Review of Literature

2. REVIEW OF LITERATURE

The literature pertaining to the study is viewed under the following heads:

2.1. Textile Wet Processing Industry and Environment

2.2. Importance of Cotton and Lycra Cotton

2.3. Weft knitting

2.4. Role of Pretreatment

2.5. Enzymes for Pretreatment

2.6. Bio Polishing

2.1. TEXTILE WET PROCESSING INDUSTRY AND ENVIRONMENT

The Indian Textile Industry is an independent industry holding a significant status in global trade. The textile sector accounts for nearly 14% of the total industrial output and about 30% of the total export. It is the largest industry in terms of employment economy and is expected to generate 12 million new jobs by 2010. As a result of various initiatives taken by the government, there has been new investment of Rs.50,000 crores in the textile industry in the last five years. Nine textile major establishments have invested Rs.2,600 crores and plan to invest another Rs.6,400 crores. Further, India's cotton production increased by 57% over the last five years and 3 million additional spindles and 30,000 shuttle-less looms have been installed.

Forecast till 2010 for textiles by the government along with the Industry and Export Promotion Councils, is to attain double the GDP and the export is likely to attain US$ 85 billion. The industry has the potential of attaining US$34 billion export earnings by the year 2010 - http://ezinearticles.com/?Textile-Industry-in-India&id=37384.

Textile wet processing is a process in which the fabric is treated with a liquid for example bleaching, shrinking and liquid colour dyes. Wet processing of textile materials require large quantities of energy and water with various reactions at elevated temperatures to transfer mass from the processing liquid medium to the surfaces of the textile materials or vice versa and are dependent on time and temperature. The homogeneity of chemical processing of textiles requires an environment that is highly water intensive as it consumes large volumes of good quality water. Water has to perform multiple activities in the industrial operations and it is the only economical process medium to conduct textile chemical processes. There is no substitute or alternative for water and is being consumed in large quantities in the textile processing industry. Today cost estimations include cost for water procurement, softening and demineralization and effluent treatment. It is therefore important to control the quality of water and its utilization for economy, states Shukla (2005).

A large number of chemicals of diverse nature are involved in processing and thus the effluents pose a definite environmental threat. Huge quantities of complex chemicals are used at different processing stages in textile processing. The textile industry has used upto 600 chemicals in production, from raw material to disposal and is generally regarded among the most polluting industries. Auxiliary chemicals added into the bath increase the total organic carbon and the chemical oxygen demand values of the effluents. Upon neutralization of the highly alkaline baths, large amounts of salts are produced. All the recent regulations have forced the processor to seriously look at the production process, the chemicals being used; dye manufacturers to look at the dyes that are being made and auxiliary manufacturers contemplate a change in the chemicals being produced, review Alaton *et al.* (2006).

Jaipura *et al.* (2004), narrate that the textile effluents contain both suspended and soluble organic impurities and have high biological oxygen demand (BOD) and chemical oxygen demand (COD). Chemical reducing agents, biological liable substances and surface active agents present in the toxic waste waters, deplete the oxygen of the receiving waters leading to environmental degradation. The unused materials from these processing operations are discharged as wastewater that are high in BOD, COD, pH, temperature, colour, odour, turbidity and toxic chemicals. The direct discharge of this waste water on water bodies like streams and rivers pollute the water and affect the flora and fauna, expresses Nayak (2006).

The BOD and COD load determines the degradability of various chemicals like surfactants which are present in the wetting oils, detergents and fabric softeners. The potential of biodegradability of a product is expressed in terms of COD to BOD. The ratio of 1:1 indicates that a chemical completely degrades in 5 days. As the ratio increases the biodegradability decreases. The high COD:BOD ratio in chemicals are problematic due to their inferior biodegradability. The ratios up to 5:1 are considered satisfactory whereas those possessing the ratios above this limit should be avoided due to their extremely low biodegradability. A surfactant has a chemical structure, namely cationic, anionic or nonionic, where molecules which are hydrophilic (affinity to water) and those which are lipophilic (affinity to fats and oils) are combined. The aquatic toxicity is related to the chemical structure and the hydrophilic-lipophilic balance HLB, of the surfactant. The hardness of the water used also contributes to the aquatic toxicity of the surfactant. The nonionic surfactants present in the concentration range of 0.1-1.0 ppm are known to kill the fish, explicates Shukla (2006).

Some of the dyes and colouring impurities present in the water prevent the penetration of light into the water hampering the photosynthetic reactions carried out by microorganisms. The harmful pollutants will make water unfit for use and also destroy the vegetation and crops in the place of discharge proving to be fatal to the invertebrate life in the water. The effluent must be decolourized, harmful chemicals converted to harmless ones, before discharging it into the environment, point out Warke and Chandratre (2003). After any wet process, the fabric may be passed through drying machines and stenter frames or cured by heating in ovens. This results in the vaporization of the organic compounds into high molecular weight volatile organic compounds (VOCs), which take the form of visible smoke and invisible but objectionable odour, express Sarkar *et al.* (2004).

Ecological or environmental problems have become global in character and there is an urgent need worldwide to tackle these problems. Ecological balance of nature is threatened by increasing environmental pollution due to rapid industrialization in the world. Textile industry being one of the largest industries, had gained attention towards pollution of water and air caused by textile mills and allied industries like dye and dyestuff industries. As the world slowly awakens to the damaging effects of some of the chemicals that were synthesized by humans, ecology and pollution have become one of the main focus issues. Environmental protection and production of quality textiles of international standards are two serious challenges before textile wet processors. Some of the major aims of the textile processing industry are to minimize the pollution of water and atmosphere during production below specified limits, to reduce the usage of harmful chemicals and to control the waste water discharge to the possible extent, emphasize Prabu and Arputharaj (2003).

The textile processing industry consumes large amount of water in its varied processing operations namely as solvent for processing chemicals and as a washing and rinsing medium. Great attention is directed towards the treatment and conditioning of water prior to processing. The growing scarcity of water is accompanied by deteriorating water quality due to increasing discharges of waste, sewage and effluents from domestic, industrial and agricultural sources and saline intrusion, report Menezes and Desai (2004). Water is the most important natural resource without which life cannot exist and industry cannot operate. It is therefore important to control the quality of water and its utilization for economy.

Greater discipline in surface and ground water abstraction and waste water discharge is the key to fresh water conservation and utilization. Good water management is a must due to lack of good water quality, more stringent demands and the increasing water cost, points out Shroff (2004).

Tirupur, an industrial hub for the knitwear sector, and one of the most important textile export centres of India, is currently facing a serve crisis due to environmental pollution and the High Court has issued immediate closure of the polluting units which has not implemented the zero discharge system. In addition the verdict of the court, based on 'Polluter's Pay Policy', ruled that the polluting industries pay Rs.55.6 crores for cleaning up the water bodies and a sum of Rs.24 crores to the farmers towards 'Loss of Ecology'. Moreover, The Tamil Nadu Government Order No.213, rules that no industry generating potentially hazardous waste can exist within 5km radius from the natural water resources. This means that all the dyeing and bleaching units which are within the 5km radius from the natural water resources come under the red category as they produce hazardous waste. Hence steps are being taken by the Government to restrict the production of potentially hazardous waste - http://sify.com/finance/supreme-court-imposes-rs-56-cr-fine-on-tirupur-industrialists -news-editors-picks-jkikab gdfjh.html.

