substrate. The rate-determining step is the formation of enzyme-substrate complex and it depends on the external factors such as pH, temperature and additives. The velocity of enzyme reaction is initially increased and reaches a maximum at the point at which all the available sites are saturated. (Nierstrasz and Warmoeskerken, 2003)

Factors affecting the rate of enzyme reaction

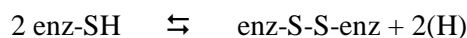
Enzyme activity on textile substrate is specific and the activity is mainly depended on the following factors (Kirk Othmer 1971; MacGraw Hill 1971):

1. **Concentration of substrate:** Rate of enzymatic action increased with increase in the substrate concentration, then there is no improvement can be observed (if the variables can be controlled).
2. **Concentration of enzyme:** Rate of enzyme action is directly proportional to the concentration of enzyme, however in presence of the products, this linear relationship may not hold, since it might has inhibition effect on enzyme.
3. **pH:** Enzymes are susceptible, when there will be change in pH. Each enzyme has its own optimum pH i.e. H⁺ concentration at which the enzyme reacts at maximum speed and has more stability. It is possible that changes in pH alter the equilibrium point between enzyme and product since, other than optimum pH each enzyme can be deactivated
4. **Temperature:** Each enzyme has its own optimum temperature i.e. temperature at which the conversion of substrate in to products in a unit time will be high. The rate of an enzyme-catalyzed reaction increased with increasing in temperature (up to its optimum temperature) and then

suddenly decreased due to deactivation of active sites.

5. **Concentration of reaction products:** The presence of higher concentration of products can decrease in the rate of decomposition of enzyme-substrate complex. It is due to the formation of stable product-enzyme than of enzyme-substrate complex, which blocks the “active centers” in certain proportion of the enzyme.
6. **Time:** Enzyme reacts in a shorter time at an optimum condition and the processing time not given sufficient consideration in discussing factors that affect the rate of enzyme action.
7. **State of oxidation:** Protease enzyme “Papain” called as “sulfhydryl enzyme” which is activated by reducing agents and inactivated by aeration or other mild oxidizing treatment. The actual reduction of disulfide linkages (-S-S-) in the enzyme molecule to sulfhydryl (-SH) may be responsible for the activation.

J
T
A
T
M



Active reduced form inactive oxidized form

8. **Activators:** Some specific bivalent metal cation act as activators, by stabilizing the enzyme-substrate complex, and so sensitize the substrate to the attack of enzyme.
9. **Additives:** Inorganic salts such as Mg²⁺ ion or complex organic molecules can be used as co-enzymes, which binds tightly to a special site on the enzyme in order to improve its reactivity
10. **Inhibitors:** Molecules chemically similar to the substrate molecules react with enzyme and blocks the active sites, which cannot be available to normal substrate. Heavy metals such as copper, mercury, lead, iron etc., and sequestering agents are lethal to enzymes.

PROTEASE ENZYMES

Protease is a class of enzyme, that actives only on protein macromolecules and

their activity begins with hydrolysis of the covalent peptide bonds that link successive amino acid residues in a polypeptide chain and this process is termed proteolysis. The initial products of proteolytic process are amino acids and small peptides. The rate of activity of the enzyme will depend on bath buffer system, ionic strength of enzyme and process history of wool fiber substrate (Nolte et.al, 1996; Shenai 2002; Shen et.al, 1993; Nierstrasz and Warmoeskerken, 2003). Protease enzymes may be classified into four categories based on their chemical reaction i.e. serine proteases, cysteine proteases, aspartic proteases and metallo-proteases.

- a) **Serine protease:** It is characterized by the presence of an essential serine residue at their active site. Trypsin, Chymotrypsin and Savinase are best-known serine proteases. *Subtilisins* particularly those produced by selected *Bacilli* have serine residue and found widespread applications as detergent additives.
- b) **Cysteine protease:** It is characterized by the presence of a cysteine and a histidine residue at the active site. The best-known enzyme is Papain and generally, activated under reducing conditions and gave optimum activity at neutral pH values.
- c) **Aspartic protease:** It contains a group of acidic proteases that contain an essential aspartic acid residue at the catalytic site. They show optimum activity at pH values between 3 and 4 and have isoelectric points between 3 and 4.5.
- d) **Metallo-protease:** It is a family of proteases characterized by their requirement for (divalent) metal ions to sustain biological activity. Most metallo-proteases shown optimum activity at neutral to alkaline pH values

WOOL

Wool fiber is mainly composed by polypeptides and small amount of lipids, so it is an ideal substrate for protease and lipase

enzymes. It has two major morphological parts i.e. the cuticle and the cortex, in which the outer cuticle cells overlapped and protected the cortex. In cortex, spindle shaped cortical cells that are separated from each other by a cell membrane complex. Cuticle, the outer layer of wool fiber has three layers called exocuticle (with A and B layer), endocuticle and epicuticle (outermost membrane made up of lipids). Epicuticle is made of 18-methyleicosanoic acid and it covalently bound to a cuticle layer (Peters 1967; King and Bradbury, 1968; Ammayappan, 2012).

