CHAPTER 1

INTRODUCTION

1.1 GENERAL INTRODUCTION

In the evolution of this research, it became apparent that the cellulase treatment applied to regular and compact yarns and production of hybrid composites needed examination through the development of various new sophisticated techniques. The initial objective of this study was therefore to develop methods to study the response of these yarns and composites to various treatments. The level of changes in mechanical properties of regular and compact yarns and hybrid composite and these translation of the property differences are important

When human life began on the earth, food and shelter were the two most important necessities. Immediately thereafter, came clothing. The first materials used for clothing were fur, hide, skin, and leaves. All of them were sheet like, two- dimensional structures, not too abundantly available and somewhat awkward to handle. A few thousand years ago, a very important invention was made to manufacture two-dimensional systems–fabrics from a simple mono-dimensional element fibres. It was the birth of the textile industry based on fibre science and technology. Fibres were readily available everywhere; they came from animals (wool, hair, silk etc.) or from plants (cotton, flex, hemp, reeds, etc.). Amongst these natural fibres, cotton is the most used fibre until today.

1.1.1 Cotton History

The word ‘cotton’ comes from an Arabic word *'qutun'* or *'kutun'* used to describe any fine fabric. Archaeologists found cotton fabric nearly 5000 years ago at ‘Mohenjo Daro’, an ancient town in the Indus River Valley of India (now West Pakistan) (NCC 2005; cotton.org 2005). Around 300BC, the army of Alexander the Great brought cotton goods into Europe, but the cloth was so expensive that only the rich could afford it (cotton.org 2005). In the early 17th century, the southern American colonies began harvesting cotton and making a coarse fabric for their own use. The development of the cotton industry took a dramatic upward turn in the 18th century as Britain acquired colonies suitable for the harvesting of cotton. Moreover, improvements in textile machinery made it possible to spin stronger yarns.

In the early 19th century, the southern American states became the biggest single supplier of cotton to the now thriving English textile mills. By the end of the 1920s, the United States was producing more than half the world's cotton (LSU 2005). Since then many other countries have increased their production, with manufacturing being carried out mainly in Europe and Asia. Today, cotton is the most widely used fibre. Almost one-half of the total world fibre demand is for cotton.

1.1.2 Cotton: from Fields to Textiles

The word Textile comes from the Latin word ‘Texere’ that means to weave, and was originally only applied to woven fabrics. It has become, however, a general term for materials made of fibres and yarns. Today the textile industry is one of the largest and basic industries worldwide. The modern textile industry covers different consumer sectors such as apparel textiles, household textiles, medical textiles, and technical textiles. The production of fabrics includes many steps starting from raw cotton. The production of cotton starts with cotton harvesting and converting it into yarns by processes like ginning and spinning. Then the yarns can be converted to stronger yarns by sizing (Rouette 2001). Sizing makes the warp yarns stronger and reduces friction during weaving. The resulting textiles are known as grey fabrics (Karmakar 1999). Grey fabrics are not ready to use, because of their hydrophobic nature (water repellent) and unwanted colours (Rouette 2001; Karmakar 1999). Therefore, grey fabrics undergo a wet-pretreatment consisting of a chain of chemical treatments that alters the properties of cotton fabric, for example – texture, converting fabrics from hydrophobic to hydrophilic and making them brighter in terms of colour (Rouette 2001). Thereafter, fabric is dyed and or printed before the final apparel production. Finally the cloths go to consumer via the outlets. Amongst the various stages of cotton preparation, wet pre-treatment is a highly energy, water and chemicals consuming step (Rouette 2001).

1.1.3 Wet Pretreatment Process for the Cotton Textiles

Wet textile processes are called 'wet' because they use water as the medium for transport of mass and heat across textile materials. Wet pre-treatment consists of desizing, scouring and bleaching (Rouette 2001; Karmakar 1999). A short description of these three stages is given below.