Due to the pollution by textile wet processing effluent, the ground water system has been totally affected, soil fertility is partially or totally lost, surface water ways and ponds are completely polluted, agricultural production in the down stream areas are severely affected, and the extent of health hazards caused to the public due to ground water contamination and through the food web is unknown. The restoration of the environment to the earlier state is totally unachievable due to non-biodegradability of the dye stuff in the environment. Furthur, the salt in the effluent has also affected the soil fertility and the ability of the biota to grow and enrich the soil. Thus the implementation of the zero discharge system has become very essential for the safety and protection of the environment - http://environsciences.com/ARTICLES/Tirupurneed%20for%20government%20aid.pdf.

Zero discharge is the treatment of all the incoming effluent and leave nothing for discharge into rivers or water bodies. This may not be practically feasible as some waste is always generated in the treatment process. Therefore the main aim is to recover usable materials such as water and salt from the effluent and minimize the generation of waste so that it can be safely used in-site without the need for discharge into the environment - http:// www.scribd.com/doc/10210123/Zero-Discharge-Treatment-Options-for-Textile-Effluent.

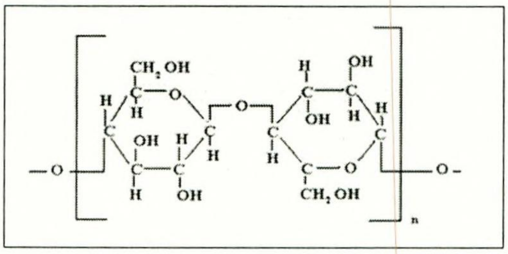
When the environmental pollution has attained its critical level that it could affect the economic progress of the country, only then the environmental concerns are properly addressed. It is essential to underline the importance of the environmental conditions on which we thrive since restoration of economy has multitude of ways, while restoration of environmental conditions has only one way –stopping pollution altogether and letting the natural curing process to get underway. Thus there is an immediate need for this industry to adopt cleaner production technologies through waste minimization, adoption of newer technologies and carefully planning resource utilization in processing units. Concept of Clean Technologies are defined as product technologies or manufacturing processes that reduce pollution or waste, energy use or material use in comparison to the technologies that they replace. The textile industry should focus on these technologies to prevent pollution while reducing costs, material consumption or improve product quality. One of the technologies that could be developed and adopted by textile industries are enzyme technology, explain Nayak (2006). The contemporary standards for environment protection are the reason behind the rising interest in the development and application of nature-friendly methods, such as enzymes, for chemical processing of textile materials, reiterate Todorova *et al.* (2007).

2.2. IMPORTANCE OF COTTON AND LYCRA COTTON

Cotton accounts for almost 50% of the worldwide consumption of textile fibre. China, the United States, the Russian Federation, India and Japan are the major cotton-consuming countries. Consumption is measured by the amount of raw cotton fibre purchased and used to manufacture textile materials. Worldwide cotton production is annually about 80 to 90 million bales (17.4 to 19.6 billion kg). China, the United States, India, Pakistan and Uzbekistan are the major cotton-producing countries, accounting for over 70% of world cotton production. The rest is produced by about 75 other countries. Raw cotton is exported from about 57 countries and cotton textiles from about 65 countries. Many countries emphasize domestic production to reduce their reliance on imports - http://www.indiaonestop.com/export-cotton.htm

Cotton is a natural fibre which is soft, versatile and strong that makes it ideal for clothing and other wear. Cotton is a natural resource that is fully renewable. Cotton is cool in warm climates, wrinkles easily, absorbs perspiration, easy to wash, with good colour retention resulting in soft, comfortable, breathable wear. Cotton clothing is extremely popular and a majority of people own some type of clothing that is either totally made of cotton, or contains at least some percentage of cotton, describe Gohl and Vilensky (2003).

CHEMICAL STRUCTURE OF COTTON FIBRE



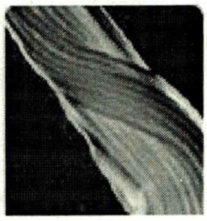
The chemical composition of cotton, when picked, is about 95 per cent cellulose; in finished fabrics it is 99 per cent cellulose. Cotton contains carbon, hydrogen, and oxygen with reactive hydroxyl groups. Glucose is the basic unit of the cellulose molecule. Cotton may have as many as 10,000 glucose monomers per molecule. The molecular chains are arranged in long spiral linear chains within the fibre. The strength of a fibre is directly related to chain length. Hydrogen bonding occurs between cellulose chains in a cotton fibre. There are three hydroxyl groups that protrude from the ring formed by one oxygen and five carbon atoms. These groups are polar meaning the electrons surrounding the atoms are not evenly distributed. The hydrogen atoms of the hydroxyl group are attracted to many of the oxygen atoms of the cellulose. This attraction is called hydrogen bonding. The bonding of hydrogen's within the ordered regions of the fibrils causes the molecules to draw closer to each other which increases the strength of the fibre. Hydrogen bonding also aids in moisture absorption. Cotton ranks among the most absorbent fibres because of Hydrogen bonding which contributes to cotton's comfort. The chemical reactivity of cellulose is related to the hydroxyl groups of the glucose unit. Moisture, dyes, and many finishes cause these groups to readily react. Chemicals like chlorine bleaches attack the oxygen atom between or within the two ring units breaking the molecular chain of the cellulose, explains Ghosh (2004).

The chemical composition of cotton fibre consists of 95 per cent cellulose, 1.3 per cent protein, 1.2 per cent ash, 0.6 per cent wax, 0.3 per cent sugar, 0.8 per cent organic acids, and other chemical compounds that make up 3.1 per cent. The non-cellulose chemicals of cotton which consist of protein, ash, wax, sugar and organic acids, are usually located in the cuticle of the fibre. Cotton wax which is primarily long chains of fatty acids and alcohols, is found on the outer surface of the fibre. The cotton wax serves as a protective barrier for the cotton fibre. Sugar comes from two sources namely plant sugar and sugar from insects. The insect sugars can cause stickiness, which can lead to problems in the textile mills. Organic acids made up of malic acid and citric acid, are found in the cotton fibre as metabolic residues. After removing all the non cellulose chemicals with selective solvents, the cotton fibre is approximately ninety-nine per cent cellulose. The adhesive quality of the fibre due to the presence of the waxes, combined with its natural twist contributes to making cotton an excellent fibre for spinning into yarn, enumerate Kalpan (2001).