Epi-cuticle is mainly responsible for hydrophobic nature of wool fiber and can be removed by treatment with alcoholic NaOH or chlorine solution in order to enhance hydro-philicity. Disulphide cross-linking is a major characteristic of cuticle. A-Layer of exocuticle is made up of cystine residues, normal peptide bonds and cross-linked by isopeptide bonds through ϵ (γ -glutamyl) lysine. Diffusion barrier of wool fiber against dyestuff might be due to the hydrophobic character of exocuticle A-Layer, which caused by the large amounts of disulfide cross-links and the bound lipid material. Cuticle scale offered felting tendency in aqueous bath, non-easy care properties and harsh feel (Mall et.al, 2002). Complete removal of the cuticle scale is damaging the mechanical properties of wool fiber. However, the partial removal is required to get improved characteristics of wool fiber. Pretreatment can also modify the composition and morphology of wool fiber.

Wool fiber has 1% lipids in which cholesterol being one of the main components. These lipids are responsible for the hydrophobic barrier of the cell membrane complex (CMC). Dyeing and diffusion properties of wool fibers are believed to be governed by the lipid structure of the intercellular spaces, which might acts as "solvents" for hydrophobic textile chemicals. However, wool has nearly 70% amorphous regions and so the processing ability of woolen products mainly depended on the presence of cuticle and epicuticle (Simpson and Crawshaw 2002).

APPLICATION OF ENZYME IN WOOL PROCESSING

Wool fiber is considered as a natural biocomposite and it has unique physical and chemical properties. The bilateral nature of caused the natural crimp and so making large number of air pockets, which are capable of retaining warmth. The drape-ability is outstanding due to its high extensibility. It absorbs a large amount of moisture, leading to comfort. Raw wool contains nearly 30 to 60% of natural as well as adhered impurities; so that its purification can be carried out in the sequence of scouring, carbonizing, bleaching, dyeing, milling and decatizing, and the sequences of the processing depends on the products and customer requirements.

Conventional wool processing consumes more energy and time for one full processing cycle for a product; however enzyme treatment might be able to reduce the processing time energy. Different enzymes can be generally used in wool processing as follows: enzyme pretreatment for each processing for the modification of wool fiber surface; enzyme-assisted processing for reducing the processing time; and enzyme processing for the improvement of performance properties of woolen products like descaling (Heine and Hocker 1995; Heine et.al, 1998; Karmakar, 1999; Walawska et.al, 2006; Ammayappan, 2009).

Preparatory Processes

Carbonization

Carbonization is the process to remove cellulosic portion (burr) from greasy wool by strong acid at baking condition. In carbonization, wool is impregnated with 5-10% sulfuric acid solution and then baked at 120°C/ 30 minutes in order to char the cellulosic impurities. The residues are then crushed and extracted from the wool as carbon dust by brushing and suction. Instead of harsh chemical, enzymes can be used to remove the adhered vegetable matters. A mixture of cellulose, pectinase and ligninase enzyme is used to remove vegetable matters from a range of wool grease. It is also reported that hydrolase, lyase and

oxidoreductase are used to remove plant impurities from wool, while the enzymes reduced the amount of sulfuric acid used for carbonization. After incubating with cellulose, enzymes burr removal easier due to a weakening of the cohesion between burr and wool. No chemical or physical damages of the wool are observed after mechanical removal of the enzyme treated burrs (Sedelnik 1993; Hein et.al, 2000).

Scouring

Scouring is carried out to remove adhered natural impurities like wax, fat and sweat with hot detergent solution. Since it involves both chemical and heat energy with large consumption of water, an alkali stable protease enzyme based scouring treatment is preferred to reduce the amount of required chemicals with improvement in the whiteness index, dye ability and softness (Ammayappan and Gupta, 2011). Enzyme based scouring led to improvement in dye-ability. It is noted that protease enzyme penetrated into the amorphous region and caused swelling, and it led to change the disulfide region of cystine than amide components. So percent content of ordered alpha helix region decreases with conversion of beta sheet form in enzyme scouring (Wojciehowska et.al, 2004).

