CHAPTER II
LITERATURE REVIEW

2.0 Introduction

In order to improve the hydrophilic property of polyester fabric, various enzymes and their application methods have been reported for the past two decades. For better understanding of the enzyme synthesis, their mechanism and application, a detailed literature review was reported in the present chapter.

2.1 Structure of polyester

Polyester fibres are man-made fibres composed of at least 85 % by weight of an ester of dihydric alcohol and terephthalic acid [12]. The linear homopolymer, polyethylene terephthalate is the dominant composition for polyester fibres. The number average molecular weight of about 15,000 is required for useful textile-fibre properties, but lower values give staple of low tendency to pilling and higher values provide high strength fibres for industrial use [13]. The length of the repeat unit in polyethylene terephthalate along the chain is 10.75 Å and the chains are nearly planar. The unit cell is triclinic; the atomic positions in the crystallite indicate that no special forces of attraction exist between the molecules [14].

2.1.1 Synthesis of polyester

Polymerisation reactions

Polyester polymer was prepared commercially as follows [15], (i) monomer formation by ester interchange of dimethyl terephthalate with
glycol or esterification of terephthalic acid with glycol (ii) polycondensation by removing excess glycol.

Step 1: Ester interchange:

\[
\text{CH}_3\text{OC} - \begin{array}{c} \text{O} \\
\text{COCH}_3 + 2\text{HOCH}_2\text{CH}_2\text{OH} \end{array} \quad \text{Ethylene glycol}
\]

\[
\text{HOCH}_2\text{CH}_2\text{OC} - \begin{array}{c} \text{O} \\
\text{COCH}_2\text{CH}_2\text{OH} + 2\text{CH}_3\text{OH} \end{array} \quad \text{Methyl alcohol}
\]

Esterification:

\[
\text{HO} - \begin{array}{c} \text{O} \\
\text{COH} + 2\text{HOCH}_2\text{CH}_2\text{OH} \end{array} \quad \text{Ethylene glycol}
\]

\[
\text{HOCH}_2\text{CH}_2\text{OC} - \begin{array}{c} \text{O} \\
\text{COCH}_2\text{CH}_2\text{OH} + \text{H}_2\text{O} \end{array} \quad \text{Phthalic acid}
\]
Step 2: Polycondensation:

\[
\text{Polyethylene terephthalate}
\]

Monomer formation (step 1) catalysed by the ester-interchange reaction between molten dimethyl terephthalate and glycol takes place at about 200°C in presence of catalyst. The product was a mixture of monomer, very low molecular weight polymer and methanol as a by-product, which distils at 150°C. Ester-interchange catalysts were divalent salts of manganese, cobalt, magnesium, zinc or calcium. An alternative monomer formation system involves terephthalic acid instead of dimethyl terephthalate and an uncatalysed direct esterification with ethylene glycol rather than ester-interchange. The monomer formed from both methods was polymerized (step 2) in the presence of an antimony catalyst. Chain extension was promoted by removal of excess glycol from the viscous melt at about 280°C, with carefully controlled agitation and a progressive reduction of pressure to about 200 Pa. Heating was continued at about 280°C until the desired degree of condensation was obtained.
2.2 Properties of polyester fibre

2.2.1 Chemical properties

Effect of alkali: Polyester fibres have good resistance to weak alkalis at high temperatures. It exhibits only moderate resistance to strong alkalis at room temperature and is degraded at elevated temperatures.

Effect of acid: Weak acids, even at the boiling point, have no effect on polyester fibres unless the fibres are exposed for several days. Polyester fibres have good resistance to strong acids at room temperature. Prolonged exposure to boiling hydrochloric acid destroys the fibres and 96 % sulphuric acid causes disintegration of the fibres.

Effect of solvent: Polyester fibres are generally resistant to organic solvents. Chemicals used in cleaning and stain removal do not damage, but hot m-cresol, mixtures of phenol and trichloromethane dissolve the polyester fibre. Oxidising agents and bleachers do not damage polyester fibres.

Miscellaneous properties: Polyester fibres exhibit good resistance to sunlight and abrasion. Soaps, synthetic detergents and other laundry aids do not damage it. One of the most serious faults with polyester is its oleophilic quality. It absorbs oily materials easily and holds the oil tenaciously [16].

2.2.2 Mechanical properties

The properties of polyester fibre vary depending on the method of manufacture [17]. Fibres produced with degree of stretch have higher crystallinity and greater molecular orientation. These fibres pose high tensile strength and Young's modulus. An increase in molecular weight increases tensile strength, modulus and extensibility. Polyethylene terephthalate shows nonlinear and time-dependant elastic behaviour. Creep occurs under load and
shows delay in recovery on removal of the load. But compared to other melt-spun fibres, creep is small.

2.2.3 Physical properties

Specific gravity: The specific gravity of polyester fibre is 1.38; density is greater than polyamide fibres and lower than rayon. Fabrics made from polyester fibres are medium in weight.

Heat effect: The melting point of polyester is close to that of polyamide, ranging from 250 to 300°C. Polyester fibres melt and shrink on exposure to flame, leaving a hard black residue. Heat setting of polyester fibres, not only stabilise the size and shape, but also enhances wrinkle resistance of the fibres [18].

Moisture regain: The moisture regain of polyester is low, ranging between 0.2 to 0.8 %. Although polyesters were non-absorbent, they do not have wicking ability. Wicking is carrying moisture on the surface of the fibre without absorption.

2.3 Hydrophilisation of polyester fibre

2.3.1 Need for hydrophilisation of polyester fibre

Polyester fabric is gaining importance among all other synthetic fibres due to its improved properties like high tensile strength, durability, lightweight, stretch resistance, stain resistance, machine washability, wrinkle resistance and abrasion resistance [19]. However demand is less when compared to natural fibres like cotton due to its hydrophobicity, low moisture regain (0.4 %) and low reactivity with most common chemical agents. The low hydrophilicity/wettability makes the fibre less suitable to be in contact with the
human skin and low reactivity makes the fibres unsuitable for other chemical finishing process. Further, the fibres have the tendency to accumulate static electricity on its surface which helps to pick up more soil during wear and washing becomes difficult.

The polyester fabrics are also notorious for pill formation and due to its increased tenacity the pill does not break easily thus leaving behind a fuzzy appearance to the garments. Thus, it has been suggested that hydrophilisation of polyester can have an effect on hand, thermal properties, permeability and hydrophilicity [20]. Several methods have been adopted to increase the hydrophilic nature of polyester fibres.

### 2.4 Methods of hydrophilisation of polyester fibre

The methods used for hydrophilisation involves hydrophilisation through block copolymer and surface modification through hydrolysis. The surface hydrolysis is carried out using grafting, chemical hydrolysis, plasma treatment and enzymatic hydrolysis.

#### 2.4.1 Hydrophilisation by grafting method

Grafting of polyester can improve hydrophilicity. The influence of graft-copolymerisation reaction between polyester fibres and mixtures of acrylamide (AAM) and acrylic acid (AA) monomers on zeta potential of the grafted polymer was reported by Lokhande and Teli [21]. The polyester fibre was rendered amphoteric in nature due to the introduction of the AAm-AA graft mixtures in the substrate.

Polyester monofilaments were grafted with methacrylic acid monomer in order to improve the water absorption and dye uptake characteristics [22]. The results show that the rate of grafting is proportional to the 0.167 power of the
monomer concentration and 0.545 power of the initiator concentration. The activation energy for grafting, calculated from an Arrhenius plot, was found to be 11.12 kcal /mol. Water absorption and dye uptake were tremendously improved by grafting.

Radiation grafting of acrylic acid to polyester fabric has been studied by an impregnation method to render its surface more hydrophilic [23]. Acrylic acid impregnated fabric was irradiated under nitrogen with gamma-ray from Co-60. The electron micrograph reveals that certain types of discontinuities on the surface of the grafted fibres exist and heavily grafted sample of polyester fibre shows a continuous structure containing occasional specks of impurity. The modified fabrics possess excellent dyeability and thermoplasticity.

The properties of polyester fabrics were evaluated by grafting with chitosan oligomers/polymers after being activated by atmospheric pressure plasma treatment [24]. The antibacterial effect was most evident when the surface of fabrics was activated by atmospheric pressure plasma treatment for 60 to 120 seconds and grafted with chitosan oligomers. The modified fabrics also exhibited good biocompatibility.

Polyelectrolyte such as poly (4-vinylpyridine) and polyacrylic acid with opposite charges have been deposited on a polyester fabric by the layer-by-layer technique [25]. The first acidic layers with carboxylic groups were produced by grafting acrylic acid onto the polyester fabric. The increase in carboxylic groups was identified by the content of methylene blue dye in fibre. The water retention depends on the character of the deposited nanolayer and they were always higher when the top nanolayer consists of polyacrylic acid.

2.4.2 Hydrophilisation by chemical hydrolysis
One of the surface modifications is the controlled hydrolysis of polyester [13]. The action of strong base leads to cleavage of ester linkages on the fibre surface. The result is the formation of terminal –OH and –COOH groups on the fibre surface. Hydrolysis is believed to increase the number of polar functional groups at the fibre surface.

Shenai and Lokre [26] have studied the action of sodium hydroxide solution on polyester fibres at various concentrations, treatment time and temperature, in terms of weight loss of the fibres. They have reported that the weight loss increased linearly with the increase of treatment conditions. Achwal [27] reports that for a satisfactory improvement in feel and silk-like finish a weight loss of 15 % was necessary. Improvement in static charge development required at least a weight loss of 10 %. Adequate improvement in hydrophilicity could be achieved by a weight loss of 5 %.

Timmis [28] reported that pilling-resistant of polyester fabric can be achieved by treating it with a 2 g/l sodium hydroxide solution at 60ºC for 30 minutes. This was accompanied by a small decrease in the tensile strength of the fabric. Shet [29] carried out treatment of polyester by padding in 25 % NaOH followed by hot air drying at 60ºC for 15 minutes and subsequent washing. Improvement in feel was observed for polyester along with wettability without affecting the strength and dimensional stability.

Elisson et al. [30] observed that untreated polyester fibres have relatively smooth surface, while NaOH treatment causes pitting of the fibre surface. The pits increase in number and depth as the time of hydrolysis was lengthened.

Namboodri and Haith [31] carried out a comparative study by treating the polyester fibres with alkalis and various alkoxides such as sodium
hydroxide in water, sodium methoxide in methanol, sodium ethoxide in ethanol, sodium isopropoxide in isopropanol and potassium tertiary butoxide in tertiary butanol at 60ºC and at different concentrations. It was found that the loss in weight of the polyester fibre was in the order sodium hydroxide < tertiary butoxide < secondary propoxide < methoxide and ethoxide.