Of the many varieties of cotton available, the most popular varieties of cotton in recent times are Organic Cotton and Bt Cotton. Cotton grown without the harmful pesticides and chemicals and manufactured into clothing without exposure to environmentally harmful chemicals is termed as Organic Cotton. Bt cotton, a transgenic plant, produces an insect controlling prote in Cry1A(c),the gene for which has been derived from the naturally occurring bacterium, Bacillus thuringiensis subsp. kurstaki (B.t.k.). The cotton hybrids containing Bt gene produces its own toxin for bollworm attack thus significantly reducing chemical insecticide use and providing a major benefit to cotton growers and the environment - http://www.envfor.nic.in/divisions/ csurv/btcotton/bgnote.pdf

The area of Bt cotton plantations in India — 3.44 million hectares — is thirty times larger than it was in 2002. In 2005, planting Bt cotton cut the use of pesticides by 42 per cent, yield losses went down and net returns increased by US$373 per hectare compared to non-Bt crops. Organic cotton is more environment friendly, better for the health of the community and for the local economy than GM cotton, according to a study by the Centre for Sustainable Agriculture in Andhra Pradesh - http://www.i-sisorg.uk/ OCBBCI.php.

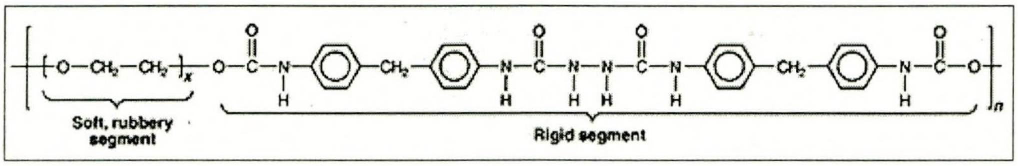
Depending on the weight, thickness and the finish, cotton materials may be classified in many ways namely cotton twill, canton cotton, French terry cotton, Egyptian cotton, honeycomb cotton and Oxford chambray. Regardless of the type of cotton present in clothing, one can always tell that it is cotton as it has a unique feeling and texture. Cotton material is great for sweaters, underwear, pajamas, shirts, shorts, pants and practically anything that is worn. Most people prefer cotton clothing as it is comfortable and feels good on the skin - http://EzineArticles.com/?expert=Victor_Epand



LYCRA FIBRE

Spandex, developed as an alternative to rubber, is a synthetic fibre that is light weight, soft, strong and very stretchable. It can be stretched to almost 500% of its length and has very high retractive ability. This exceptional characteristic of elasticity has earned the name elastane. Lycra is the trademark brand but it has become so popular that all the varieties of spandex are popularly referred to as Lycra - http://spandexfabric.com.

Spandex is mostly used to make sports wear and work wear and is ideal for risk involved jobs as it acts as a second skin. It gives the best fit and comfort and also prevents sagging of the garment. Spandex fibres or fabrics can be easily dyed and damage by body oils, perspiration, lotions or detergents are resisted. These fabrics are also abrasion resistant. The spandex fibre diameters range from 10 denier to 2500 denier and can be found in both, clear and opaque lustres, narrates Bhatnagar (2002).

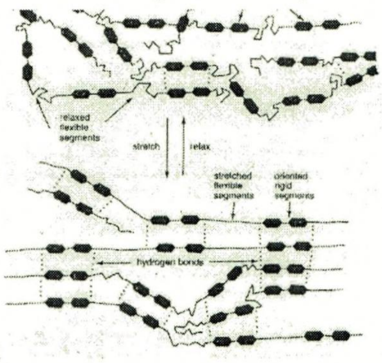


CHEMICAL STRUCTURE OF SPANDEX

Two types of pre polymers namely macro glycol and diisocyanate, are reacted to produce the spandex fibre polymer. The macro-glycol can be a polyester, polyether, polycarbonate, polycaprolactone or some combination of these. These are long chain polymers, which have hydroxyl groups (-OH) on both ends. The important feature of these molecules is that they are long and flexible. This part of the spandex fibre is responsible for its stretching characteristic. The other prepolymer used to produce spandex is a polymeric diisocyanate. This is a shorter chain polymer, which has an isocyanate (-NCO) group on both ends. The principal characteristic of this molecule is its rigidity which provides strength to the fibre. When the two types of prepolymers react, the hydroxyl groups (-OH)on the macro-glycols react with the isocyanates to form a long chain polymer by addition polymerization in the presence of a catalyst diazobicyclo[2.2.2]octane, explain Collier and Tortora (2001).

Spandex is a long-chain synthetic polymeric fibre. Soft and rubbery segments of polyester or polyether polyols allow the fibre to % stretch up to 600% and then recover to its original shape. Hard segments, usually urethanes or urethane-ureas, provide rigidity and so impart tensile strength and limit plastic flow - http://www.answers.com/topic/spandex

Unstretched and Stretched State of Spandex Polymer



Customer satisfaction is of highest importance today. To cater to their satisfaction the manufacturer must be in constant touch with the needs and requirements of the customers which results in continuous improvement and upgradation of their products using different techniques. Blended and mixture fabrics are developed using different techniques to achieve and satisfy both the manufacturer and consumer's requirements, view Awashthi and Singh (2003). Blended fabrics are made of different types of fibres twisted together, for example Polyester blended with cotton, Silk blended with wool and Ramie blended with acrylic. Mixture fabrics are developed by combining two or more different kinds of fibres or yarns for colour or textured effects or to achieve certain fabric qualities. Lycra cotton fabrics have two significant differences from all-natural fibres: a degree of stretch not present in the natural fibre and a greater resistance to wrinkling. The advantage of Lycra cotton combination is obvious. The tiny bit of synthetic added to a natural-fibre yarn means a wool-and-Lycra or cotton-and-Lycra jacket can shake off creases and still offer the warm or cool comfort that could be expected from plain wool or cotton - http://www.teonline.com /knowledge-centre/fabrics.html.

2.3. WEFT KNITTING

A variety of different materials and technologies can be used for garment production. One of the commonly used method for developing fabric is knitting technology. Knitted fabrics used for clothing production must be of high quality. Structural parameters of knitted fabrics, as well as finishing processes directly influence their mechanical and physical properties and thus are closely connected with wearing properties of knitted garments. The structure of knitted fabric is a system of yarns, bent into stitches. Integrity and friction of a yarn bent into the stitch determine the form of a knitted fabric stitch - http://www.teonline.com/knowledge-centre/industrial-knitting-process.html

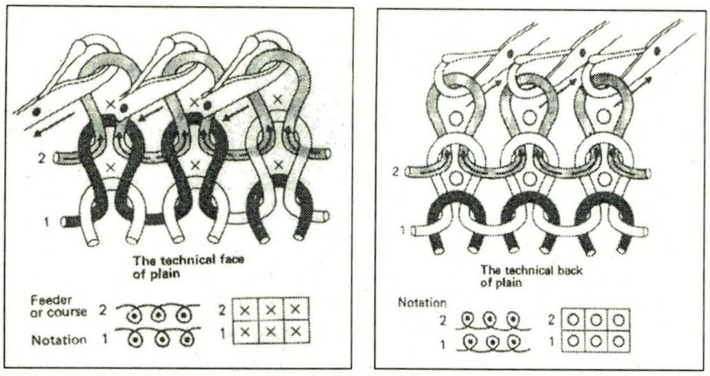
Weft knitting is a process of manufacturing fabric by the intermeshing of loops of yarns. When one loop is drawn through another loop, a stitch is formed. Weft knitting is a method of forming a fabric by knitting, in which the loops are made in a horizontal way from a single yarn and the intermeshing of loops takes place in a circular or flat form on a course-wise basis. One or more yarns (called feeds) are fed one at a time, to the multiplicity of knitting needles, placed either in a lateral or circular fashion. Most weft knitted structures come out in a tubular form or in open width, presents Ajgoankar (1998).