Bleaching

Wool fiber has a pronounced natural yellow color called canary coloration. During growth and also on exposure to light, alkali or by microbial degradation, canary coloration is high in Indian wool due to tropical condition (Anon 1980). Bleaching of wool fiber can be predominantly done by hydrogen peroxide employing a variety of conditions i.e. treatment with different reducing agents followed by hydrogen peroxides. Research works revealed that peroxide bleaching can be enhanced by the presence of a protease enzyme in the same bath (Cegarra et.al, 1995).

Jovancic et. al., (2001) reported that the partial removal of the cuticle cells takes place during peroxide bleaching in presence of protease enzyme, which positively

influenced the whiteness. Addition of small quantities of enzyme in the peroxide bath can considerably accelerated the peroxide decomposition or acted as catalyst and so simultaneously enhanced wool fiber whiteness (Levene et.al, 1997). They also inferred that cysteic acid content of the wool fiber in cuticle significantly decreased with increase in the enzyme concentration in the peroxide-bleaching bath, probably due to the loss of the sulfur in the A-Layer of the exocuticle.

They also observed that the enzyme retained only 5% of the initial activity after 15 minutes in the alkaline peroxide bath and its activity diminished sharply. Shan et.al (2001) formulated an optimized bleaching condition for wool with hydrogen peroxide as follows: 10ml/l H₂O₂, pH 5.5, 60 minutes, 8 ml/l stabilizer, 4 ml/l enzyme with 1:20 bath ratio and found that the enzyme used as catalyst under acidic conditions and at low temperatures for bleaching of wool fiber with hydrogen peroxide. Treating of wool fiber with a haloperoxidase (hydrogen peroxide+halide) and a protease enzyme resulted in improved shrink resistance. Wool cuticle degrading enzyme called *Bacillus cereus strain NS-11* modified the cuticle components preferentially without damaging the inner components of wool fiber in presence of hydrogen peroxide (Karmakar 1999).

Dyeing

Wool fiber can be dyed wide range of dyestuff like acid, basic, reactive and metal complex dyes. Among those, acid and metal complex dyes are mainly used for dyeing owing to their brilliancy of shades, all round fastness properties and ease of application. However, the conventional dyeing process can be executed at high temperature for longer duration to achieve the desired shade (Pailthroe 1992; Russell et.al, 2002). Higher dyeing temperature may deteriorate the quality of wool and may causes wool to shrink considerably. Thus, always there is a demand to identify eco-friendly and economic dyeing process which will leave

the wool fiber in a good condition after the dyeing has been completed.

Researches made continuous efforts to explore alternative methods that will reduce cost, retain quality and maximum production. Enzyme pretreatment on wool fabric can decrease the resistance of the fiber against dye diffusion and so it will increase the adsorption rate constant of dyeing and decrease the apparent activation energy for the dyestuff when compared to untreated fabric (Riva et al 2002). Yoon et.al, (1998) inferred that dyeing and diffusion properties of wool fibers are believed to be governed by the lipid structure of the intercellular spaces of wool fiber since they act as “solvent” for hydrophobic chemicals.

The improvement in the dye ability of wool fiber due to enzyme pretreatment may be varied according to the characteristics of wool fiber and dye. Enzyme can digest the amorphous region and induced the dyeing rate positively and decreased the affinity for small molecular weight dye molecule like leveling acid dye. However, with proper enzymatic hydrolysis of wool fiber, both the dyeing rate and the dye affinity may be increased, particularly with the dyes of large molecular size like metal complex dye. Lipase enzyme treatment is considerably improved the dye ability of wool fiber due to degradation of the hydrophobic F-layer and so the accessibility of the fiber to the aqueous dye liquor increased (Monlleo et.al, 1994; Kantouch et.al, 2005).

Moreover, the degradation of protein compounds within the fiber allowed greater mobility for the dye molecules. Even a mild enzyme treatment of wool markedly can improve the dye ability without causing significant fiber damage. Riva et.al (1993) inferred that the enzymatic treatment degraded the fiber surface partially, which can make the dye diffusion easier. This effect is more notable at the low dyeing temperatures than conventional dyeing condition, since the diffusion energy is insufficient when untreated wool is dyed at these temperatures.

Cegarra (1992) stated that the enzyme treated wool had more amine

J
T
A
T
M

terminal groups than untreated wool, so enzyme treated wool fiber capable of attracting the dye as well as dyed more intensely dyed than the untreated fibers. Trypsin enzyme treatment can increase the exhaustion of natural dye like crocin, beta-carotene, curcumin, chlorophyll and carmine from 40% to 62% on wool fabric without change in both washing and light fastness properties (Liakopoulou et al 1998, Tsatsaroni et al 1995, Tsatsaroni et al 1998).