Bendak [32] studied the topochemical degradation of polyester fibres caused by methanolic sodium hydroxide solution treatment. The treatment of samples with methanolic sodium hydroxide solutions was observed to have a weight loss of about 5-8 %, with a significant decrease in wicking time and sinking time. Shenai et al. [33] studied the hot alkaline treatment on the polyester fibres. The treatment was carried out by a 4 % solution of sodium hydroxide at 100ºC and it was observed that there was 30 % loss in weight after two-hours of treatment.

Prorokova et al. [34] reported the surface activation of polyethylene terephthalate fibre materials by weak surface hydrolysis. Sodium hydroxide solutions with a concentration of 10-15 g/l at the boiling point for 10-15 minutes were the most favourable condition for surface activation of polyester fibre material. An additional number of carboxyl and hydroxyl groups that have a significant positive effect on the surface properties of fibre material were formed.

Reaction of an amine with an ester group of the polyethylene terephthalate led to chain scission at the reacting site giving rise to amide formation and etching. Chauhan et al. [35] carried out etching experiment on polyester filament at room temperature (27ºC) using a 40 % aqueous methylamine solution. The fibre to liquor ratio was kept high. The observed chemical etching with aqueous methylamine has revealed a complex stress
cracking behaviour, which varied with orientation and thermal crystallisation conditions. The surface of etched polyester filaments exhibited a complex mosaic pattern of cracks.

Mikhailova et al. [36] reports on modification of polyester fibres with metal salts containing highly charged cations. The treatment increased the hydrophilicity of the fibres covered with a multilayer of continuous polymeric metal oxide. The calculation of its thickness was in the nanosystem category.

A chemical method based on the use of cyclodextrins (CDs) and citric acid (CTR) as finishing chemicals for the modification of polyester fibres was reported by Ducoroy et al. [37] It was observed that the reaction between these reactants yielded a cross-linked polymer, by formation of ester between the polyol (CD) and the polycarboxylic acid (CTR). This polymer (called polyCTR-CD) permanently coated the polyester fibres. The chemical structure of polyCTR-CD consisted of CD moieties and unreacted carboxylate groups. These groups resulted from the partial reaction of CTR and yielded ion exchange property to the fibres.

The literature on chemical hydrolysis of polyester clearly shows that sodium hydroxide treatment enhances the properties such as pilling resistance and reduction in static charges. These properties are achieved with the reduction in the strength of the fabric. Aminolysis and other chemical methods of polyester treatment improve the dyeability only at the cost of etching polyester surfaces.

2.4.3 Hydrophilisation by plasma treatment

Plasma technology is employed for surface treatment of polyester. Plasma treatment for surface modification of textiles was performed by two
methods, one method is depositing plasmas and the other is non-depositing plasmas [38]. Depositing plasmas were applied by using saturated and unsaturated gases (e.g., fluorocarbons, C₂H₄) or vapours (e.g., acetone, methanol, allylamine, acrylic acid) to develop a layer of the exposed gas. In nondepositing plasmas several reactive etching (i.e., Ar, He, O₂, N₂, F₂) or nonpolymerizable gases (H₂O, NH₃) was exposed to react with the substrate and produce new functional groups on the surface. Low-temperature plasma technology is used to improve the surface properties of polymeric materials without changing the bulk properties.

Functional groups were introduced on the surface of polyethylene terephthalate and polyamide fabrics using five different plasma treatments [39]. Fabrics were directly treated in acrylic acid, water, air, O₂ and argon plasma. The plasma conditions were changed to control the extent of plasma surface modification. Plasma modifications resulted in unsaturated bonds and/or free radicals on the surface of the fabrics and found to have a significant improvement on the overall surface charges and consequently on dyeability and soil resistance.

Kabajev et al. [40] studied about the effect of glow discharge plasma of air, oxygen and helium treatment on polyethylene terephthalate films and fibres. Samples were treated in low-temperature plasma of various gases (air, oxygen and helium). The SEM images conclude that considerable long time exposure resulted in a removal of the material almost up to the middle of the object diameter. The various orientation and density of elements in the morphological structure were well seen in the fibre longitudinal section. IR spectra show the occurrence of new absorption bands near 780, 1615 and 3370 nm⁻¹ that were caused by new functional groups such as carboxyl and nitrile.
Consequence of these structural changes was the sharp increase of surface energy that was shown as increase in capillarity of fabrics.

Jahagirdar et al. [41] studied plasma treatment of polyester fabric to impart the water repellency property. Polyester fabric were treated with dichlorodimethyl-silane (DCDMS) solution by two methods: (i) dipping the fabric directly in DCDMS solution for different intervals, (ii) dipping the fabric in DCDMS solution after its exposure into air plasma chamber for different durations at optimized exposure power conditions. The effectiveness of the water repellency property of modified polyester fabric was checked by repeated washing up to ten cycles. Prior exposure of plasma before treatment of DCDMS solution modifies the fabric leading to deposition of more and more silane groups making it water repellent as compared to those treated directly with DCDMS.

Klenko et al. [42] studied on the treatment of polyester fabric by an atmospheric dielectric barrier discharge (DBD) as an alternative to low-pressure plasma technology. Operation at atmospheric pressure with implementation of DBD was more profitable in comparison with the low-pressure treatment, due to its simplicity and low operation costs. The most stable modification was achieved with the modification time of 360 seconds. The stability of modification effect was observed in 17 days after the treatment.

Helium-oxygen plasma treatments were conducted to modify polytrimethylene terephthalate (PTT) and polyethylene terephthalate (PET) warp knitted fabrics under atmospheric pressure [43]. Surface oxidation by plasma treatments resulted in formation of hydrophilic groups and moisture regain enhancement. Low-stress mechanical and bulk properties were enhanced by plasma treatment. Increasing interfibre and interyarn frictions
might play important roles in enhancing surface property, low-stress mechanical property and bulk property for both fabrics.

Plasma technology is advantageous than alkaline hydrolysis as the fibre acquires the desirable properties such as wicking property and chemical reactivity. But such improvement is possible only by means of the low pressure plasma treatments, which are governed by purchase of necessary equipment, technical gases etc. To overcome the disadvantages of alkaline hydrolysis and plasma technology, enzymatic treatment of polyester fibres was developed.

2.5 Enzymatic treatment

Enzymes are naturally occurring high molecular weight protein composed of various amino acids [44]. They are capable of catalysing chemical reaction of biological processes and hence are known as biocatalysts. Due to extraordinary catalytic power of enzymes, they speed up chemical process by its mere presence and without being consumed in the process.

2.5.1 Mechanism of enzyme action

The most widely accepted mechanism of action is based on the enzyme substrate complex theory. The molecule that is bounded by the active site and acted upon by the enzymes is called the substrate. The active sites of the enzyme completely fits with substrate known as the ‘Lock and key’ fashion (Fig.2.1) [45, 46], interaction between substrate and active site takes place resulting in the formation of a number of weak bonds including hydrogen bond and Vander Waals interaction. Formation of weak interaction in the enzyme-substrate complex is associated by a small release of free energy known as the binding energy. The binding energy is the major source of free energy used by
enzyme to lower the activation energy of reactions so that the reaction proceeds at a much faster rate (Fig.2.2) [47].

![Figure 2.1: Lock and key mechanism [46]](image)

![Figure 2.2: Enzymes lower the activation energy of a reaction (E_a) [47]](image)

### 2.5.2 Advantages of enzymatic treatment over chemical process

- Enzymes are generally safer than the chemicals [48]. Chemicals used in textile manufacturing and textile processing are hazardous to the workers handling them.
- Enzymes are very specific as each type can only affect one chemical bond. Chemicals commonly used are very broad in their actions and much less specific.

- Enzymes perform best under normal, mild conditions of 100-140 F temperature, pH 4-8 and normal pressure. Many chemicals require extreme conditions of high temperature, high pressure or extreme pH to be effective. Because of the mild conditions required, working with enzymes is much safer and more energy efficient.

- Enzymes are also clean and “green” to manufacture.

- In terms of effluent, the enzymes are less polluting. Chemicals used in textile processing cause toxic products to be released in the effluent.

- Most enzyme treatments are compatible with other types of treatments, such as detergents or stones, to save time or achieve specific effects.

**Disadvantages of enzymatic treatment**

- The major disadvantage of enzymes is cost - they are more expensive

- Enzymes are sensitive to temperature, pH, humidity and contaminants.

- Storage is more difficult because they have a shorter self-life than most chemicals.
2.5.3 General classification of enzymes used for textile processing

Enzymes for textile use can be classified based on their action [49].

- Amylase, starch degrading hydrolytic enzyme converts amylose or amylpectin polymers to water-soluble shorter chain sugars.

- Lipase, fat solublising hydrolytic enzymes converts fatty esters into constituent alcohol and acid.

- Pectinase, hydrolytic enzyme acts on pectin, which is linear polymer of galacturonic acid and converts to soluble fragments.

- Cellulase, hydrolytic enzymes that hydrolysis cellulosic materials.

- Proteases catalyse the hydrolysis reaction of protein molecule into the component amino acids.

- Catalases, catalysis the hydrogen peroxide into water and oxygen.

2.5.4 Application of enzymes on polyester

Some of the attempts to modify polyethylene terephthalate by enzymatic treatment have not resulted in any change [50] since PET is one of the aromatic polyester, which seem to be more resistant to biodegradation than aliphatic polyester. But still much research has been carried out for improved textile properties such as wettability (or) hydrophilicity using enzymes due to high demand of polyester among the other synthetic fibres. Potentially a great variety of enzymes have been identified based on their natural role to hydrolyse ester bonds in lipids and polyesters.
2.5.4.1 Polyester hydrolysis using lipase enzyme

The effects of five hydrolyzing enzymes on improving the hydrophilicity of several polyester fabrics have been studied [10]. Four lipases were reported to improve the water wetting and absorbent properties of the regular polyester fabric than alkaline hydrolysis. Compared to aqueous hydrolysis, the enzyme reactions have shown to be effective under more moderate conditions, including a relatively low concentration (0.01 g/l), a shorter reaction time (10 minutes) at an ambient temperature (25ºC). Enzymatic hydrolysis improved water wettability, accompanied by full strength retention, which is not possible with the alkaline treatment of polyester. Lipase was also effective in improving the wetting and absorbent properties of sulphonated polyester and microdenier polyester fabrics.

Xie et al. [51] reported that treatment of polyester with lipases has been shown to improve wetting and absorbency while strength was retained. They compared to chemical hydrolysis by alkaline treatment. Enzymatic surface hydrolysis has been advantageous in maintaining mechanical stability, because enzyme cannot penetrate into the fibre and is therefore restricted to reacting on the very surface only.