Weft knitting is more diverse and widely spread and accounts for one quarter of the total yardage of apparel fabric. Weft knitting machines are attractive to small manufacturers because of their versatility, relatively low capital costs, small floor space requirements, quick pattern and machine changing facilities and the potential for short production runs and low stock holding requirements of yarn and fabric.

Excellent comfort properties of weft knits have made their entry into formal wears for men and women. With the technological advancement in manufacturing of cloths and the awareness of consumers to quality, the expectations in knit goods have gone high. However, knit goods are known for their high structural sensitiveness to deformation during manufacturing process or at their end use. On usage, knitwear change their dimensions according to the body movements. They undergo either reiterated single or a double directional stretching. The value of the deformation in different parts of knitwear can reach 10% to 20%, if a deformation is large enough, a stitch form and a yarn orientation change and contact points between the stitches move, explain Mikučionienė and Laureckienė (2009).

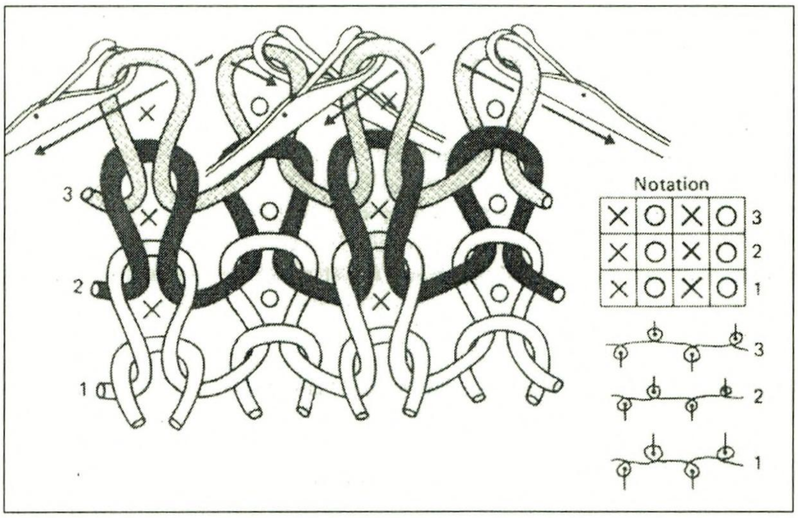
There are four basic stitches in weft knitting namely Plain-knit stitch, Rib stitch , Interlock and Purl stitch. All other stitches are variations of the above four basic structures. Plain knit, the basic form of knitting can be produced in flat knit or in tubular (or circular) form. It is also called jersey stitch or balbriggan stitch. It is the base structure of ladies hosiery, fully fashioned knitwear and single jersey fabrics. A row of latch or beard needles is arranged in a linear position on a needle plate or in a circular position on a cylinder. The side by side evenly spaced needles are moved by cams, which act on the needle butts. The spacing of the needles is called guage, gage or cut which refers to the number of needles in one and a half inches, for example, a 60 guage machine will have 40 needles per inch. The needles intermesh loops drawn to one side of the fabric, forming vertical herringbone like ribs or wales on the right side or technical face of the fabric. On the reverse side or the technical back, courses are visible as interlocking rows of opposed half circles. These fabrics have the tendency of curling up at the edges which is controlled to a level through certain finishes. If a yarn breaks, needle loops successfully unmesh leading to a structural breakdown known as laddering.

Plain knit allows the use of single or plied yarns, produces comparatively lightweight fabrics than that produced by other stitches. The production rate is higher, about 5 times more than weaving. It is inexpensive and a variety of designs may be produced including stripes, multi-coloured patterns, textured surfaces produced by raised designs and pile effects. Plain-knit fabrics stretch more in the width than in the length and as such, they are widely used for making underwear, gloves, hosiery and sweaters. Plain knit structures are the simplest and most economical weft knitted structure to produce and has a potential recovery of forty percent in width after stretching, narrates Brackenbury (2000).



TECHNICAL FACE AND TECHNICAL BACK OF PLAIN KNIT FABRICS

Rib stitch produces alternate lengthwise rows of plain and purl stitches and as such the face and back of the fabrics are similar. Rib stitch can be produced on a flat rib machine as well as circular rib machine. In the flat rib machine, one set of needles is placed opposite the other set of needles in an inverted V position. In the circular rib machine, one set of needles is placed vertically in a cylinder and the other set of needles is placed horizontally on a dial. In both the machines, one set of needles pulls the loops to the front and the other set of needles pulls the loops to the back of the fabric. Each set of needles alternately draw loops in its own direction, depending on the width of the rib desired. For instance, rib stitches can be 1x1, 2x2, 2x1, 3x1, and the like. Accordion rib is the combination of 1x1 and 2x2. As a greater amount of yarn is required for rib stitch and the rate of production is also slower, it is an expensive method of fabric construction. The fabric does not curl at the edges and as the fabric possess an excellent widthwise elasticity, it is widely used for making such clothing that needs an excellent fit such as wristbands of sleeves and waistbands of garments, underwear and socks for men and children.

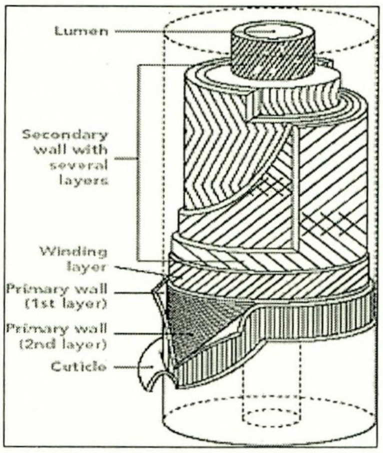


FACE AND REVERSE LOOP WALES IN 1 X 1 RIB

1x1 rib is balanced by alternate wales of face loops on each side and therefore it lies flat without curling when cut. It is expensive to produce and heavier than the plain structure and require very fine yarns for knitting. Relaxed 1x1 rib is twice the thickness and half the width of an equivalent plain fabric but has twice as much width wise recoverable stretch. A 1x1 rib normally relaxes by approximately thirty percent compared to its knitting width. Rib structures are elastic, form fitting and retain warmth than plain structures, outlines Spencer (2001).