Mangovskha (2001) inferred that protease enzyme called *Novolan L* on the wool yarn can improve the shrink resistance of the garments made of them. He also found that chlorine and enzyme treated yarns have higher rates of dye exhaustion and great accessibility for dyes than untreated and enzyme treated yarns. De La Maza et al (1997a) worked on dyeing of wool and wool blends in presence of an enzyme called Liposome that acts like vesicles formed by the surface-active biological lipids. He inferred that liposomes made with pure phosphatidylcholine acted as vehicles for commercial dyes in dyeing untreated samples to improve the dyeability of wool fiber. Wool has an internal aqueous domain is trapped between the lipid bilayers, in which liposome carried the dyestuff for easier diffusion (De La Maza et.al, 1997b; Marti et.al, 2001).

Finishing

Enzymes are used to improve the softness or to improve the efficiency of the subsequent finishing process either as pretreatment and enzyme-assisted finishing or bio-finishing. Selection of enzyme and the extent of enzyme treatment depends on the final product. For wool top enzyme treatment can be given to impart shrink-resistance finish and for woolen fabric, it can be given to improve the dye ability.

Enzyme assisted finishing

Wool fabric has a tendency to shrink in hot rubbing under wet condition which might be due to presence of cuticle scales. It is generally well known that felting of wool and caused by the tangle / friction between the cuticles exerted between two wool fibers.

Partial removal of cuticle layer can prevent such shortcoming. However, hydrophobic character, fiber fineness and scaly structure are the main factors behind the differential frictional effect, so these factors caused all the fibers to move towards their root direction and when mechanical action is applied (King and Bradbury, 1968; Simpson and Crawshaw 2002). Shrink proofing process can modify the fiber surface either by oxidative or reductive method and/or by the application of a polymer resin (Chen et.al, 2000).

Chlorination is commonly used to modify the scales of wool fibers in order to confer resistance to felting shrinkage. The most frequently used commercial process (chlorine/Hercosett process) consists of chlorination followed by dechlorination and polymer application (McLaren and Milligan, 1981; Ammayappan and Moses, 2007). Chlorination produces AOX by-products; these increase the effluent load and ultimately may generate toxicity in the whole food chain by being taken up by aquatic organisms.

Nowadays enzymatic treatment of woolen fabric can consider as an alternative shrink proofing process (Levene et.al, 1996). He found that, prior reducing treatment on wool fiber by sodium bisulphate, could enhance the enzyme' activity in subsequent processing on woolen materials and imparted shrink resistance. He inferred that *Esperase* has good active with least damage to wool fiber. Novolan-L enzyme treated wool tops gave yarn with less number of neps, low breaking per spindle, low co-efficient of hairiness and the final knitted woolen fabric have soft feel with good pilling performance and dimensional stability.

El Sayed et al. (2002) developed an enzyme-based anti-felting process with the objective of developing an AOX-free process. In this process, lipase enzyme in the pretreatment step, glutathione reductase in the reduction step and papain enzyme in the after treatment step are used. The lipase removed lipids from the outer surface of wool fiber; glutathione reductase reduced the disulfide bonds in wool keratin together with nicotineamide adenine dinucleotide

J
T
A
T
M

phosphate in the reduced form and papain hydrolysed and so smoothened the wool scales. Wool fabric treated with this system shown good felting resistance as compared with untreated wool, but still was inferior to that treated with the conventional chlorine/Hercosett process.

It is reported that cuticle cells of wool fiber can be removed completely by treating it with either gas chlorination or hydrogen peroxide followed by incubating the fibers with papain in presence of sodium bisulphate. This process is called CHLORZYME and PERZYME process respectively, however both are very costly processes (Karmakar 1999). Brier (2000) stated 100% enzyme based process called LANAZYM process in which wool fabric was treated with Perizym-AFW to give shrink resistance with improved whiteness, pilling behavior, dyeability and washability. Nakanishi et al. (2001) described a low temperature plasma treatment followed by enzyme treatment can remove the protruding fibers from the surface of the fabric for increasing its softness.

Cortez et.al, (2004) applied a microbial transglutaminase isolated from *strptoverialium mobaraense* to wool fabric either alone or following a protease treatment in order to increase the strength of woolen fabric (25% increase compared to a control). This improvement in strength indicated that transglutaminase can remediated the negative effects of proteolytic treatments in terms of loss in fiber strength, by forming chemical bonding between newly formed functional groups, through crosslinking without impairing the texture of the fabric. (Mcderitt and Wrinkler, 1998; Ogawa.M et.al, 2002).