Bide et al. [52] studied on alkaline hydrolysis and enzyme treatment of polyester. The treatment resulted in the creation of surface carboxylic acid groups which improved hydrophilicity and functionality. Functionalised polyester was used to link soil release finishes and biological active proteins. The presence of functional groups provides opportunity for the development of multifunctional biomaterials and possibilities for unique finishing effects.
Yoon et al. [11] reports that improved strain resistance, wettability and/or dyeability of polyester fabrics were observed by treatment with pectases, which include lipases, esterases or cutinases.

The effects of enzymatic hydrolysis on drawn polyester filament yarns were investigated. Two multifilament yarns were drawn with different draw ratios at different temperatures and they were hydrolyzed using lipase in similar conditions. Results of Koddami et al. [53] showed that the hydrolysis decreases the weight of polyester hanks by less than 0.5 %. The strength loss due to hydrolysis reached a maximum of 10 %, whereas the elongation-at-break of samples decreases by 7-25 % due to hydrolysis. Hydrolysis also increased the moisture absorption of the polyester by up to 50 %. The FTIR spectra as well as other results show that the effect of hydrolysis was limited to the surface of the substrate and hydrolysis were more affected by the increase in surface area rather than drawing.

Kim et al. [54] studied on effect of nine commercial lipases from different sources with activator calcium chloride and non-ionic surfactant Triton X-100 on the moisture regain of polyester fabric. The lipase treatments were compared with alkaline treatment. The weight loss of polyester fabrics was 0.165±0.07 %. The moisture regain of lipase treated samples improved by about two times compared with buffer-treated samples. However, alkaline treatment does not show any improvement in moisture regain. The moisture regain of sample treated with lipase from Rhizopus niveus in the presence of calcium chloride improved by 1.3 times compared with sample in the absence of calcium chloride. The presence of non-ionic surfactant inhibits hydrolytic activity of lipase on polyester fabrics. Nitrogen content of samples was 0.034 %. K/S values improved confirming the formation of carboxyl and hydroxyl groups on the surface of polyester fabrics by lipase hydrolysis. The SEM
images show a great deal of cracks and voids in comparison with the untreated sample.

The optimization of enzymatic treatment of polyester fabric by lipase enzyme from *Porcine pancreas* at different pH, temperature, reaction time and concentration were reported [55]. The hydrolytic activity of lipase was evaluated by the number of carboxylic groups, using the titration method. The lipase treatment condition was controlled at pH 7.5, temperature 40°C, treatment time 90 minutes and concentration 6.25 g/l. The moisture regain of the polyester fabrics treated with lipase improved 3.2 times compared to that of the untreated polyester. The surface of the lipase-treated polyester fabrics showed cracks and voids. The nitrogen content of the lipase-treated polyester fabrics were measured as 0.072 %. Thus, the improvement of the surface wettability of the lipase-treated polyester surface was associated with the hydrolytic action of lipase rather than with protein absorption.

Effect of commercial *Porcine pancreas* lipase (PPL) treatment in the presence of a calcium chloride and Triton X-100 on the wettability and moisture regain of polyester fabrics have been studied [56]. The results conclude that moisture regain of polyester fabric in the presence of 0.5 % surfactant showed 1.5 fold decrease. The surfactant changes the surface property of polyester to hydrophilic which inhibits the hydrolytic activity of lipase. The lipases could attach efficiently to the hydrophobic polyester surface. The moisture regain and wettability of PPL treated polyester fabrics improved when calcium chloride was added as activator to the treatment solution. Voids and cracks caused by PPL treatment were largely responsible for increasing water-related properties.
Aspergillus oryzae CCUG 33812 was used to produce a specific PET hydrolysing lipase [57]. The cultivation conditions for lipase production were optimized in presence of several inducers. Results show that bis(2-hydroxyethyl) terephthalate (BHT) was the best inducer. The BHT-induced extracellular lipase could catalyse the hydrolysis of the PET model substrate. The formation of new carboxyl groups is consistent with the increase in $K/S$ values of dyed polyester fabrics after the enzymatic treatment. Additionally, treatment with the BHT-induced lipase resulted in increased moisture regain and weight loss of polyester fibre/fabric, while the water contact angle and the static half decay time decreased slightly. This indicates that hydrophilicity and anti-static ability were improved after the treatment with the BHT-induced lipase. Spectrophotometry and high performance liquid chromatography (HPLC) with UV detection indicated that hydrolysis of polyester occurred and that products were formed due to the catalytic action of the BHT-induced lipase.

Donelli et al. [58] investigated the changes induced by a lipolytic enzyme on the surface properties of amorphous and crystalline polyester membranes. The lipolytic enzyme displayed higher hydrolytic activity towards the amorphous polyester substrate, as demonstrated by the decrease of the water contact angle values. Minor changes were observed on the crystalline polyester membrane. The protease after-treatment removed the residual enzyme protein adhering to the surface of polyester. The enzyme treatment did not induce any detectable change of surface morphology of the polyester substrate, whereas alkali caused the formation of holes as confirmed by SEM. The lipolytic enzyme was able to increase the hydrophilic character of the amorphous polyester membranes without altering the surface and bulk properties of the substrate. FTIR analysis highlights the chemical and structural
features involving the effect of the enzyme on the outermost layers of the polyester polymer. The esterification of free carboxylic acid groups with a fluorescent alkyl bromide indicates that the enzymatically treated polyester films were the most reactive. The obtained results demonstrate the ability to modify polyester films through enzymatic surface hydrolysis, and functionalise the enzymatically modified polyester surface.

Vertommen et al. [59] used commercial lipase from *C.antartica* for treatment of PET film substrate and PET granules. Using X-ray photoelectron spectroscopic (XPS) analysis an increase in nitrogen content up to 7.2% owing to adsorption of lipase on polyester were measured and angle-resolved XPS confirms the presence of protein layers with thickness of 2.5-2.8 nm. Removal of adsorbed protein was done using ultra sound, demineralised water and isopropyl alcohol and reports to be ineffective.

Eberl et al. [60] reported on the treatment of linear aromatic polyester polytrimethylene terphthalate (PTT) films and fabric with lipase from *T.langinosus* and cutinase from *T.fusca*. The lipase was able to hydrolyse the PTT fibres measured as soluble products using HPLC, but they were unable to hydrolyse PTT films. The cutinase was reported to hydrolyse the PTT fibre and film. The activity of cutinase on PTT film was due to activity optimum was close to *T_\text{g}* of PTT. The increase in K/S value after cutinase treatment was reported. The ESEM images conclude that the surface structure was not damaged and mechanical stability was still maintained. The DSC results show an increase in crystallinity after enzymatic treatment.

A lipase from *Thermomyces lanuginosus* and cutinases from *Thermobifida fusca* and *Fusarium solani* hydrolysed polyethylene terephthalate fabric and films and bis (benzoyloxyethyl) terephthalate (3PET) [61]. The
influence of the non-ionic detergent Triton X-100 and plasticizer N, N-diethyl-2-phenylacetamide (DEPA) was investigated. Due to interfacial activation of the lipase in the presence of Triton X-100, a seven fold increase of hydrolysis products released from 3PET was measured. In the presence of the plasticizer DEPA, increased hydrolysis rates of semi-crystalline PET films and fabric were measured both for lipase and cutinase. The formation of novel polar groups resulted in enhanced dye ability with additional increase in colour depth by 130 % and 300 % for cutinase and lipase respectively, in the presence of plasticizer.

Heumann et al. [62] reported on the hydrolysis of polyester fabric with commercial and crude enzyme. Commercial enzyme Lipase PS, hydrolase from T.fusca, esterase Texazym PES and crude enzyme preparation from Aspergillus sp., Beauvesia sp. and F.solani was used for the study. The increase of hydrophilicity of polyester fabrics was higher for commercial Lipase PS and crude enzyme from Aspergillus sp. and relative decrease of water absorption time upto 76 % than control was reported. The hydrolase from T.fusca showed highest activity on PET model substrate.

The enzymatic treatment with different lipases caused adequate effects, especially, referring to water penetration, absorption and the mechanical parameters of the processed fabric [63]. The process does not cause major damage of the fibre surface or major reorganisation of the surface layers of the polyester fibres therefore their mechanical characteristics are satisfactory. The lipases significantly improve water penetration and the absorbent properties of regular polyester fabric. The surface of polyester fibres modified by enzyme treatment had unique characteristics as shown by SEM. These appearances reflect different degrees of enzymatic modification of the control polyester surface corresponding to different treatment conditions.
2.5.4.2 Polyester hydrolysis using cutinase and other enzymes

Braaz et al. [64] and Calado et al. [65] reported that amongst the hydrolytic enzymes besides esterases and lipases, enzymes acting on natural polyesters such as cutinases or Polyhydroxyalkanoate depolymerases could have potential to modify polyester polymer.

Cutinase was chosen for the modification of synthetic fibres because it is described as esterase that degrades cutin, structural polyester of plants [2]. Cutinase is a serine hydrolase with low specificity that is known to hydrolyze p-nitrophenyl esters, soluble and insoluble triglycerides. Wild type cutinase from fusarium solani pisi, was obtained in the extracellular medium in a crude form with a purification degree between 50 and 70 % was used for the surface modification of synthetic fibres like polyester, polyamide 6.6 and acrylics. The activity on polyester and polyamide was measured as soluble products produced by enzymatic action and dyeing hydrolysed fibres with reactive dyes. Results of solubility data indicate that cutinase have a higher activity on polyamide than on polyester. This was due to higher solubility of adipic acid than terephthalic acid, as well as oligomers of polyester was less soluble than the short oligomers of polyamide 6.6. But the higher K/S value of polyester dyed samples indicates the formation of end groups at the fibre surface was high for polyester fibre yielding high colour intensities.

Micro fungi were selectively isolated from plant surface and soil samples for production of polyethylene terephthalate fibre degrading enzymes and used to modify the surface of polyester fabric [66]. Twenty two of 115 isolate showed clearing, indicating the production of cutinase. All isolates exhibited activity towards p-nitrophenyl butyrate (p-NPB) and one isolate identified as Fusarium solani gave the highest activity with polyester fibre as
an inducer. Enzymatic modification of polyester cloth material properties using crude enzyme from *Fusarium solani* showed hydrolysis of ester bonds of the polyester fibre. The modification of the polyester fabric resulted in increase of water and moisture absorption and general enhancement of hydrophilicity of the fabric properties that could facilitate processing of fabric ranging from easier dyeing and softer feel.

Vertommen et al. [59] reports on hydrolysis of synthetic polymer polyethylene terephthalate using cutinase by direct measurement and identification of the different hydrolysis products. In aqueous heterogeneous system, dissolved cutinase from *Fusarium solani pisi* acts on solid polyethylene terephthalate substrates. The extent of hydrolysis was detected by measuring the amount of soluble degradation products in solution using reversed-phase HPLC. The DSC analysis reported that crystallinity greatly affects the capability of the enzyme to hydrolyze the ester bonds, displaying relatively high activity towards an amorphous polyester film and little activity on a highly crystalline substrate. The enzyme was sufficiently stable, hydrolysis rate on the amorphous substrate maintained at sufficient high level over a long period of time of at least five days.