2.4. ROLE OF PRETREATMENT

The three basic categories of wet processing are Pretreatment, Colouration and Finishing. The basic pretreatment process is a cleaning operation, using chemicals to remove the extraneous matter attached to the textile forms and to diminish its hydrophobicity, which is the most essential primary requirement for further value addition processes, says Shukla (2005). One of the most serious problems faced by the processor is reproducibility of a processed fabric as per the approved buyer's sample. It has been estimated that 60-70% of textile processing faults can be attributed to faulty pretreatment of fabrics. This is because the pretreatment process holds a key position within the finishing industry, practically every textile material has to pass through them in order to become the desired product, comment Singh and Tiwari, (2005).



COTTON FIBRE STRUCTURE

Cotton Fibre Structure: A cotton fibre is a single biological cell. The layers in the cell structure area, from the outside of the fibres to the inside, cuticle (wax, proteins and pectins: 2.5% of fibre weight and amorphous), primary wall (cellulose:2.5% of fibre weight and 30% crystallinity index), secondary wall (cellulose: 91.5% of fibre weight and 70% crystallinity index), and lumen (protoplasmic residues). Non cellulosic materials are amorphous and located in the cuticle and lumen. The cuticle forms a protective layer, shielding the cotton from environmental attacks and water penetration - www.cottoninc.com.

Waxes are very complex substances composed of high molecular weight alcohols and fatty acids in free or esterified form. They are chemically linked to cellulose or pectin or alternatively to residual proteins. Waxy materials are mainly responsible for the non absorbent characteristics of raw cotton. Waxes and pectin prevent wetting by interfering with further aqueous wet and chemical processing, points out Ismal (2008).

Non-cellulosic components are present in matured cotton fibres and in the primary cell wall, which is the outermost concentric layer that makes up the cotton fibre. The surface layers which contain liquids, waxes, pectins, organic acids, protein/nitrogenous matters, non cellulosic polysaccharides and other unidentified substances constitute approximately 10% of total fibre weight. The surface layers protect the fibre against the environment during the growth and lubricate them during yarn spinning and fabric forming. Normal cotton has contaminants which may originate from the base fibre during cultivation and from spinning preparation, spinning and knitting processes. Before hydrogen peroxide bleaching, the fabric should be free from all types of contaminants since most of these substances are hydrophobic in nature and interferes with further aqueous chemical processing, narrate Ramasamy and Kandasamy (2004).

The conventional process widely practiced is boiling with sodium hydroxide to remove such impurities and to improve the wetting and aqueous penetration of the dyeing and finishing solution. During high temperature alkali scouring, the pectinous material is hydrolyzed and loosens the fats and waxes which gets saponified as fatty acids. The fatty acids are then converted to sodium salt and removed during washing. This process is very effective as it removes the impurities and leaves the fabric with 99% cellulose content on a dry basis but generates huge amounts of alkaline waste effluents with high BOD , COD and salt content. About 75% of the organic pollutants arising from textile finishing come from the preparation of cotton goods, narrate Ramachandran and Saravanan, (2008).

Due to the non specific nature of the chemical processing not only are the impurities but also the cellulose is attacked, leading to damages in strength and other desirable fabric properties. Moreover, on the fibre level, oxidative damage may occur and is reflected in the lower degree of polymerization and decreased tensile strength. The high temperature strong alkali scouring is nonspecific and removes both the natural cotton lubricants and the manufacturing introduced lubricants. This process completely removes the natural cotton waxes which contribute to the softness of the cellulosic fabric. The increase of bath temperature means higher energy costs and can contribute to the formation of aggregates of products present in the impregnation bath, expresses Roda (2008).

Current awareness about the negative environmental impact of the textile preparatory processes, combined with increasingly strict regulations on industrial effluents have forced the textile processors to minimize the pollution load in textile chemical processes. The use of enzymes in chemical processing of textiles is gaining wider recognition because of their non-toxic, eco-friendly and bio-degradable characteristics coupled with the specificity of action. They can be safely used in a wide selection of textile processes, where conventional processes make use of extensive chemicals whose disposal into the environment leads to many problems, inform Shukla *et al.* (2005)

The term bio processing has been used to refer all textile chemical processing which are based on enzymes, eliminating use of chemicals. Bio scouring is a new concept in scouring of cellulosic material with an enzyme based formulation for efficient removal of natural impurities with minimal damage to the fibre. Enzymes are biocatalysts without which no life in plant or animal kingdom can be sustained. Their technological application can be considered as the ultimate aspect in eco-friendly concepts. As enzymes are effective over mild conditions of pH and temperatures and as they are easily biodegradable, they are no threat to the environment. The use of the gentle enzyme process replaces the need for harsh processing with sodium hydroxide as there is less contribution to the textile effluent and a softer textile product, view Etters *et al.* (2004).

The bleaching of textile cotton and its blend is mainly done by hydrogen peroxide, which is not fully eliminated after the bleaching process. The presence of peroxide left in the bleached fabrics creates severe problems to the subsequent processes. It hydrolyses the reactive dyestuffs and also leaves the dyeing process with unlevelled dyeing and shade variation. Hence critical shades and light shades require complete removal of peroxide for perfect trouble free levelled dyeing. Catalase enzymes are used as peroxide killers, explains Mahapatra (2007).

Bio preparation process decreases both effluent load and water usage that the new technology becomes economically viable. Replacement of caustic scouring of cotton substrates by Bio preparation with selected enzymes would result in lower BOD, COD, TDS, Alkalinity, Process time, Cotton Weight Loss and Harshness of Hand, focus Sundar *et al.* (2007). The application of bio auxiliaries would open a number of research opportunities in textile processing. Enzymes are the tools for development of new biotechnology based solutions for textile wet processing and finishing, remarks Menezes (2007).

2.5. ENZYMES FOR PRETREATMENT

In the recent times, with growing environment awareness, important legislation on ecotoxicological considerations have been introduced. These have imposed changes in the chemical processes and finishing methods. Hence integrated pollution control is necessary for developing eco friendly processes in the new millennium. One such tool for eco friendly processing is the use of enzymes in textile wet processing, remark Kannan and Geethamalini (2004).

The term enzyme is derived from the Greek word 'enzymos' which means 'in the cell or ferments'. Enzymes are made up of more than 250 amino acids and based on the medium for their preparation, they are classified as bacterial, pancreatic(blood, liver) and malt (germinated barley). Based on specificity, enzymes are grouped under the following classes – Oxidoreductases : oxidation, reduction reaction, Transferases – transfer of functional group, Hydrolases: hydrolysis reactions, Lyases : addition to double bond or its reverse, Isomerases: isomerization and Ligases : formation of bonds with ATP clevages, informs Rai (2004).