El.Sayed et.al (2001) found that shrink-resistance of wool tops and woven fabrics have been enhanced by lipase/sodium monoperoxyphthalate/sodium sulphite based pretreatment. IR spectroscopy and XPS showed that the bunte salt together with low concentrations of cystine monoxide and cystine dioxide are formed in the reaction and SEM pictures shown the complete absence of wool scales. They also proposed the mechanism for shrink resistance imparted by

this enzyme combination. Proteolytic enzyme along with a haloperoxidase (together with a hydrogen peroxide source and a halide source) on wool used to improve its luster and whiteness index due to removal of scales as well as coloring matter (Lanatto et.al, 2005).

Handle modification

Softness plays an important role in the selection criteria of a textile product. In order to reduce prickleness and enhancement of softness and luster, woolen textiles generally treated with enzymes as per their end-uses. In most of the enzyme treatments, partial descaling of wool is carried out in order to improve the handle of woolen products (Levene et.al, 1995). Sawada et.al (2001) found that that anti-felting property and tensile strength of protease enzyme treated wool fabrics in a reverse micellular system is superior to conventional scoured wool fabric.

J
T
A
T
M
Kondo et.al (2001) inferred that wool fibers treated with potassium permanganate in presence of ammonium sulphate, acetic acid and sodium bisulphate and subsequent proteolytic enzyme treatment gave good descaling and so shown better softness than bleached ones. El Sayed and coworkers (2002) developed an enzyme-based wool felt-proofing process in which glutathione reductase used as a catalyst for reducing the disulphide bonds (cystine) together with nicotine amide adenine dinucleotide phosphate (NADPH) in the reduced form. Successive cellulase and protease enzyme treatment on wool/cotton blended fabric can improve its handle due to improvement in moisture regain, drape ability, crease recovery angle, however it reduces the tearing strength (Moses and Ammayappan 2008).

Levene et.al, found that a chlorination pretreatment followed by an alkaline protease treatment on wool fiber made wool fiber with enhanced luster. The handle of the product fiber can be retained in the post softening treatment (1995). Cardamone et.al, (2004) inferred that pretreatment of woven and knitted wool

fabric of various weights with peroxy carboximide, ruptured peptide linkages and cystine disulphide cross-linkages through hydrolysis and oxidation reaction and further proteolytic enzyme treatment biopolishes and controls the shrinkage without appreciable loss in strength and elastic recovery.

Pretreatment for polymer finishing

Cuticle scale and lipid layer on the external surface of wool fiber hinders the performance of final end-products like suiting, shawl and hosiery, and so processors prefer either pretreatments or polymer finishing or both for the improvement of its properties (King and Bradbury 1968). Among the pretreatments, bio-finishing of wool using enzymes is used to impart softening as well as shrink-resistant (Shridhar et.al, 1995; Ammayappan, 2008). The proteolytic enzyme pre-treatment increased the number of acidic groups on the wool surface, which enhanced the hydrophilicity of wool fiber; while lipolytic enzyme treatment removed the hydrophobic barrier on the wool surface, which resulted in chemical homogeneity of the scale surface and also increased surface free energy of wool fiber. This modification of the wool fiber is providing the driving force for the uniform and better spreading and adhesion of finishing chemicals on the surface of fabric (Ammayappan and Moses, 2010a).

Proteolytic / lipolytic enzyme pre-treatment followed by different chemical finishing can impart a broad range of handle properties. It is also observed that physical and handle properties of the wool based blended fabric could be improved by successive treatment with cellulase and protease enzyme followed by finishing with cationic softener or silicone softener (Ammayappan and Moses 2010b; Ammayappan, 2008). It is also found that prior enzyme treatment on woolen materials also improves the performance like wrinkle recovery, antimicrobial activity, softening and shrink resistant properties due to better encapsulation of wool fiber than untreated ones.

Protease-treatment using Savinase 16.0L Ex followed by combination of polyurethane based softener and micro polysiloxane emulsion finishing imparted shrink-resist and softening finishing, while cellulase enzyme treatment followed by β -Cyclodextrin+Finish-VLF+Sanitized-9919 combination finishing imparted antimicrobial and shrink-resist finishing on the wool/cotton blend fabric. It is inferred that enzyme pretreatment had potential applications on woolen textiles as per consumer needs for the development of multi-functional finished products (Ammayappan et.al, 2011)

FUTURE APPLICATIONS OF ENZYMES IN WOOL PROCESSING

Enzymatic processes for cotton are already well established and considered as environmentally acceptable process since they could be easily adopted on equipment already existed in textile processing units. The composite nature and ease of accessibility of wool fiber complicate the control of the enzyme catalytic activity on the fiber surface and so enzymatic processes using proteases still not met with extensive commercial acceptability because of excessive losses of weight and strength. Therefore, reaction control plays an important role in the wool finishing because of the possibility of enzymes diffusing into and damages the wool fiber. Hence technology has to be developed for the application of suitable enzymes on woolen material, through enzyme pretreatment or enzyme-assisted processing or bio-finishing which can improve or facilitate the performance of final products.