Stefanie et al. [67] evaluated bio-polishing of polyester and polyester/cotton blend using two different cutinases for 100 % polyester fabric and a blend of cutinase and cellulase for polyester/cotton blended fabric treatment. The enzyme treated fabric samples were evaluated for weight loss, pilling note and high performance liquid chromatography (HPLC) analysis of the treatment liquors for degradation products of polyester. Cutinase B gave higher weight loss than that of cutinase A, whereas cutinase A gave little to no weight loss compared with a blank. Both cutinases gave improvement on pilling note compared to the blank at 2000 revolutions. The Cutinase B showed
considerably higher degradation of polyester as reported by HPLC analysis. The treatment of 50/50 polyester/cotton at different dosages of combination of cutinase and cellulase shows that the weight loss increased with increased dosage of both enzymes. Both cellulase and cutinase A gave an improvement in pilling note as compared to the blank.

Cutinase hydrolysis at the surface of polyester fibres have been studied [68] by colour intensity measured as K/S value of reactive dyed samples and terephthalic acid solution formed after reaction with peroxide by fluorimetric determination of the resulting hydroxyterephthalic acid. The K/S values were shown to increase due to the increase in the number of –OH end groups after enzymatic hydrolysis. This confirms that significant enzymatic hydrolysis occurred even over short incubation time, with the K/S value increasing from 0.09 to 0.37. Terephthalic acid formed by enzymatic hydrolysis increased with incubation time and the intensity of the sharp peak at 425 nm increased over 24 hours of incubation. The amount of protein present in the enzymatic treatment solution decreased during the incubation, mainly due to its adsorption on the polyester fibres.

The effect of agitation on adsorption, desorption and hydrolytic efficiency of a native and a genetically modified cutinase on polyethylene terephthalate was reported [69]. The higher level of agitation results in greater amount of hydrolysis for both enzymes in terms of terephthalic acid in solution and equal amounts of hydroxyl and carboxyl groups in fabric. The hydrolysis rate was two-fold lower using orbital agitation. Therefore, the highest K/S increase was obtained for the sample. Among two cutinases the treatment with the genetically modified cutinase at the lowest mechanical agitation have highest K/S value.
For comparison of the aromatic polyester-hydrolyzing activity of the esterases from *F. oxysporum* LCH 1 and cutinase from *F. solani* f. sp. *pisi*, polyester fibres were incubated with 80 U of hydrolases for 168 hours [70]. Determination of the amount of terephthalic acid released showed a considerably higher activity of the enzyme from *F. oxysporum* LCH 1 on polyester compared to *F. solani* f. sp. *pisi*. The water adsorption ability of polyester fabrics treated with enzyme preparations from *F. oxysporum* LCH1 and *F. solani* f. sp. *pisi* was increased compared to untreated samples. Treatments with inactivated enzymes did not result in increased rising heights of water in the fabrics. Therefore, the observed changes in water adsorption of the enzyme treated fabrics cannot be attributed to protein adsorbed to the fibres and indicate an increase in the hydrophilicity of the polyester fabric caused by the hydrolytic action of the enzymes on polyester. The results obtained with esterases and cutinases from various fungi and bacteria provide accumulating evidence for the hydrolysis of ester bonds in polyester catalysed by microbial enzymes.

Hooker et al. [71] reports on a new method for the efficient removal of cyclic trimer (CTR) present in polyester fibres by enzyme catalysed hydrolysis. The enzymatic hydrolysis of CTR produced three significant hydrolyzed products, terephthalic acid (TA), bis (hydroxyethyl) terephthalate (BHET) and monohydroxyethyl terephthalate (MHET). TA and MHET were the predominant products, and BHET was found in trace amounts. The rate of cutinase-catalysed hydrolysis was high initially and decreased as the reaction proceeded. CTR hydrolysis began to level off after 16 hours, with the first 8 hours being the most effective. Increasing the rate of agitation from 0 to 150 rpm increased the amount of hydrolysis by almost 10 times. Higher
concentrations of the enzyme facilitated more complete continued hydrolysis of the ester bonds of MHET after all of the CTR had been hydrolyzed.

Cutinase from *Fusarium solani pisi* was genetically modified near the active site, by site-directed mutagenesis, to enhance its activity towards polyethylene terephthalate and polyamide 6, 6 (PA 6, 6) fibres [72]. The mutations L81A, N84A, L182A, V184A and L189A were done to enlarge the active site in order to better fit a larger polymer chain. Modelling studies of polymer reported enhanced free energy stabilization of model substrate tetrahedral intermediate (TI) bound at the enzyme active site for all mutants, for both model polymers. L81A and L182A showed an activity increase of four- and five-fold, respectively, when compared with the wild type, for PET fibres. L182A showed the one- and two-fold higher ability to biodegrade aliphatic polyester substrates. Further studies in aliphatic polyesters seem to indicate that cutinase has higher ability to recognize aliphatic substrates.

Gudrun et al. [9] in his work describes about newly isolated organisms and their potential to modify the surface of polyethylene terephthalate (PET). Out of the different screening processes, four bacterial and five fungal strains were isolated. A PET model substrate bis(benzoyloxyethyl) terephthalate was synthesized and used in the screening process. On this model substrate, extracellular enzyme preparations from the isolated micro organism showed a maximum activity. All enzyme preparations showed esterase activity on p-nitrophenyl-acetate while no activity was found on p-nitrophenyl decanoate or p-nitrophenyl palmitate. Increased hydrophilicity of polyester fabrics after enzyme treatment was found based on rising height and water dissipation measurements.
Alisch et al. [10] compared the treatment of polyethylene terephthalate fibres with hydrolase preparations from *Thermomonospora* (*Thermobifida*) *fusca* and *Fusarium solani f. sp. pisi* with caustic hydrolysis. As a result of enzymatic hydrolysis there was an increase in hydrophilicity of the fibres determined by measurement of their dyeing behaviour with reactive dyes and their water absorption ability. Comparing with untreated, increased K/S values for the polyester fabric swatches incubated with the two hydrolase preparations were reported. This indicates an increase in the amount of hydroxyl groups as a result of a partial enzymatic hydrolysis of the polyester fibres. The colour intensities obtained with the *F. solani* hydrolase were higher compared to those obtained with the *T. fusca* enzyme; at the same amount of enzyme activity. The rising height measurements of water show an increase in water absorption ability of the enzyme treated sample and it was almost the same as could be achieved by the alkaline treatment of the polyester fabrics.

*Melanocarpus albomyces* recombinant steryl esterase (rSTE1) from *Trichoderma reesei* was studied for hydrolysis activity on polyester [73]. The effect of hydrolytic activity of rSTE1 on the textile properties of polyethylene terephthalate was evaluated by determining wetting and dyeing behaviour. Polyester fabric reported a significant reduction in hydrophobicity after the enzyme treatments since contact angle and penetration time of water were clearly decreased. Improved hydrophilicity is most probably caused by hydrolysis of ester bonds in the polyester backbone, leading to increase of polar carboxyl and hydroxyl groups on the surface of polyester. The increased polarity on the surface enables polar interaction and hydrogen bonding with water molecules and, thus, increases the water wettability of the fibres. Treatment of polyester by rSTE1 also improved binding of methylene blue dye on the polyester surface.
Andersan et al. [74] reports that pilling properties of polyester fabrics were found to be improved by treatment with enzyme preparations from *Humicola sp.*, *Candida sp.*, and *Pseudomonas sp*.

Paulo and Gubitz [3] review on several PET hydrolysing enzymes. Polymer hydrolysing enzymes should be highly active on water insoluble polymers. Surface functionalisation is effective when enzyme hydrolysis takes place in the middle of the chain as well as chain ends. The mode of enzymatic action on PET substrate can be modified with changes to reaction conditions. High crystallinity negatively affects the ability of the enzymes to hydrolyse. In addition to enzymatic hydrolysis, the simple adsorption of enzyme protein to the polymer can also increase hydrophilicity owing to the hydrophilicity of protein. Hence a better understanding of the interaction of enzyme with the substrate with regard to factors such as sorption, movement on the polymer surface and role of hydrophobic or binding material is necessary to develop enzymes with further enhanced activity.

### 2.5.5 Enzymatic hydrolysis of aliphatic polyesters

Enzymes have shown potential both for synthesis of functional polyesters and surface functionalisation by grafting. Lipases have been used for the synthesis of bifunctional polyesters [75], biocompatible sorbitol containing polyesters [76] and polyester coating of cellulose [77]. Attachment of novel side chains on poly (styrene-co-4-vinylbenzyl alcohol) was achieved by lipase-catalysed ring-opening polymerisation [78].

Muller et al. [7] and Walter et al. [79] have given number of reports on the hydrolysis of synthetic aliphatic polyesters while aromatic polyesters seem to be more recalcitrant to microbial/enzyme attack.
Tokiwa & Calabia reviews the degradation of microbial polyesters. The degradability of biodegradable polyesters depends on the degrading organisms available in the environment [80]. Polymers are degraded in soils by the action of a wide range of microorganisms. Lipases can hydrolyze aliphatic polyesters other than optically active polyesters such as polyhydroxy butyrate (PHB) and polylactic acid (PLA). Molecular weight is one of the factors determining the biodegradation of plastics. Low molecular weight is favourable for biodegradation. The rate of enzymatic hydrolysis of polycaprolactum (PCL) diol by *Rhizopus delemar* lipase was faster at the smaller molecular weight. Higher the melting point of polyester, the lower the biodegradability. Higher order structure properties such as crystallinity and modulus of elasticity suppressed the polymer degradability.

Commercial lipases were examined for their degradation efficiency of aliphatic polyester films [81]. Lipase Asahi derived from *Chromobacterium viscosum* degraded polybutylene succinate-co-adipate (PBSA), poly (ε-caprolactum) (PCL) and polybutylene succinate (PBS). Lipase F derived from *Rhizopus niveus* degraded PBSA and PCL during 4–17 days. Lipase F-AP15 derived from *Rhizopus orizae* could degrade PBSA in 22 days. These results were explained with the sequential reactions of the chemical hydrolysis of the polymer to oligomers at higher pH and temperature, and the succeeding enzymatic hydrolysis of oligomers to the monomers.

Work published by Ryou et al. [82] studied on the rate of enzymatic degradation of plasma surface modified microbial polyester, poly [(R)-3-hydroxybutyrate] and poly [(R)-3-hydroxybutyrate-co-3-hydroxyvalerate]. The CHF₃ plasma treated polyesters exhibited significant retardation of enzymatic erosion, because of the introduction of surface fluorocarbon groups. The increased surface hydrophilicity of the O-plasma
treated polyesters gave no significant acceleration of the enzymatic erosion.