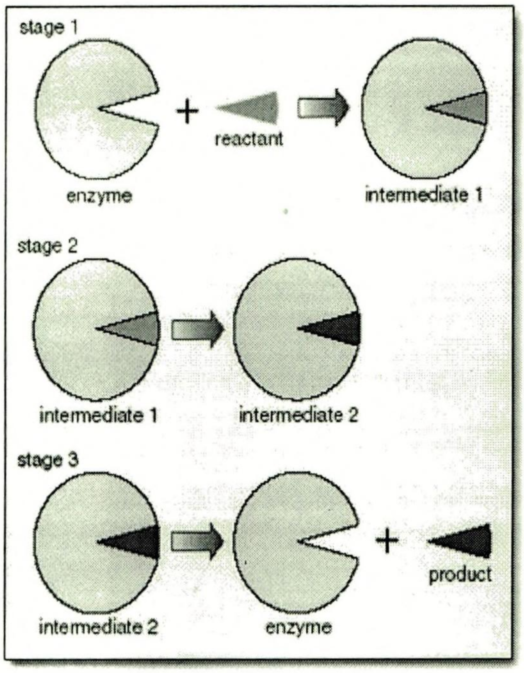
Enzymes are protein molecules that catalyze specific biochemical reactions in life processes. Their efficacy, specificity, sensitivity to control and nature to work in mild conditions serve to distinguish them from catalysts of non-biological origin. A definite three dimensional shape is essential for enzyme activity and specificity. When an enzyme is exposed to conditions different from its normal biological environment, a structural change occurs called denaturation, leading to functional ineffectiveness, highlight Singh and Goel (2004).

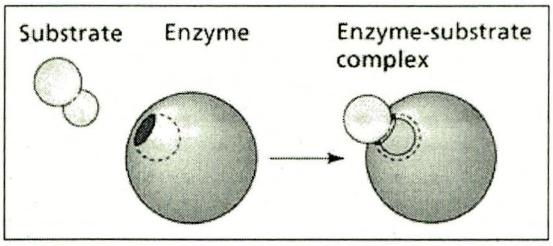
Many enzymes consist of a protein combined with a low molecular weight organic molecule called a coenzyme. The protein portion is referred to apoenzyme. When united the two form a complete enzyme identified as holoenzyme. In some cases the protein portion of the enzyme may be a metal for example, Iron in catalase enzyme. Many enzymes may require the addition of metal ions (Mg^{2+}, Mn^{2+}, Fe^{2+}, Zn^{2+}) to get activated. The metal ions function in combination with the enzyme proteins and are called inorganic coenzymes or cofactors. Sometimes the cofactors and the coenzyme are required to get the enzyme activated, explain Sunder *et al.* (2007).

The specificity of an enzyme for certain substrates and also the precise control of the catalytic activity in living cells is based on the concept of the binding sites. A protein possesses regions on its surface where small solute molecules or ions called ligands can bind reversibly. Although many ligand binding sites may be on the surface of the protein, each site has the power to bind only to a specific ligand due to the character of the site. The character of the site includes the three dimensional shape of the site, the charge character and its hydrophobicity or hydrophilicity. The character of the binding site is a function of the amino acid side chains that are brought together by the folding of the polypeptide chain - www.freshwap.net/tag/fundamentals-of-enzymology.

Apoenzyme +	**Coenzyme**	→ **Holozyme**
High molecular	Low molecular	Active system
Weight inactive	Weight inactive	
Protein	organic molecule	

Enzymes have active centers, which are the points where the substrate molecule attaches to the enzyme like a key that fits into a lock. The substrate forms a complex with the enzyme. Later the substrate molecule is converted into the end-product and the enzyme is regenerated, explain Nalankilli (1998).





Nature of Enzyme Action – Lock and Key Mechanism

Ping pong mechanism of enzymes : Enzymes activate or accelerate the rate of reactions. The active centres in the enzymes (fissures, holes, pockets, cavities or hollows) forms a complex with the substrate in lock and key fashion. The bio reaction takes place in this complex and its destruction leads to the release of the original enzyme (with altered shape) and the product. The altered enzyme binds to the second substrate releases its products and returns to its original shape. After the reaction has taken place, the enzyme is released to be re-adsorbed into another substrate surface of the substrate. This process continues until the enzyme is poisoned by a chemical bogie or inactivated by extreme temperature, pH or by other negative conditions in the processing environment, discuss Manickam and Ganeshprasad (2004).

A competitive bogie is a molecule other than that of substrate, that becomes attatched to the active site of the enzyme and prevents the enzyme from being adsorbed by the substrate. This bogie competes with the substrate for the enzyme. A non- competitive bogie is a molecule that becomes attatched to the other sites of the enzyme and causes change in the three dimensional shape of the enzyme. Hence the lock and key mechanism is inactivated and the substrate can no longer get attached to the enzyme molecule - www.ebook computer.com/Handbook_of_Enzyme_biotechnology_rapidshare -ebook.html.

Certain enzymes require metal ions as activators which stabilize the structure of the enzyme substrate complex and make the action more effective. Inhibitors are chemicals such as alkalis, antiseptics and acid liberating salts which blocks certain useful groups and inhibit enzyme activity , which may be either reversible or irreversible, narrate Moghe and Khera (2005).

There are different parameters which influence the performance of the enzymes for producing desired effects. They are as follows:

pH: pH of the bath should be maintained as per the recommendation as variation reduces the activity of the enzyme eg. Acid cellulase has maximum activity in the pH range of 4.5 to 5.5.

Temperature: The recommended temperature should be maintained in the bath otherwise adverse results may be produced.

Dosage : depends on the effect desired. Acid cellulase can be used to remove micro fibrils from the cotton surface and it can produce a peach effect on lyocell depending on the dosage.

Mechanical Action: Abrasion is a must to achieve the desired results in bio polishing; hence it is an important factor for producing the required results.

Auxiliaries : Non ionic types are most compatible with enzymes. Presence of heavy metals in the bath are not desirable as they may interfere with the activity of the enzymes, state Chand and Mishra (2000).

Novozymes from Denmark introduced a commercial pectate lyase enzyme for the bioscouring of cotton in 1999. It has been established that the pectins in native cotton fibres are present in the fibre primary wall and function as water soluble substances that bind the waxes and the proteins together in the primary wall matrix - www.novozymes.com/.

Pectate lyase enzymes act by hydrolyzing the pectins, thereby degrading the pectin-wax interface in between the wax and the primary cotton wall. The cotton waxes are further broken down by the enzyme enabling a bio scouring action to be accomplished. The reduction in the residual pectin levels in the cotton fibres are sufficient to ensure that the enzyme treated fibres exhibited good wetting ability and dyeing properties, states Holme (2009).

Mechanism of scouring with pectate lyase enzyme: Cleavage of glycosidic linkages present in pectic acid by trans elimination and deesterification of methyl esterified group present in pectic polymer backbone takes place during enzymatic scouring. Saponification of the methyl esterified group present in the pectin occur due to the usage of alkaline solution at low temperature in the enzyme treatment. The latter reaction results in the production of pectic acid which in turn would undergo trans elimination reaction in the presence of pectate lyase enzyme. The dissolution and removal of the unsaturated product formed during washing would reduce the amount of pectic substances in the primary wall and in turn destabilizes it. The destabilization of the primary wall will help the easy removal of cuticle present on it when subjected to hot soap washes and cold washes, giving required absorbency to cotton, reiterates Weddell (2002).