The **desizing** process involves the removal of starch from the fabric. Starch is added to yarns before weaving to strengthen them. Traditionally desizing was carried out using hydrogen peroxide (H_2O_2) and sodium hydroxide (NaOH), however since the 1950's, enzymatic desizing processes based on α-amylases have been widely introduced and implemented successfully in the textile industry. Nowadays thermostable α-amylases produced by bacteria, especially from *Bacillus subtilis*, are widely available and active in the temperature range of 40-110°C (Neierstrasz & Warmoeskerker 2003).

Scouring - also known as boil off, kiering, kier boiling or caustization is the first process step in which the fibre surface is treated (Rouette 2001). The objective of a scouring process is to make the material hydrophilic, before it undergoes other processes like bleaching and dyeing. A desired hydrophilicity during scouring can be achieved by removing non-cellulosic material from the cotton fabric, especially from the cuticle (waxes and fats) and the primary wall (e.g. pectin, protein and organic acids). More precisely scouring not only removes non-cellulosic material from cotton fibres but also removes substances that have adhered to the fibres during the production of the yarn or fabric. Substances like, dirt, lint, pesticides, oils, and any sizing agent applied to yarns to facilitate weaving (Rouette 2001; Karmakar 1999; Hardin & Li 1997; Lin & Hsieh 2001; Buchert 2000; Etter et al 1999; Lenting et al 2002). Effective scouring is essential for subsequent processing of any cotton made substrate, regardless of its natural source.

Bleaching is the last chemical process before dyeing that eliminates unwanted coloured matter from fibres, yarns or fabrics. Bleaching of cotton fabric needs intense reaction conditions, to make the fabric free from seed coat fragments, and to achieve a required degree of whiteness (Rouette 2001; Karmakar 1999). Traditionally, a bleaching process is performed oxidatively at an elevated temperature (90°C to 100°C) and at high concentrations of H_2O_2 and NaOH. In the past, the enzyme laccase has been tried for bio-bleaching but the results have not been promising (Tzanko et al 2001).

Tzanko et al (2002) claimed that, under controlled laboratory conditions, a whiteness equivalent to industrial bleach can be achieved by H_2O_2, generated via the enzyme glucose oxidase. However, till date no bio-bleaching process has been introduced on the industrial level. Recently the focus has been shifted towards the use of low-temperature oxidative catalyst for the bleaching of cotton fabrics (Topalovic 2002).

Wet pre-treatment steps for fabrics involve the addition or removal of solid-liquid substances to or from the fibre surfaces. Therefore, mass transfer is an important phenomenon in wet pre-treatment of textile finishing (Moholkar 2002). In order to improve existing wet pre-treatment processes, knowledge of several scientific disciplines such as enzyme technology, biochemistry, fibre science, polymer technology, colour chemistry, mechanical engineering, chemical engineering and applied physics is required. Thus, wet textile processing can be seen as the most knowledge-intensive area of the entire textile processing chain.

1.1.4 Overview of the Alkaline Scouring for Grey Cotton

One of the earliest techniques for the scouring of cotton fabric involved the use of potash, the by-product of wood combustion (Rouette 2001; Karmakar 1999). A major component of wood ash is potassium oxide, and when wood ash is added to water, the potassium oxide reacts to produce potassium hydroxide, a strong alkali. Early textile chemists prepared their fabric by treating the fabric in hot slurries of potash, followed by neutralisation of the treated fabric in solutions of buttermilk (Rouette 2001; Karmakar 1999). Although it can be argued that the chemicals used by ancient textile chemists were of *'natural'* origin, the release of these natural substances did not have a positive impact on the environment. Soap is an example of a supporting scouring agent, before the introduction of synthetic detergents. The major drawback with soap as a supporting agent is its tendency to form insoluble calcium salts or *'scum'* in hard water (Menachem & Pearce 1998).