2.6 Application of enzymatic treatment to other textile processing

2.6.1 Enzymatic treatment of cellulose with cellulase

Cellulases are hydrolase class of enzymes, which cleave 1-4, β-glucosidic linkage of celllobiose chain or cellulose. The cellulases are a mixture of enzymes viz., endoglucanases, cellobiohydrolases, and β-glucosidases [83-85]. Endoglucanases cleave bonds along the length of the cellulose chains in the middle of the amorphous regions, resulting in decrease in the degree of polymerisation of the substrate [86].

Cellulolytic fungi generally produce two different cellobiohydrolases (CBHI and CBHII). CBHI attacks the reducing end, whereas CBHII acts at the non-reducing end. Cellobiohydrolases are processive enzymes, initiating their action from the ends of the cellulose chains. They attack the crystalline parts of the substrate, produce primarily celllobiose and decrease the degree of polymerisation of the substrate very slowly [87]. The cellobiohydrolases and endoglucanases act synergistically with each other and they have a higher activity in mixtures than the sum of the activities of the individual enzymes acting alone [88]. Cellobiohydrolase and endoglucanases act together to hydrolyse cellulose to small cello-oligosaccharides. In the final β-glucosidases hydrolyse the soluble oligosaccharides and celllobiose to glucose.
Ozdić et al. [89] worked on treatment of cellulase with single jersey fabrics, knitted with 100% combed, carded and open-end cotton yarns. The pilling behaviour of enzyme treated fabric samples did not display any significant difference whether they were pre-treated or dyed. It is evident that single enzymatic treatment reduces pilling tendency and double enzymatic treatment reduces it more. Double enzymatic treatment interfaces with the weight and the strength of fabrics severely, even beyond the acceptable limits. The results demonstrate that enzymatic treatment causes weight loss in carded yarns to the highest degree. Single and twice enzymatic-treated fabric samples display severe colour deviations.

Extracellular extracts of cellulase from *Myrothecium verrucaria* have been used to study the mechanism of cellulase action on unmercerized and mercerized cotton cellulose [90] and compared with acid degradation. These comparisons suggest that the enzyme, being composed of large molecules with restricted mobility in the substrate, removes a number of adjacent glucose residues from the few sites of attack.
Evaluation on changes in the low-stress mechanical behaviour of 100 % cotton and cotton/polyester yarns after treatment with a cellulase enzyme was done [91]. The enzyme treated cotton yarns show weight losses, due to fibre erosion and fibre separation, improved compressive softness and reduced bending stiffness due to improved yarn flexibility. The extent of changes in yarn properties was different for different spun yarns. Thus, the open end friction yarn accounts for the maximum changes in hand-related mechanical properties among the cotton yarns, while the air-jet yarn accounts for the maximum change among the polyester/cotton yarns, suggesting that the treatment probably offers maximum tactile benefit. The woven and knitted fabrics made from these yarns will feel softer and more flexible.

Enzymatic hydrolysis of cellulose in cotton fibres by a cellulase mixture was monitored by measuring products of hydrolysis as a function of time in a test reaction vessel [92]. Subsequently, an empirical equation was applied to the data to characterize the cotton cellulose-cellulase system. In spite of its simple form, the empirical equation provided a good fit to the experimental data. In addition, the empirical equation provided pertinent mechanistic information without resorting to the use of complex kinetic models.

Verenich et al. [93] studied the effect of enzymatic pretreatment of cotton fibres on the properties of resulting nonwoven fabric. Enzymatic treatment is known to improve the aesthetical properties of fabrics with reduction in strength. In the case of nonwovens the strength loss can be even more drastic as cellulase may attack bonded areas of the fabric. The pretreatment of cotton fibres prior to fabric formation showed that the resulting nonwovens could be stronger and more drapeable than the same fabric composed of untreated fibres.
Paulo et al. [94] studied on the kinetic parameters during cellulase treatment of cotton using classical Michaelis-Menten equation with a slight modification. Two different type cellulases i.e. total cellulase and ageing cellulase were taken for the studies. The comparison was made between original fabrics and scoured fibres, mercerized and raised fibres. On comparing both cellulase treatments of all fabrics, the mercerized fabrics and raised fabrics have the maximum reaction rate then the original fabrics. This was because the mercerized cellulose has more accessible structure and the raised fabrics have higher damaged fibres and more open structure on the surface. The increase in mechanical friction was more synergistic with cellulase action on fabrics than on a bundle of fibres. The synergism between increasing mechanical friction and cellulase action is to increase the dissociation of the enzyme-bound species leaving more free enzymes for catalysis.

Samples of jute-cotton blended fabric were treated with commercial cellulases, xylanases and pectinases individually and in combination at various concentrations in order to smooth and soften the fabric [95]. Addition of commercial cellulases alone extensively removed protruding jute and cotton fibres from the fabric, whereas addition of commercial pectinases or xylanases mainly loosened the protruding long jute fibre bundle. Combined treatment of pectinases and xylanases with reduced amounts of cellulases was equally effective as high levels of cellulases results in the removal of surface protruding fibres. Thus, the fabric surface was smoother in enzyme-treated samples compared to untreated control. The treatments with mixtures of enzymes were more effective than cellulase alone.

Biopolishing of jute-cotton union fabric have been studied with Biocellulase ZK. The treatment led to the removal of surface hairs from the fabric and induced improvement in soft feeling. The handle of the fabric was
improved due to increased drapeability, compressibility, reduced stiffness and rigidity. Enzymatic softening of semi-top-grade TD3 jute enhanced its spinning properties to the level of a high-speed modern worsted ring spinning machine [96]. The improved spinnability of the treated fibre aroused from the improved fineness and pliability of its filament.

2.6.2 Cellulase treatment on non-cotton cellulosic materials

Kumar et al. [97] studied treatment of cellulase on several man-made cellulosic fabrics-lyocell (Tencel), rayon (viscose) and cellulose acetate. The treated fabrics and untreated control were tested for surface fuzz removal, softening, pilling, weight loss and strength. The effect of cellulase on these different cellulosics varied. On both rayon and lyocell, cellulase altered the handle and drapeability and removed surface fuzz. Cellulase also reduced the pill tendency of rayon and fibrillation of lyocell. Cellulose acetate was minimally affected by cellulase under the selected test conditions.

An enzyme based process was applied in finishing viscose fabrics. Viscose fabrics are very susceptible to pilling because of individual loose fibre ends, which protrude from surface and fizzes [98]. A commercial enzyme of cellulase type Econase CE and experimental cellulases such as endoglucanase II (EGII), cellobiohydrolase (CBHI) and cellulase enriched with EGII from the Trichoderma reesei strain were used for modification of viscose woven fabrics. Based on the results obtained, it was found that no significant changes in the molecular structure of modified viscose fabrics were caused after enzymatic treatment with either commercial or experimental cellulases. Enzymatic treatment carried out in presence of cellulase type Econase CE allows smoothing of the surface of viscose fabric, removal of impurities and
individual loose fibre ends, which protrudes from the surface of the untreated fabric.

Lyocell (tencel), rayon (viscose) and cellulose acetate woven fabrics were treated with acid cellulase [99]. The benefits indicated from the study were softening, defuzzing, depilling and pill prevention, improved drapeability and appearance of rayon and lyocell fabrics after multiple laundering. Cellulase treatment performed best on lyocell followed closely by rayon. Cellulase had little effect on acetate rayon. A study on kinetics of enzymatic hydrolysis of lyocell fibres showed that the maximum hydrolysis rate occurred in the initial stage of the process, becoming progressively lower as time lapses due to the influence of inhibition effect by the accumulation of products.

Depilling mechanism of lyocell has been studied by Jose Morgado et al. [100]. The study shows that cellulase first attacks the cellulose from the microfibrills and then onto the surface of the fabrics that are more externally exposed. The hydrolysed cellulose from the microfibrills moved from the base fabric by cellulase enzymes and released to the treatment medium, where it has been widely attacked by enzymes present in the bath. Cellulase proved to be a thorough surface finishing agents, since they change only the fibre surface, not the crystallinity.

The commercial cellulolytic complex Econase CE, prepared from the *Trichoderma reesei* strain was used to treat three different types of regenerated cellulosic fibre. Celsol fibres made from enzyme treated cellulose pulp, AW fibres made from hydrothermally modified cellulose pulp and commercial viscose fibres were used [101]. The enzymatic treatment does not affect the molecular structure of cellulosic AW and celsol fibres. The tensile properties of the modified fibres remained at acceptable levels. It has been reported that the
changes in physical-mechanical parameters which takes place during the enzymatic modification of selected cellulosic fibres may improve the utility and comfort properties such as pilling and wrinkle resistance, wettability, dyeability, drapeability and soft feel of the fabric.

Pure jute finished with Biosoft (cellulase enzyme) under different conditions selected using Box and Behnken model and then tested for mechanical properties [102]. It was observed that enzymatic treatment caused considerable reduction in protruding surface hairs on the fabric and improvement in softness of the fabric. The treatment was found to improve ‘Fukrami’ and ‘Numeri’ and reduce the ‘Koshi’ and ‘Hari’. The total hand value of the fabric increased by more than 15 % for the sample treated with 4 % enzyme at 50ºC for 90 minutes.

The brightness of peroxide bleached jute material is increased by about 3 % when pretreated with an enzyme mix containing cellulase and xylanase [103]. Pretreatment reduced the peroxide requirement for bleaching. Treatment of jute with polysaccharide degrading enzyme reduced the inherent coarseness and rigidity of jute fibres and rendered them distinctly softer [104, 105].

Ramie fabrics were treated with three kinds of commercial enzyme mixtures and evaluated for scouring effects on pectic substances removal, whiteness, surface structure and mechanical properties [106]. Cellusoft, made from cellulase, acted on the surface of the fibres and removed fibrillar fuzz from the surface. Treatment by Ultrazyme, consisting mainly of pectinase, showed drastic effect on the removal of pectic substances in the fibre. Measurement of mechanical properties with Kawabata evaluation system revealed that untreated and treated ramie fabrics are still stiff with low elongation. Enzyme treatment made the fibre stiffer and less elastic.
Hemp fabric was hydrolysed with cellulase, hemicellulase and cellulase with additional β-glucosidase [107]. Crystallinity changed regardless of enzyme system and treatment conditions. The largest total porosity and the highest number of small pores occur when treated only with cellulase. The hemicellulase admixture helped to generate small sized pores initially but appeared to promote the formation of larger pores at longer treatment time. Celllobiose assisted in the creation of bigger pores from the start of the hydrolysis reaction.