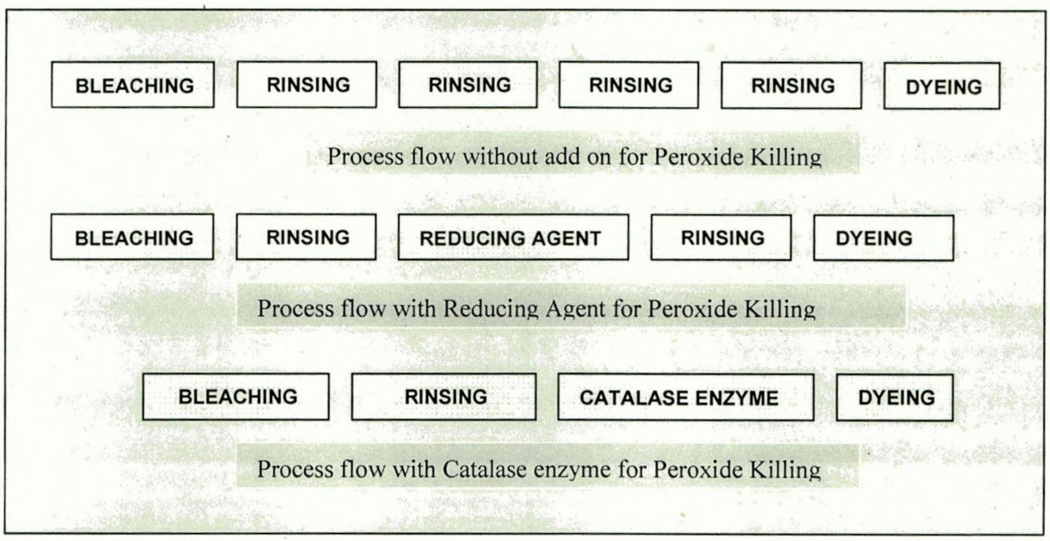
Today's textile processing industry uses a lot of Hydrogen peroxide for bleaching of greige goods before dyeing and printing. After the bleaching process, the residual peroxide in the bath needs to be removed before the fabric enters the dyeing process, as the presence of peroxide changes the dye shade and causes an uneven dyeing result. Traditionally, peroxide removal has been done using several consecutive rinses with plentiful water, or using reducing chemicals such as bisulphate to break down the peroxide. Both methods are unreliable and call for high water consumption. A more modern way to remove peroxide involves the use of catalase enzymes, which breaks down hydrogen peroxide into water and molecular oxygen. The advantage of this process is the end products are natural to the environment and do not disturb the dyeing process. The catalase enzyme is specific and does not react with anything else, and thus there is no need to remove or inactivate it. The use of catalases has been the fastest growing enzyme application in textiles in recent years, focuses Auterinen (2006).

Bleach Cleanup is a process of removing residual hydrogen peroxide prior to dyeing. The dyes sensitive to oxidation causes a shade change in the presence of residual hydrogen peroxide. Hence a peroxide killer treatment is very essential. The conventional bleach cleaning process with reducing agent involves three rinsing steps but the use of catalase enzyme reduces it to one with the effect in same dyeing bath. 1 molecule of the enzyme can convert five million molecules of hydrogen peroxide to water and oxygen in one minute, discusses Murthy (2004).

$$\text{Catalase} + 2H_2O_2 \rightarrow 2H_20 + O_2 + \text{Catalase}$$

Traces of the hydrogen peroxide present after bleaching, has to be removed to prevent oxidation effect which causes uneven dyeing. Conventionally reducing agents like sodium thiosulphate was used for removal of the peroxide remaining in the bleached goods. The traces of the reducing agents had to be removed to prevent the reduction of the dye bath which causes uneven dyeing. Use of the catalase enzyme eliminates the residual peroxide on the bleached goods and also saves water, energy and chemical besides helping in achieve uniform dyeing, express Gowda *et al.* (2004).

PROCESS FLOW USING DIFFERENT AGENTS FOR PEROXIDE KILLING



The traditional method of removing the residual hydrogen peroxide is by rinsing the fabric with water a number of times. Alternatively, a mild reducing agent may be used to neutralize the bleach. In either case, large amounts of water (upto 40 litres per kg of fabric) are required for rinsing the fabric to remove residual hydrogen peroxide. The presence of

Hydrogen peroxide in the dye bath causes decolourisation of reactive dyes which are sensitive to oxidization. Even small colour changes can render the dyed fabric commercially not acceptable due to stringent contemporary quality requirements. Catalase enzyme ensures dye shade quality when reactive dyes are used after peroxide bleaching; reduces the complexity cost and time of using reducing chemicals to neutralize residual peroxide; conserves water as the number of rinses are less and conserves energy as the enzyme works at low temperatures, report Menezes (2003).

Catalase enzyme, widely distributed in nature, is well known for its ability to catalyse the conversion of five million molecules of hydrogen peroxide to water and oxygen in one minute, with one enzyme molecule. The various advantages of using the enzyme are that there is no adverse effects on dyestuffs, no heating required, no rinsing prior to dyeing, no risk of overdosing and no formation of by products in waste water. Thus catalase enzyme can be efficiently used to reduce hydrogen peroxide instead of using a reducing agent like thiosulphite, recommend Kannan and Nityanandan (2006).

2.6 BIO POLISHING

Cotton fabric often shows harsh handle and stiff appearance. The surface of the fabrics are not smooth because of the small protruding fuzzy micro fibrils followed by pilling after wear. Treatment with cellulase enzyme eliminates the superficial micro fibrils by the controlled hydrolysis of cellulose leading to permanent improvement in fabric softness and smoothness. Cellulases are derived from both fungal and bacterial sources. Cellulases derived from the fungus Tricoderma resei is widely used in textile finishing since it gives higher yield in industrial production. Cellulases derived from Tricoderma resei contains a group of enzymes namely endoglucanases (EG), cellobiohydrolases (CBH) or exoglucanases and they act synergistically to hydolyse cellulose, inform Yadav *et al.* (2004).

The removal of cellulosic micro fibrils to improve pilling performance, soften hand and to create a smooth even surface is accomplished by the effective usage of cellulases. The final result from the partial hydrolysis of cellulose is affected by both mechanical agitation and chemical composition. These enzymes are usually incorporated into detergents to give the washed garments a smooth feel and bright outlook - www.informaworld.com/ index/795280496.pdf.

This process is particularly suitable for the pretreatment of napped, knoppy goods when there are no suitable cleaning, beating, brushing and shearing machines available. These enzymatic processes can be adopted to run in the equipment already available in the textile processing industries. The clean chemistry approaches is an advantage in comparison to the powerful alkalies, acids, oxidizers and reducers needed in traditional processes, tending to attack the textile material and as well as causing contamination in the environment, express Sinitsyn *et al.* (2005)

Once the enzyme reaction stops, residues are present only in the primary structure, while there are no chemical residues likely to affect the skin. More over, no chemical residues are present on the processed materials and the colour change of the dyed goods are minimal. The only disadvantage which is still unsolved in the practical application of the cellulase treatment are the other elements, apart from pH and temperature, like the coexisting dyes or surfactants in the treatment solution or substrate which may affect the activity of the enzyme, focuses Durai (2007).