REFERENCES

- Ammayappan, L., 2008. Study on improvement in aesthetic properties of woolen products by different chemical finishes. *Ph.D., Thesis*, Anna University, Chennai.
- Ammayappan, L., and Gupta, N.P., 2011. A study on the effect of enzymatic pretreatment on physio-chemical and

- mechanical properties of woolen yarn, *Manmade Textiles in India*, 54(7):244-248
- Ammayappan, L., and J. Jeyakodi Moses, 2010a, Study on improvement in handle properties of wool/cotton union fabric by enzyme treatment and subsequent polysiloxane-based combination finishing, *Asian Journal of Textile*, 1 (1): 1-13.
- Ammayappan, L., and Jeyakodi Moses, J. 2010b, Study on physical and handle properties of wool/cotton union fabric treated with enzymes and different pre-polymer finishing chemicals, *Current Chemical Research*, 1(1): 19-25
- Ammayappan, L., and Jeyakodi Moses, J., 2007. Functional finishes for woolen textiles, *The Indian Textile Journal*, 118(1):25-32
- Ammayappan, L., J. Jeyakodi Moses, K. Asok Senthil, A. S. M. Raja and Lam K. C. Jimmy, 2011, Performance properties of multi-functional finishes on the enzyme-pretreated wool/cotton blend fabrics, *Textile Coloration and Finishing*, 23 (1): 1-9
- Ammayappan, L., 2009, Quality improvement of woolen products through chemical finishing techniques, *Wool Technology*, Eds: Karim, S.A., Shakyawar, D.B. and Anil Joshi, M/s Agrotech Publishing Academy, Udaipur, India, 349-363
- Ammayappan, L., Nayak, L.K., Ray, D.P., and Basu, G., 2012, Role of quality attributes of Indian wool in performance of woolen product: Present status and Future perspectives -A review, *Agriculture Reviews*, 33 (1): 37 – 45
- Anon, 1980. *Final report of the PL 480 project: Evaluation of the characteristics processing performance and end use suitability of various Indian wools*, Wool Research Association, Mumbai.
- Breir, R., 2000. Lanazym process: Purely enzymatic anti-felt finishing of wool, *Melliand-Textilberichte*. 123: 49-62
- Cardamonme, M., 2002. Proteolytic activity of *Aspergillus flavus* on wool, *AATCC review*, 2(5):30-35
- Cavaco-Paulo, A., 1998. Processing Textile Fibres with Enzymes: An overview, *ACS Symposium Series*, 687:180–189.
- Cavaco-Paulo, A., and Gübitz, G.M., 2003. *Textile processing with enzymes*, 1st Edition, Wood head Pub., Ltd., Cambridge, UK
- Cegarra, J., Gacén, J., Cayuela, D. and Bernades, A., 1995. Wool bleaching with hydrogen peroxide in the presence of enzymes. *Tintoria*. 92 (1): 32-36
- Cegarra, J., Riva, A., Gacén, J., and Naik, A., 1992. Influence of enzymatic treatments on wool dyeing, *Tintoria*, 89(4): 64-67
- Chen, Q.H., Au, K.F., Yuen, C.M.W., and Yeung, K.W., 2000. Development of wool shrink proofing, *Textile Asia*, 31(4), 38-43.
- Cortez, J., Bonner, P.L.R., and Griffin, M.R., 2004. Application of transglutaminases in the modification of wool textile, *Enzyme and Microbial Technology*, 34:64-72
- De La Maza, A., Coderch, L., Parra, J.L., and Marti, M., 1997a. Multi lamellar Liposomes including cholesterol as carrier of a 1:2 metal complex dye in wool dyeing, *Textile Research Journal*, 67(5):325-333.
- De La Maza, A., Coderch, L., Serra, S. and Parra, J.L., 1997b. Multilamellar Liposomes including cholesterol as carrier of a 1:2 metal complex dye in wool dyeing, *Journal for Society for Dyers and Colorists*, 113(5/6) :165-169
- Devlin, T.M., 1997. *Textbook of Biochemistry*, 4th Edition, John Wiley & Sons Publications, New York, pp. 127-178.
- El Sayed, H., Hamed, R.R., Kantouch, A., Heine, E., and Höcker, H., 2002. Enzyme wool enzyme-based felt proofing of wool, *AATCC Review*, 2(1): 25-28
- El-Sayed, H., Kantouch, A., Heine, E., and Höcker, H., 2001. Developing a zero-AOX shrink-resist process for wool, Part-I: Preliminary results, *Colouration Technology*, 117(4): 234-238.
- Heine E. 1991. *Fundamental research on the action of enzymes on wool*. PhD Thesis. Reinisch-Westfaelish Technischen Hochschule.