2.6.3 Enzymatic treatment of polyester/cotton blended fabrics

Cotton fabric samples present in the polyester/cotton blended fabrics were treated with a formulation of a total crude *Trichoderma reesei* cellulase in a two step procedure to remove only the cotton portion [108]. In the first step, samples were treated at a low liquor ratio by padding through the enzyme formulation at 21°C with a wet pickup of 100 % and batched for 12 hours. As a second step, the samples were then treated at a high liquor ratio (1:25) with an identical enzyme formulation at 55°C, with intensive agitation. The pre-treatment influenced the overall weight loss and rate of hydrolysis in samples and the protein concentration in the liquor of the second step. The overall weight loss was 25–28 % (w/w) in the two-step procedure compared to a weight loss of 22 % (w/w) in the one-step batch hydrolysis.

Cotton samples were removed from polyester/cotton blended fabric by treatment with different concentrations of Cellusoft L in a rotawash machine with beating effects [109]. The high level of the beating effects enhanced enzymatic activity, thereby the weight loss increased from 7.5 to 100 % in the presence of discs and 100 mg/g Cellusoft L. The optimal conditions obtained for 100 % cotton samples were applied to the polyester/cotton fabric; the
maximum weight loss obtained was 45%. The cellulose hydrolysis of the blend remained relatively constant as the treatment continued; therefore, the total weight loss of the samples would not increase with the increase in treatment time, mechanical agitation and enzyme dosage.

2.6.4 Desizing of cotton fabrics

Malt extract was used originally for the desizing of amylaceous sizes present in the fabric. Later the enzyme amylase was isolated and marketed. A variety of these products are available commercially. They are mainly based on amyllopectic enzymes [110]. These enzymes are effective at various temperatures ranging from 20 to 115°C covering all means of application. Recently, an improved desizing process using a combination of amylase and lipase has been developed.

2.6.5 Enzymatic scouring of cotton fabrics

The dirt, sizes and natural impurities which are hydrophobic in nature are usually removed by alkaline scouring to achieve good absorbency of cotton. Enzymatic treatment of unscoured cotton fabric can be done with pectinase, cellulase, protease, lipase and other enzymes [111-113]. Cellulases are especially suited to scouring of cotton fabrics. The degree of whiteness of a cotton sample treated with cellulase alone was observed to slightly lower by 8-10 % than the degree of whiteness of alkaline boiled-off treatment. Pectinolytic enzymes can be used for enzymatic degradation of pectin adhering to cotton [114]. Pectinases and cellulases are very effective compared to the proteases and lipases [115].

Karapinar et al. [116] studies on three different pre-treatments of cotton fabric A, which was only boiled with water at 100°C; fabric B, which was only
de-sized with amylase; and fabric C, which was both boiled with water at 100°C and de-sized with amylase was treated with 6 different enzyme combinations for 3 different reaction times (30, 60, and 90 minutes) and compared with alkaline scouring. De-sizing a fabric alone is enough for effective scouring. Treatment time of 30 minutes is insufficient for effective scouring when compared with reaction times of 60 and 90 minutes. The combinations in which cellulase was present show more improvements than the other enzymatic combinations. The most similar results to alkaline scouring by means of wettability and pectin removal were achieved with cellulase + pectinase and cellulase + protease + pectinase.

Research work was undertaken to find optimum conditions of pH, temperature and incubation time and enzyme concentration for bioscouring of cotton knitted fabrics with an alkaline pectinase isolated from *Bacillus subtilis* WSHB04-02 by use of response surface methodology [117]. At optimum parameters such as pH 9.1, temperature 57°C, incubation time 1.25 hour and pectinase concentration 1.0 g/l in pectin removal combined with adequate wettability were reported. In addition, a boiling water pretreatment of 30 minutes before enzymatic scouring was found to be useful for subsequent pectinase treatment due to the improvement of the accessibility of pectinase to the pectin in cotton fibres.

An attempt has been made by Presja et al. [118] to develop a single bath treatment of pectinase and bleaching using peracetic acid. Viscometric method was used to prove that pectinases retained their activity in the presence of peracetic acid. An improvement in the efficiency of the single-bath treatment was observed with the addition of a chelator, tetrasodium pyrophosphate. A sufficient quantity of wax and pectin was removed and results in improved water absorbency of the treated fabric. The damage to the
cotton fibres was negligible and the degree of whiteness obtained was uniform and adequate for further dyeing.

Adamsen et al. [119] studied chelating agents and enzymatic retting of flax. Chelators added to pectinase-rich enzyme mixtures increased the efficiency of enzymatic retting of flax fibre fineness over chemical retting at an alkaline pH.

2.6.6 Enzymes in bleaching process of textiles

The residual hydrogen peroxide remaining after the bleaching process in textile material oxidises the dyes during dyeing process and results in uneven dyeing. Enzymes such as peroxidases or catalase commercially available as peroxide killer are used to kill the residual peroxide [120]. The catalase enzyme catalyses the decomposition of hydrogen peroxide into water and molecular oxygen. Besides peroxide decomposition, this treatment saves water, energy and chemicals.

2.6.7 Enzymes application in resin finishing of cotton

Lipase was used as an alternative to conventional alkaline treatment to restore the tensile strength of cotton fabrics treated with 1,2,3,4-butane tetracarboxylic acid (BTCA) [121]. The application of lipases in low concentration for short treatment time restored partially the strength loss of the fabrics due to the polycarboxylic cross linking. The lipase treatment improved the tensile strength with up to 10 %, causing 4 % alteration of the crease-resistance of the fabrics. A steady state of the tensile recovery was reached, possibly due to steric difficulties to form the enzyme/substrate intermediate complex or due to electrostatic repulsion between the negatively charged
binding/catalytic site of the lipase and the increasing negative charge of the cotton during the hydrolysis.

2.6.8 Dyeing of textile materials with enzymes

Cho et al. [122] describe a one-step chemoenzymatic reaction for the production of natural blue pigments, in which the geniposide from gardenia extracts was transformed by glycosidases enzyme to genipin. Genipin was then allowed to react with amino acids, thereby generating a natural pigment. Among the 20 tested amino acids, glycine and tyrosine were associated with the highest dye production yields. The natural blue pigments produced were used to dye cotton, silk and wool. The colour yields of the pigments were significantly higher than those of other natural dyes. The colourfastness properties of these dyes were fairly good, even in the absence of mordant.

Although it is not possible to reproduce the colours of nature by enzymatically catalysed reaction, the use of oxidoreductases catalysed in reduction/oxidation of vat dyes is an area worth exploring [123]. An enzymatic system can replace the hydrogen sulphide in the bath to prevent premature oxidation.

Commercial azo, triarylmethane, anthraquinonic and Indigoid textile dyes are efficiently decolourised with enzymes [124]. The presence of lignin peroxidase and or manganese peroxidase in addition to laccase increase decolourisation by upto 25%. The effect of textile dyeing auxiliaries depends on the individual enzymes.

2.6.9 Enzymes for wool and silk finishing

Wool is made of protein and the enzyme most widely used for modification is protease [44]. Ruffling up of the surface of wool garments by
abrasive action during dyeing to improve pilling resistance and softness is done using chlorine. Protease treatment on wool significantly improves the pilling performance of garments and increases softness. Proteases were also used to treat silk. Threads of raw silk must be degummed to remove sericin, a proteinaceous substance that covers the silk fibre. Degumming was performed in an alkaline solution containing soap which attacks fibroin, the fibre. However, the use of proteolytic enzymes is a better method because they remove the sericin without attacking the fibroin. Test with high concentration of enzymes show that there was no fibre damage and the silk threads are stronger than traditional treatments.

Chlorination is commonly used to modify the scales of wool fibres to confer resistance to felting shrinkage [125]. The enzyme that has been most successfully used to reduce shrinkability was papain, a vegetable protease. Among the sixteen proteases, esperase 8.0 L was found to be the most active, which reports the least damage when applied after sulphite treatment. Wool prickliness was eliminated by proteases treatment without detriment to other fibre properties. Bio-polishing of wool fibre with proteases removes the protruding fibres and keeps the fabric looking new after repeated washing.

Effect of biofinishing on cotton/wool blended fabric was studied with both cellulase and protease enzymes [126]. The enzyme treatment had significant effect on the physical and aesthetic properties of blended fabrics. The enzyme treatment reduced the protruding fibres and increased resistance to wrinkling, pilling and shrinkage.

Studies were carried out on multivoltine silk yarn and optimum conditions for degumming with proteolytic enzymes [127]. From the study, it was concluded that the twisted mulberry can be effectively degummed with
proteolytic enzyme (Biopril). This process can be carried out in a single bath without pretreatment or after treatment resulting in saving of time and energy.

Two proteases, viz Degummase and protease ‘A’ Amano 2, were used for biopolishing of different varieties of bleached and semi-bleached tasar silk fabrics [128]. Gum was completely removed by enzyme treatment in bleached tasar silk samples. Whereas some gum was left on semi-bleached and unbleached tasar silk. Improvement in lustre was observed in case of all varieties of tasar silk fabrics due to the cleaning of the fibre surface by enzyme. Degummase gave a higher weight loss with all the varieties of tasar silk and was more effective than protease A Amano 2.

A study on enzymatic treatment of silk showed that 5% concentration of protease and 10% concentration of degummase were sufficient for removal of gum [129]. Enzyme treatment followed by bleaching gave the best results of whiteness. The enzyme treatment increased the lustre and absorbency of silk fabric.

2.6.10 Enzymes for polyamide fibres

Polyamide fibres are obtained by the condensation of adipic acid and hexamethylenediamine. These fibres are hydrophobic and have poor wettability in an aqueous medium. Alkaline hydrolysis is an effective way to improve fibre wettability, but the action of concentrated solutions of NaOH or KOH is hard to control and results in extensive damage [130].

The use of hydrolytic enzymes can lead only to superficial hydrolysis of polyamide fibres. This is due to the fact that enzymes are relatively large molecules and do not penetrate into the tight hydrogen bonded structure of polyamide. These superficial changes would improve the fibre hydrophilicity
and chemical reactivity towards other agents for new finishing effects of polyamide, without causing significant damage. It is been reported cutinase can be used to modify the surface of polyamide fibres by hydrolysis of the amide linkages with the formation of amino and carboxylic groups [131]. Enzyme action produces some superficial cuts along the polymer, corresponding to breakage of the amide linkages. From the breakage of these linkages two hydrolysis products might result, adipic acid and hexamethylenediamine. Enzymatic hydrolysis of polyamide fabrics was followed by determination of amino groups in the solution and on the fibre surface [132].

2.6.11 Enzymes for acrylic fibres

Polyacrylonitrile or acrylic fibre is gaining importance because of its wool-like handle; easy care properties, good colourfastness, dimensional stability, moth and mildew resistance, pressed-in crease retention, resiliency, warmth, wrinkle resistance and chemical resistance. Like polyester, acrylic has the undesirable properties of poor abrasion resistance and pilling resistance [133]. Several attempts have been made to improve the eco-efficiencies of acrylic fibre production processes, including its subsequent dyeing. The chemical methods tried to make acrylic more hydrophilic and thereby enhance dye uptake, have not been successful. In turn, these methods affected the physio-chemical properties of acrylic because of elevated temperatures, aggressive chemicals and higher concentrations of dimethyl sulphoxide [134].