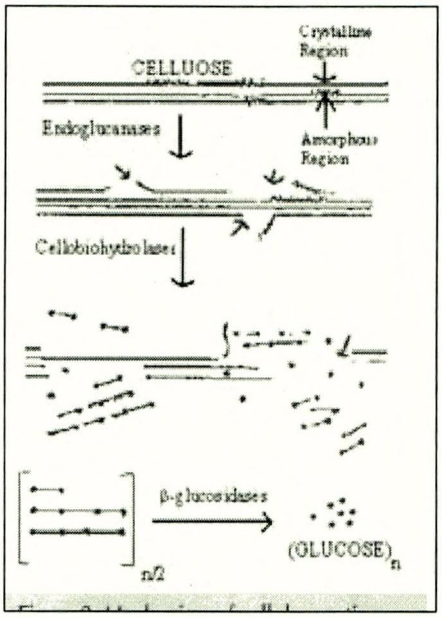
Alat (2001) recommends the following parameters for efficient bio polishing. Liquor ratio should be sufficient to allow free movement of the fabric or garment but low enough to create the required mechanical action. Conditions are similar to dyeing. Secondly the active pH range for acid cellulase enzymes are 4.5 to 6, but the best result are obtained at pH 4.75 for acid cellulase. The pH should be maintained between 4.5 to 4.7 by using sodium acetate – acetic acid. Similarly though the acid enzyme is active between 40 -58°C, the ideal temperature is between 50 -55°C. Enzyme dosage is to be adjusted depending on the fabric type, blend ratio and construction of the fabric. As a thumb rule, viscose requires less dosage than cotton and thick fabrics or tightly woven or knitted fabric requires more dosage than thin fabrics. Weight loss for 100% cotton upto 3-5% is ideal. Excessive dosage or treatment will lead to loss in tensile strength. Process time of less than 30 minutes is not recommended even though the enzyme dosage is increased proportionately.

When cotton fibre is treated with an aqueous solution of cellulase, the enzyme is adsorbed onto the surface of the fibre to form a primary wall/cellulose complex. At the interface, hydrolysis of the cellulose occurs very rapidly, releasing products of decomposition of cellulose and non-cellulosic components which were dispersed in the primary wall matrix. The process is repeated over and over again at an extremely rapid rate, producing pathways in the primary wall that permit the enzyme to reach and accelerate the hydrolysis of the cellulose that constitutes the very substance of the cotton fibre –secondary wall. The enzymatic destruction of cotton by the use of cellulase will result in an absorbent fibre at the expense of weight and strength loss, present Etters *et al.* (2004).

Cotton fibres consist of macro fibrils which are composed of organized micro fibrils (microcrystals). Micro fibrils are formed through the association of individual cellulose molecules, which form intermolecular hydrogen bonds and hydrophobic bonds, states Chanzy (1993). Cellulose in cotton consists of crystalline fibrils which vary in its length and complexity and are connected by less organized amorphous regions with an average ratio of about two thirds crystalline and one third non-crystalline material. Structurally the crystalline cellulose can occur in different lattice types, namely cellulose I, cellulose II, cellulose III, cellulose IV or cellulose X, but cellulose I and cellulose II are of relevance to textile processing. The degree of polymerization (DP) of cotton may be as high as 14,000, but it can be reduced to 1000 -2000 through processing treatments. The crystalline regions of cotton reportedly have a degree of polymerization (DP) of 200 to 300, whereas the molecular weight of cotton can range between 50,000 to 150,000, outline Kirubahar *et al.* (2007).

Gokarneshan (2004) defines bio polishing as a finishing process which consists of a cellulase enzyme treatment to give a partial hydrolysis of cotton fibre. The hydrolysis of cotton leads to a weight loss of around 3-5% and a strength loss of 2-7%. Enzymatic treatment of cotton and cotton blended fabric results in less fuzz and pilling, better fabric feel, increased gloss or lustre and increased durable softness.

Cellulase catalyses the hydrolytic cleavage of the cellulosic chains producing soluble products leading to weight loss and strength loss. Loss in weight of the fabric treated with acid cellulase enzyme increases by increasing the enzyme dosage or concentration. It has also been studied that strength loss can be reduced by using less aggressive cellulose mixtures or monocomponent solutions. Cellulases rich in endoglucanases will be ideal to achieve the desired surface improvements with minimum strength loss, discuss Arumugam *et al* . (2007).



Mechanism of Cellulase Enzyme

Cellulases typically consist of two cellobiohydrolases (CBH I and CBH II), several endoglucanases (EG I-V) and two betaglucosidases (BGL I and BGL II). All these enzymes act in a synergistic fashion during the reaction, which is very efficient for the degradation of the crystalline cellulose. At first the endoglucanases (EGs) randomly attack the cellulose polysaccharide chain generating new chain ends. The exo type enzymes act in a progressive way on the chain ends to form glucose or cellobiose as main reaction products. The latter is decomposed to glucose by betaglucosidases, explain Saravanan *et al.* (2008).

Reports of cellulase characteristics and activity reveal that cellulases are used in the textile industry to improve the appearance of the fabric surfaces by effecting a stone washed appearance in denim, by biopolishing or softening fabrics, by removing surface fuzz fibres to impart a smooth appearance or by removing 'white specks' which are tangled bundles of surface fibres which do not take up dyes, presents Synder (1997). Cavaco-Paulo and Almeida (1996) point out that cellulase activity does not change the crystallinity index of cellulose, indicating that the cellulose activity is not confined to the non crystalline regions. The mode of action supports the concept that the cellulose behaves as a one phase polymer with crystalline regions with varying degrees of accessibility during cellulase treatment.

Rousselle *et al.* (2003) present that treatment with total cellulase produced moderate to high losses in weight and strength but no change in moisture-related properties, molecular weight distribution, pore size distribution or hydrogen bonding patterns, when comparing cellulase-treated fabric with fabric treated with buffer only. These results substantiate the presumed one chain mechanism for enzymatic hydrolysis of cellulose, where the endoglucanase (EG) components of the whole cellulase break cellulose chains on the surface of the molecule, after which the polymer molecule is rapidly and completely removed by cleavage of cellobiose units by the exoglucanase (CBH) components. This total removal of some cellulose chains by the combined action of CBH and EG components leaves behind the remaining microfibril consisting of chains that are essentially unchanged that is a cellulose polymer similar in structure to the starting material, but in a smaller quantity.

The textile industry is extremely competitive and cost conscious. Since enzymes are often regarded as expensive reagents, there continues to be some resistance to their more widespread use. Though cellulases were introduced only a decade ago, they have become the third largest group of enzymes used and also their worth has been proved in textiles. Today cellulases account for twenty per cent of the world enzyme market, indicate Kumar *et al.* (2008). The applications of enzymes modifies the surface properties of textiles which acts favorably for dye uptake and other finishes. Thus, enzyme technology is a fast growing, eco friendly emerging field of science which has found innumerable applications for textile wet processing.