Even today, alkaline scouring of cotton is still the most wide spread commercial technique for removing or rupturing the fibre cuticle to make the fibre absorbent for the cotton processing. Various scouring agents used in the textile industry are listed in the Table 1.1. Although sodium hydroxide is used generally for the scouring, sodium carbonate and calcium hydroxide are also mentioned as a scouring agent (Rouette 2001; Karmakar 1999; Menachem Lewin & Pearce 1998; Throtman ; Carr 1995). Scouring of cotton fabric is typically done with a hot solution (90°C to 100°C) of sodium hydroxide (± 1 mol/L) for up to one hour (Rouette 2001). The concentration of alkali used and the time and temperature conditions needed depend on the condition of the starting materials and the desired quality of the scoured fabric. Reducing agents are added during the scouring process to prevent oxidation of cellulose by air oxygen at high pH.

Other chemicals for instance, wetting agents, emulsifying agents and chelating agents (Menachem Lewin & Pearce 1998; Throtman 1984 ; Carr 1995) are also included in typical preparation baths for scouring. Wetting agents act by reducing the surface tension of water enabling improved penetration of the chemicals into the cotton fabric. Emulsifying agents assist in removing waxy materials. Chelating agents remove polyvalent metal ions such as calcium, magnesium, iron or other salts that can have a harmful effect on subsequent wet-processing operations. Polymeric materials can also act as chelating agents or as pickup enhancing agents for the application in continuous preparation processes. These various chemicals tend to be used in excessively high amounts (Rouette 2001; Karmakar 1999; Throtman 1984).

The key factors for a successful industrial scouring process are the concentration of the NaOH, the treatment temperature, the reaction time and the exclusion of air to avoid weakening the fibre by the formation of oxy-cellulose (Karmakar 1999). In view of the high extracting action of the scouring process, the final effect obtained also depends on the efficiency of the subsequent rinsing steps.

Table 1.1 Classification of traditional scouring agent (Karmakar 1999)

S. No.	Scouring	Chemicals
1	Alkaline agents	NaOH, KOH, Na_2CO_3, Liquid NH_3 sod. metasilicate, sodium silicate, sodium phosphate, trisodium phosphate, tetrasodium phosphate, sodium tripolyphosphate and borax
2	Surfactants	Anionic activator, non-ionic activator
3	Organic solvent	Chlorine system: Carbonate trichloride, trichloroethylene, perchloro ethylene, methyl chloroform, trichloro methane, fluorine
		Hydrocarbon system: Benzene, industrial gasoline, white spirit, solvent naphtha

Cotton fabrics arrive at mills with a number of impurities. This includes motes, seed coat fragments, pesticides, dirt, chemical residues, metallic salts of various kinds, and immature fibres. The clear mechanism of action of alkaline scouring on various non-cellulosic materials in the cotton fibre is given in Table 1.2.

Scouring with NaOH cleans by physical loosening fragments from the fabric and by dissolution of metallic salts and chemical residues. It softens and preconditions the seed coat fragment materials entrapped in the yarns and the fabrics. The dilute alkali swells the seed coat fragment material and opens up the cell structure to access the hydrogen peroxide in bleaching that takes place later. The swelling process helps to loosen the attachment of the seed coat fragments from the yarn and fibres. High temperature in the presence of sodium hydroxide melts some of the waxy material and converts some of it to a water-soluble form. It also converts non-cellulosic material (pectins, hemicelluloses and proteins) in the cuticle-primary wall to water soluble forms to effect removal.