The enzymes nitratalase, nitrile hydralase and amidase catalyse the hydrolysis of acrylic fibres to corresponding amides, carbonic acid and ammonia. Studies have demonstrated that these enzymes improve many undesirable properties of acrylic under mild conditions. Surfacial nitrile groups of acrylic fibres were hydrolysed by the enzyme preparation to a maximum of
16 %, although acrylonitrile was known to be a very good substrate for both nitrilases and nitrile hydralases enzyme organisms [135]. However, the enzyme action on polyacrylonitrile is restricted to certain factors relating to the properties of the polymer. Firstly, rate of adsorption and de-sorption of enzymes to the polymer may affect the hydrolysis rate. Secondly, the crystallinity and hydrophobicity of acrylic fibres may limit the accessibility of nitrile groups to the enzyme [132]. More research is required to explore the high potential of nitrile degrading enzymes in the modification of acrylic fibres.

Cavaco-Paulo et al. [2] reported for the first time the action of cutinase on vinyl acetate, co-monomer in acrylic commercial fibre. The cutinase hydrolysis of acrylics (constituted by polyacrylonitrile and 7% of vinyl acetate as co-monomer) yields acetic acid, leaving vinyl alcohol at the fibre surface. Table 2.0 gives the cutinase enzyme activity on synthetic heterogeneous substrate.

**Table 2.1: Cutinase enzyme activity on synthetic heterogeneous substrate [2]**

<table>
<thead>
<tr>
<th>Substrates</th>
<th>Activity (U*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-nitrophenyl palmitate (PNPP)</td>
<td>1</td>
</tr>
<tr>
<td>Polyamide</td>
<td>( \sim 2.3 \times 10^{-3} )</td>
</tr>
<tr>
<td>Polyester</td>
<td>( \sim 2.5 \times 10^{-5} )</td>
</tr>
<tr>
<td>Acrylic</td>
<td>( \sim 4 \times 10^{-4} )</td>
</tr>
</tbody>
</table>
Guibitz and Paulo [136] review about the recent studies which clearly indicate that the modification of synthetic and natural polymers with enzymes is an environmental friendly alternative to harsh chemical methods. New processes using lipases, proteases, nitrilases and glycosidases have been developed for the specific non-destructive functionalisation of polymer surfaces. The specificity of enzymes has also been exploited in polymer synthesis; for example, lipases have been used for the production of optically active polyesters. Oxidoreductases have been used for the cross linking and grafting of lignaceous materials and for the production of polymers from phenolics. Enzyme engineering combined with sophisticated analysis techniques and screening assays should lead to the development of more efficient enzymes with higher turnover rates and stabilities in organic solvents.

2.7 Objective assessments of textile materials for handle properties

The effects of polyester content, pick density and weave on the thermal comfort and tactile properties of polyester/viscose blended yarn fabrics have been studied using low-stress mechanical properties of Kawabata evaluation system [137]. The fabrics with higher polyester content reported higher total hand value and higher thermal insulation, but lower air permeability and lower moisture vapour transfer. The fabrics with higher polyester content showed lower extensibility and twill woven fabrics reported higher extensibility than the plain woven fabrics.

Mechanical and surface properties were determined for polyester, cotton, and polyester/cotton blend knit fabrics [138]. The polyester fabric showed a higher resistance to tensile deformation than the cotton fabric, while the blend fabrics showed an intermediate resistance in accordance with the blend level. This behaviour was due to better packing efficiency of polyester fibres,
resulting in a yarn with a higher modulus. The compression behaviour, friction behaviour and contacting surface fibre counts increases with increasing cotton content in the fabrics; however, the 50/50 polyester/cotton blend fabric showed almost an identical behaviour as 100% cotton fabric.

Objective and subjective analysis of knitted fabric bagging was studied by Ucar et al. [139]. In that work fabric-bagging tests are performed on set of knitted fabrics that vary in design, tightness and blend ratio. The relationship between residual bagging heights ($R_{\text{residual}}$) obtained from the fabric-bagging test and the mechanical characterization determined from the KES-FB (Kawabata evaluation system) system is determined. The work showed that it is possible to predict $R_{\text{residual}}$ for knitted fabrics by using the standard KES-FB test and without performing fabric bagging fatigue tests.

Identification of the handle and sensibility of woven silk fabric and determination of relation between them were studied by Chunjeong Kim et al. [140]. Four hand factors such as surface, thermal, flexibility and dryness senses and three sensibility factors of classic, modern character and natural are determined. The hand factors are deeply related to the sensibility factor, a smooth and cool hand showed a modern sensibility, a smooth and warm hand showed a classic sensibility and a rough and warm hand showed a natural sensibility. The hand and sensibility of silk fabrics were deeply related to their mechanical properties, such as surface, bending, shearing, compression and thickness. The hand of smoothness, flexible and the sensibility of modern and classic were preferred than the hand of rough and stiff sensibility of natural character by consumer.

The treatment of wool fibre with potassium permanganate and proteolytic enzymatic treatment on the KES measurement for fabrics that
impact on fabric handle was monitored by Bahi et al. [141]. While the effect of the permanganate treatments alone on the wool fabric was relatively small, the combined effect with the proteolytic enzyme treatment was much more obvious. In particular, the shear hysteresis, which is the sensitive indicator of fabric softness and inter-yarn friction, increased significantly for the combined treatments. Subjective analysis clearly differentiates the enzyme treated wools.

The effects of mercerization, dyeing and printing with pigments on the hand properties of the woven fabrics produced with compact spun yarns were reported [142]. The handle properties of the fabrics tested in Shirley stiffness tester, circular bending rigidity tester and thickness tester. It was determined that yarn count, fabric weave and finishing treatment have a statistically significant effect on handle properties of the fabrics woven with compact spun yarns. All finishing processes results in stiffening of fabric of which pigment printing reported high. Although mercerization before dyeing and printing results in improvements in various fabric properties, this process influences the fabric softness in a negative way.

A method of calculating the general handle factor (GHF) of a woven fabric was developed on the basis of mechanical parameters determined at small stresses with the use of an Instron tension tester [143]. From the analysis it was reported that raw woven fabrics were characterised by the lowest value of GHF factor, whereas woven fabrics with elastomeric finishing have the highest GHF factor value. When considering the type of weave, fabrics with twill and combined weave were characterized by the best handle, whereas those with a plain weave by the worst. The highest values of the GHF factor were obtained for fabrics with the lowest weft density.
An objective approach to assess the handle of various knitted fabrics has been made by analyzing the force displacement curves [144]. In comparison to the conventional pulling through method, a rounded sample was pulled through a hole and from the space between two horizontal plates and the required pulling force was measured with respect to the displacement of specimen, recorded as a force-displacement curve. The results of the correlation test show that the features of the pulling-through curves associate with all mechanical and surface properties, except fabric thickness and compression energy.

The influence of different methods of industrial washing on denim properties was reported [145]. The denim has been processed by different industrial washing techniques, namely simple and silicone softening, washing with chlorine solution, enzyme and double enzyme washing. It can be concluded that the silicone softening made the greatest influence on the change of denim properties, whereas the simple softening the least one.

The effect of nano-ZnO coating on the frictional properties of cotton fabric–to–fabric and fabric–to–metal was reported by Yadav et al. [146]. The bulk-ZnO coated fabric resulted in significant increase in friction with both fabric and metal in comparison with control. In case of nano-ZnO coated fabric, due to its nano-size and uniform distribution, friction was significantly lower than the bulk-ZnO coated fabric.

The material properties important to fabric draping was measured using the Kawabata fabric evaluation system and the experimental data was incorporated into the system to calculate internal forces, so that the draping behaviour of a particular type of fabric can be dynamically demonstrated [147]. The simulation results prove that this system can reasonably reproduce the dynamical draping behaviour of the selected woven and knitted fabrics. In
dynamic simulation, it was found that the knitted fabrics have more deformation but smoother appearance than the woven fabrics due to their lower bending and shear moduli.

Factor analysis of assessment of the handle of a range of 156 men's summer fabrics by a panel of 56 judges who constitute Japanese and Chinese judges as one group and Australia, New Zealand and India associated with western judges as other group [148]. The analysis has been extended to include KES-F data on the mechanical and physical properties of these fabrics. The western judges indicate a preference for light-weight fabrics which have low thickness and low bending rigidity. A small deviation of surface roughness is preferred. The Japanese and Chinese judges appear to like materials with low bending and shear hysteresis and high tensile resilience. Fabric surface roughness, weight and thickness surprisingly seem to be unimportant.

Mitsuo et al. [149] in review paper on fabric handle and its basic mechanical properties reports that KES system has been used for various kinds of fabrics. Statistical investigation by neural network model has been very popular and the accuracy of prediction is higher than that of conventional regression methods. The drape behaviour of fabrics was studied using image processing system and new dynamic drape coefficients were defined. Image analysis is widely used for evaluating surface appearance.

A mathematical cantilever testing method was explained by Pierce [150]. It is possible to calculate flexural rigidity of the fabric by dividing the measured bending length by fabric weight, which is a measure of stiffness that would be appreciated by fingers. If flexural rigidity is divided by fabric thickness, we get bending modulus. This is a measure of fabric hand, using which one can differentiate full handle from paperiness.
2.8 Synthesis of enzyme from microorganisms

Microorganisms are attractive enzyme sources and these enzymes could be described as bio-chemically identifiable characters [151]. Enzymes are biocatalysts and they are responsible for running the cellular factory, mainly in the case of microbes. These microbes are unicellular known for their efficiency in production of different enzymes according to the environmental stimuli.

2.8.1 Microbial lipase

Nearly 100 years ago the microbiologist Eijkmann reported that several bacteria could produce and secrete lipases. When results confirmed that lipases remain enzymatically active in organic solvents [152], studies began to develop these enzymes as ideal tools in the synthesis and reactions. Lipase finds wide application in synthetic organic chemistry [153-157] because they display exquisite chemo selectivity, regioselectivity and stereo selectivity. They can also function in a synthetic mode in esterification (ester synthesis from alcohol and acids) or trans-esterification reactions [158, 159]. They are readily available in large quantities and many of them can be produced in high yield from microbial organisms, namely fungi and bacteria. The crystal structures of many lipases have been solved, facilitating considerably the design of rational engineering strategies. It is worthy to note that they do not usually require cofactors and they do not catalyse side reactions.