J
T
A
T
M

- Heine E. and Hocker H., 1995. Enzyme treatments for wool and cotton, *Review of Progress in Coloration*, 25: 57-63.
- Heine, E., Hollfelder, B., Lorenz, W., Thomas, H., Wortmann, G., and Höcker, H., 1998. Enzyme applications in fiber processing, Chapter 23: Enzymes for wool fiber modification, ACS Symposium Series, 687: pp 279–293
- Heine, E., Ruers, A., and Hocker, H., 2000, Enzymatic degradation of vegetable residues in wool, *DWI reports*, 123:475-479
- Jovancic, P., and Jovic, D., 2001. Shrinkage properties of peroxide-wool-biopolymer treated wool, *Textile Research Journal*, 71 (11):948-953
- Kantouch A., Raslan W.M. and El-Sayed H., 2005. Effect of lipase pretreatment on the dye ability of wool fabric, *Journal of Natural Fibers*, 2: 35-48.
- Karmakar, S.R., 1999. *Chemical technology in the pre-treatment processes of textiles, Chapter 15: Application of biotechnology in the pre-treatment processes of textiles*, Elsevier Pub., London, 12: 418-440
- King, N.L.R., and Bradbury, J.H., 1968. The chemical composition of wool. V. The epicuticle. *Australian Journal of Biological Science*, 21:375–384.
- Kirk-Othmer, 1971. *Encyclopedia of Chemical Technology*, John Wiley & Sons, New York, Vol 9, Third Edition, pp.173-225.
- Kondo, T., Sakai, C., and Karakawa, T., The process for modifying animal fibers, *Eur.Pat. Appl.*, 16pp, EP 134267 A1 850320.
- Lantto, R., Heine, E., Freddi, G., Lappalainen, A., Oinonen A.M., Paavola M.L. N., and Buchert, J., 2005. Enzymatic modification of wool with tyrosinase and peroxidase, *Journal of the Textile Institute*, 96 (2): 109-116
- Levene, R., 1997. Enzyme-enhanced bleaching of wool, *Journal for Society for Dyers and Colorists*, 113(7/8): 206-210.
- Levene, R., Cohen, Y., and Barkai, D., 1996. Applying protease to confer improved shrink resistance to wool, *Journal for Society for Dyers and Colorists*, 112(1):6-10
- Levene, R. and Shakkour, G., 1995. Wool fibers of enhanced luster obtained by enzymatic descaling, *Journal for Society for Dyers and Colorists*, 111(11): 352-359
- Liako poulou-kyriakides, M., Tratsaroni, E., Laderros, P., and Georgiadon, K., 1998. Dyeing of cotton and wool fibers with pigments from Crocus Sativus- Effect of enzymatic treatment, *Dyes and Pigments*, 36(3):215-221
- Maclaren, J.A., and Milligan, B., 1981. *Wool Science: The chemical reactivity of the wool fiber*, Science Press, Marrickville, Australia.
- MaGraw-Hill, 1971. *Encyclopedia of Science and Technology*, 3rd edition, MaGraw-Hill Book Company, New York.
- Mall, J.K., Sims P., and Carr C.M., 2002. Surface chemical analysis of lipase enzyme treatments on wool and mohair, *Journal of the Textile Institute*, 93: 43–51.
- Mangovska, B., 2001. Dyeing properties of chlorine and enzyme treated wool, *Vlanka-Textil*, 8(4): 257-262
- Marti, M., De La Maza, A., Parra, J.L., and Coderch, L., 2001. Dyeing wool at low temperatures: New method using Liposomes, *Textile Research Journal*, 71(8):678-682
- Mcderitt, J.P., and Wrinkler, J., 1998. *Novo Nordisk Brochem*, 28: 6051033-161824
- Monlleo, D., Julia, M., Pinazo, A., Erra, P., 1994. Use of lipases for wool modification, *Melliand Text*, 5: 402–405
- Moses, J.J., and Ammayappan, L. 2008, Effect of silicone and urethane finishing treatment on performance properties of enzyme treated wool/cotton union fabric, *Journal of the Textile Association*, 69(2):68-74.
- Nakanishi, T., and Iwasaki, K., Shrink proofing method for animal hair fiber product, *Jpn. Kokai Tokkyo*, 4pp, JP 04327274 A2 921116
- Nierstrasz V.A., and Warmoeskerken M.M.C.G., 2003. *Process engineering and industrial enzyme applications*,