Lipases are enzymes belonging to the group of serine hydrolases (EC 3.1.1.3). Their natural substrates are triglycerides and their mode of action is similar to that of esterases. However their activity is considerably increased when they are located at the polar or non-polar interface [160]. This flexibility of different substrate specificity among the different lipases gave these
enzymes an enormous potential application [161]. The lipases can also bring about deterioration of dairy products and oils [162].

### 2.8.2 Extracellular lipases

A large number of microorganisms are capable of using natural oils and fats as carbon source for their growth. The lipase enzyme is responsible for the breakdown of the oils and fats prior to their digestion by the microorganisms and catalysis the hydrolysis of triglycerides to free fatty acids, partial glycerides (mono and diglycerides) and glycerol [163]. The activity of extracellular enzymes is many times greater than the activity of intracellular enzymes. Most of these enzymes are inducible in nature. Generally bacterial lipases are glycoprotein but some are extracellular lipases, which are lipoproteins. The production of extracellular lipases from bacteria depends on carbon and nitrogen sources, inorganic salts, presence of lipids, temperature and availability of oxygen. Most lipases are non-specific in substrate specificity and a few bacterial lipases are thermostable [164, 165]. Chief producers include *Pseudomonas sp.*, *Bacillus sp.*, *Staphylococcus sp.*, *Chromobacterium*, *Propionibacterium*, *Achromobacter* etc., [166].

### 2.8.3 Source of lipases

Lipases can be found in plants, animals, vegetable cells and microorganisms. Lipase-producing microorganisms have been found in diverse habitats such as industrial wastes, vegetable oil processing factories, dairies, soil contaminated with oil, oilseeds and decaying food [167], compost heaps, coal dips and hot springs [168]. The screening strategies for lipase producing organisms reported by Sztazjer et al. [169], says that a relatively small number of bacterial lipases have been well studied as compared to plant and fungal lipases.
2.8.4 Structure of lipases

The basic features of 3D structure of the *Rhizomucor miehei* lipase was described first by Brady et al. [170]. All lipases whose three dimensional structures are known belong to the class of the $\alpha/\beta$ hydrolase fold family [171]. Together with other members of this family like serine esterases, thioesterases, dinelactone hydrolase and bromoperoxidase A2, they share a common fold composed of a central $\beta$-sheet of up to eight different $\beta$-strands connected by up to six $\alpha$-helices and a common catalytic mechanism composed of five subsequent steps. A catalytic triad consisting of the residual serine, glutamate or aspartate and histidine forms the active site of lipases [172].

2.8.5 Screening for microbial lipases

To characterize the enzyme a quantitative assay for lipase activity was needed, particularly for lipolytic enzymes present in the extracellular fluid. Lipase activity screening procedures such as titrimetric and calorimetric methods are time consuming and are not suitable for routine large scale screening operations. Lawrence et al. [173] reports screening procedure for lipase activity on agar plates can be done more conveniently and quickly using tributyrin.

2.8.6 Synthesis of extracellular enzyme

Samad et al., [174] reported that the glycerol and lecithine in the production medium can stimulate the production of lipases. Maltose was found to be the best carbon source and peptone the best nitrogen source for the synthesis of enzymes from *Rhizopus rhizopodiformis*. Shabti and Dayamishne [175] reported that soybean oil containing medium would be the best one for the synthesis. Kamini et al., [176] said that olive oil would be the best
for replacing soybean oil. Groundnut oil was recommended by Kumar et al., [177]. Savitha and Ratledge found sunflower oil [178] as effective inducers of lipase enzymes. Tween 80 [179] and latex for *Calotropis gigentea* [180] was found to be effective inducers. Sauer Kraut Brine could serve as a substrate for the synthesis of extracellular lipase from *Geotrichum candidum* ATCC 34614 and wheat bran, rice bran and bagasse have been widely used as the solid substrates for the fermentation [181].

Otero et al. [182] studied fourteen noncommercial microbial lipase preparations using different culture media. In spite of the low concentrations of active proteins in the culture media, all of these preparations displayed significant activities for both hydrolysis and synthesis reactions. *A. murorum, M. mucoroides, F. poae, O. sulphureo-ochraceum, R. araucariae, S. halstedii, F. oxysporum, P. chrysogenum, B. linens* and *S. fradiae* have been studied and characterized. Fungi provide a huge potential source of enzymes. Most of the enzymes of interest are active in a polar solvent. Lipase preparations from *P. cepacia, S. halstedii, Streptomyces* sp. and *R. araucariae* could be suitable biocatalysts for the synthesis of esters in polar media.

*Serratia marcescens* isolated from raw milk was found to produce extracellular lipase [183]. The growth of this organism could contribute to flavour defects in milk and dairy products. *Serratia marcescens* was streaked onto spirit blue agar medium, and lipolytic activity was detected after 6 hours at 30°C and after 12 hours at 6°C. The purified lipase had a final recovered activity of 45.42 %. Its molecular mass was estimated by SDS-PAGE assay to be 52 kDa. The purified lipase reported the optimum pH between 8 and 9 and showed about 70 % of its activity at pH 6.6. The optimum temperature was observed at 37°C and exhibited high activity at 5°C. The thermal inactivation
of *S. marcescens* lipase was more obvious at 80°C and was completely inactivated after heating at 90°C for 5 minutes.

Extracellular lipase was isolated and purified from the culture broth of *Pseudomonas aeruginosa*, an extremophile which naturally grows in water-soluble mineral cutting oil used for cooling and lubrication in industrial metal works [184]. The molecular mass of the purified lipase was estimated by SDS-PAGE to be 54 kDa. The optimum pH and temperature were 11 and 70°C respectively. The enzyme is stable over a broad pH range (pH 4-11.5). The lipase preferably acted on triacylglycerols with medium chain fatty acids. The lipase was inhibited strongly by Zn$^{2+}$, Hg$^{2+}$, Cu$^{2+}$ and slightly by Ca$^{2+}$ and Mg$^{2+}$. Non-ionic detergents and sodiumdeoxycholate enhanced lipase activity. Lipase from *P. aeruginosa*, finds applications in the metal industry and organosynthetic reactions.

An expression vector system was developed for the secretory production of recombinant *Bacillus stearothermophilus* lipase in *Saccharomyces cerevisiae* [185]. The mature lipase gene was fused to α-amylase signal sequence from *Aspergillus oryzae* for the effective secretion into the culture broth and the expression was controlled under GAL10 (the gene coding UDP-galactose epimerase of *S. cerevisiae*) promoter. *S. cerevisiae* successfully secreted lipase into the culture broth. To examine an optimum condition for lipase expression in the fed-batch culture, lipase expression was induced at three different growth phases (early, mid, late). Maximum production of lipase (1,254,000 U/l) was found when the culture was induced at an early growth phase. Secreted recombinant lipase was purified only through CM-Sepharose chromatography, and the purified enzyme showed 1,963 U/mg of specific activity and thermoalkalophilic properties similar to those reported for the enzyme expressed in *Escherichia coli*. 
Kamzolova et al. [186] studied about lipase secretion from *Y. lipolytica* and citric acid synthesis on media containing animal fat or rapeseed oil as a sole carbon and energy source. Rapeseed oil of concentration not less than 5 g/l was observed as the optimal medium. Under optimal conditions of cultivation, citric acid production by rapeseed oil-grown yeast *Yarrow lipolytica* 187/1 amounted to 135 g/l; specific rate of citric acid production reached 127 mg/hour.

Sibel et al. [187] studied the synthesis of lipase by *Candida rugosa*. High yields of enzyme activity (5.58 U/ml) were obtained with yeast extract and protease-peptone as nitrogen source in the medium with olive oil, the minimum lipase activity (2.81 U/ml) was observed with tryptone and lactose. Biomass concentration ranged from 1.76 to 2.05 mg/ml and 0.09 to 0.23 mg/ml in the medium with and without olive oil respectively. The lipase activity and lipase specific activity were higher in bran than in soybean flour and cheese whey.

Lipase production in *Aspergillus niger* J-1 was tested using both submerged fermentation (SmF) on a mineral culture medium and solid-state fermentation (SSF) on wheat bran [188]. The maximum lipase activity was obtained during the submerged fermentation in a medium containing glucose at 2 % and olive oil at 2 %. However, 4.8 U/ml of lipase activity was reached using solid-state fermentation process with a medium containing 0.75 % of ammonium sulphate and 0.34 % of urea. The optimum pH and temperature for enzymatic activity were 6 and 40°C respectively. The enzyme also exhibited 80 % of its initial activity in neutral and mildly acid media and at temperatures between 20 and 30°C for a period of 24 hours.
Koblitz et al. [189] studied the purification and characterization of lipase from *Rhizopus sp.* and reports that lipase extracted could be purified to SDS-PAGE homogeneity, although the lipolytic fraction seemed to contain two lipase isoforms. The lipase studies showed a high optimum temperature and also good stability in hydrophobic solvents. Lipase can be used for esterification reactions in organic media.

The preparation of triglyceride lipase from defatted pig adipose tissue powder was extracted and their properties were compared with hormone sensitive lipase [190]. The triglyceride lipase is active in the absence of serum and is clearly separable from lipoprotein lipase by heparin/sepharose affinity chromatography. The triglyceride lipase was able to hydrolyze the triolein emulsified in gum arabic. The specific activity of the purified triglyceride lipase was low. This may be due to partial inactivation of the lipase during the preparation of delipicted tissue powder with organic solvents.

Micro organisms isolated from soil samples were screened for their ability to degrade various biodegradable polyester-based plastics [191]. The most active strain, designated as strain TB-13, was selected as the best strain for degrading these plastics. From its phenotypic and genetic characteristics, strain TB-13 was closely related to *Paenibacillus amylolyticus*. It could degrade poly (lactic acid), poly (butylene succinate), poly (butylene succinateco- adipate), poly (caprolactone) and poly (ethylene succinate) but not poly (hydroxybutylate-co-valerate). However, it could not utilize these plastics as sole carbon sources. Both protease and esterase activities, which may be involved in the degradation of plastic, were constitutively detected in the culture broth.
2.9 Conclusion

It is evident from the literature that most of the reported works on the surface modification of polyester fabric were with enzymes synthesized from different microbial organisms and few commercially available enzymes. The commercially available enzymes for polyester do not have much activity on surface functionalisation and hence there is a necessity to find a suitable microorganism to synthesis lipase enzyme which could have potential to hydrolyse the surface of polyester fabric.

Further, it is also evident from the reported works that the hydrolysed polyester fabric by either alkali or enzymatic treatment was characterized by any few of the following methods such as the assessment of hydrophilicity by percent weight loss and capillary rise test, determination of hydroxyl and carboxyl groups by reactive and basic dyes, identification of functional groups by FTIR, crystallinity measurement by XRD methods, thermal properties by DSC, surface morphological changes by scanning electron microscope, surface roughness by atomic force microscope and handle property by Kawabata analysis and no one reported on the testing the enzyme treated samples with all the above methods.