- Cavaco P.A., and Gubiz G.M (Eds.), Woodhead Publishing Limited; Cambridge, 120-134.
- Nolte H., Bishop D.P. and Hocker H., 1996. Effects of Proteolytic and Lipolytic Enzymes on Untreated and Shrink-resistant wool, *Journal of the Textile Institute*, 87:212-226.
- Ogawa.M., Ito, N., and Seguro, K., 2002. Japanese P 03213574.
- Pailthorpe, M.T., 1992. *The theoretical basis for wool dyeing*. In: *Wool Dyeing* (Ed. D.M.Lewis), Society of Dyers and Colourists, Bradford, UK, pp.52-87
- Pardeshi,P.D., Paul, R., and Manjrekar,S.G., 2002. Wool processing,- Challenges and prospects, *Asian Textile Journal*, 11(4):52-57
- Peters.R.H, 1967.*Textile Chemistry*, Vol 2, Elsevier Pub. Co., London.
- Riva A, Algaba J and Prieto R, 2002. Dyeing kinetics of wool fabrics pretreated with a protease, *Colouration Technology*, 118(2): 59-63
- Riva A., Cegarra, J., and Prieto, R., 1993. The role of an enzyme in reducing wool shrinkage', *Journal of Society for Dyers and Colourists*, 109(5/6):210-213
- Sawada, K., and Ueda, N., 2001. Enzyme processing of textiles in reverse micellar solution, *Journal of Biotechnology*, 89:263-269
- Sedelnik, N., 1993. Biotechnology to remove vegetable impurities from wool, *Przegląd Włokienniczy*, 47(7): 178-181.
- Shan,Y., Hua, Y.K., and Zhu, R.Y., 2001. Research on wool bleaching with hydrogen peroxide and catalyzing with enzyme, *Journal of Tianjin Institute of Textile Science and Technology*, 20(1):14-17
- Shen, J., Bishop, D.P., Heine, E., and Hollfelder. B., 1993. Some factors affecting the control of proteolytic enzyme reactions on wool, *Journal of the Textile Institute*. 90 (3): 404-408
- Shenai.V.A, 2002. Wool-enzyme reaction, *The Indian Textile Journal*, 112(11):19-21
- Shridhar, V.C., S. Khan and R.D. Mehta, 1995. Effects of biofinishing on cotton /wool blended fabrics, *Textile Research Journal*, 65:564-569.
- Shukla S.R., 2001. Environment friendly processing of protein fibers, *Indian Journal of Fibre and Textile Research*, 26(2):116-124.
- Simpson W.S. and Crawshaw G., 2005. *Wool: Science and Technology*, Woodhead Publication Ltd., Cambridge, UK
- Tsatsaroni E., and Kyriakides M.L., 1995. Effect of enzymatic pretreatment on the dyeing of cotton and wool fibers with natural dyes. *Dyes and Pigments*. 29 (3):203-209.
- Tsatsaroni E., Kyriakides M.L., and Eleftheriads. I., 1998. Comparative study of dyeing of properties of two natural pigments-Effects of enzymes and proteins. *Dyes and Pigments*. 37(4):307-315.
- Walawska, A., Rubkki E., and Filipowska B., 2006. Physicochemical changes on wool surface after an enzymatic treatment, *Progress in Colloidal Polymer and Science*, 132:131-137.
- West, E.S., and Todd,W.R., 1961. *Biochemistry*, 3rd Edition, The Macmillan Company, New York, pp.373-436.
- West, E.S., and Todd, W.R., 1961. *Biochemistry*, The MacMillan Company, New York, 3rd Edition, pp.373-436
- Wojciehowska. E., Wlochowicz. M.R.A., Wysocki, M., and Birczynska. A.W., 2004. The use of Fourier transform-infrared and Raman spectroscopy for the investigation of structural changes in wool after enzymatic treatment. *Journal of Molecular Structure*. 704:315-321.
- Yoon, N.S., Lim, Y.J., Tahara, M., and Takagishi, T., 1996. Mechanical and dyeing properties of wool and cotton fabrics treated with low temperature plasma and enzyme, *Textile Research Journal*, 66(5):329-336.
- Zubay, G.I., Parson, W.W., and Vance, D.E., 1995. *Principles of Biochemistry*, Wm.C.Brown Publications, Oxford, pp.136-159.