More precisely, the scouring process is based on the reaction between cotton impurities and alkali hydroxide. Traditional scouring implies a certain alkali consumption that determines the minimum concentration of sodium hydroxide to be used. When sodium hydroxide is brought into contact with the cotton fabric, some of the alkali absorbs, since the hydroxyl groups of cellulose have a weak acidic character (Rouette 2001). So, at pH around 13-14, cellulose absorbs about 1% or 10g/kg of sodium hydroxide. Alkali is also required to neutralise the carboxyl group of the pectins. About 0.5% of the sodium hydroxide concentration is required to change the pectins into water soluble salts of pectic or meta-pectic acid (Karmakar 1999). . Neutralisation of the amino acids obtained by hydrolysis of the protein used around 1% of sodium hydroxide. It is evident that around 3% to 4% (±1 mol/L) of sodium hydroxide is necessary for the saponification of waxes and to maintain sufficient alkalinity (Rouette 2001; Karmakar 1999). Literature reveals that fats are esters of fatty acids with glycerol which constitute around 37% to 47% of the total fat constituents. They have low melting points and are hydrolysed into soaps and glycerol (saponification reaction) quite easily using an aqueous solution of NaOH (Nierstrasz & Warmoeskerkern 2003; Manchem & Pearce 1998; Throtman 2001)

So, during the scouring process, the intra and intermolecular hydrogen bridges of the cellulose are cleaved and the polar hydroxyl groups of the polysaccharides are solvated. The fabric swells, and this facilitates transport of the impurities from the interior of the fibre to the outside.

Table 1.2: The removal of impurities of cotton fibre during alkaline scouring process (Rouette 2001; Karmakar 1999; Nierstrasz & Warmoeskerkern 2003; Manchem, Lewin & Pearce 1998; Throtman 2001)

Impurities	Mechanism of impurity removal
Fats and waxes	• Saponification: The saponifiable parts of waxes (fatty acid, glycerides, and esters) are converted in to soap. • Emulsification: The non-saponifiable parts of the waxes such as alcohols and hydrocarbons are emulsified by the soap formed. • High temperature: melts some of the waxy materials and converts some of it to a water soluble form. • In extreme cases the use of solvent is necessary.
Pectin and related substances	• Solubilisation: by the action of alkali, which also acts as a swelling agent to facilitate removal • Pectins are converted to water soluble salts of pectic or meta-pectic acid
Proteins and amino acids	• Hydrolysis: Proteins are hydrolysed with the formation of soluble sodium salts of amino acid.
Hemicelluloses	• Dissolution: Hemicelluloses with low DP are dissolved in NaOH.
Inorganic substances, minerals and heavy metals	• Partially dissolve in NaOH • By producing more soluble salt e.g. acid demineralisation • By use of sequestering or chelating agents.

1.1.5 Drawbacks associated with the alkaline scouring

The scouring process requires large quantities of chemicals, energy and water and is rather time consuming (Nierstrasz & Warmoeskerkern 2003). Owing to the high sodium hydroxide concentration and its corrosive nature, intensive rinsing is required that leads to a high water consumption. The use of high concentrations of sodium hydroxide also requires the neutralisation of waste water, which requires additional acid chemicals. Furthermore, the alkaline effluent requires special handling because of very high BOD and COD values. Apart from the above wet processing problems, the biggest drawback of alkaline scouring is a non-specific degradation of cellulose that produces fabrics of lower tensile strength and therefore of lower quality. Moreover, alkaline scouring is hazardous to the workers and creates an unpleasant work atmosphere. Although alkaline scouring is effective and the costs of NaOH are low, this process can be improved considerably to meet today's energy and environmental demands.

1.1.6 Overview of Enzymatic Scouring

Enzymes are substrate specific bio-catalysts; they operate best at ambient pressures, mild temperatures and often at a neutral pH range. Enzymes are gaining an increasingly important role as a tool in various wet textile pre-treatment and finishing processes (Nierstrasz & Warmoeskerken 2003; Hardin 1997; Stephen 1957). Biocatalysts have proven to be a flexible and reliable tool in wet textile processing and a promising technology to fulfil the expected future requirements. Enzymatic scouring has been investigated extensively by various institutes and laboratories now for nearly one decade (Lin & Hsieh 2001; Buchert & Pere 2000; Etters et al 1994; Buschle-Diller et al 1998; Cavaco-Paulo et al 1996). Initial investigations explored the possibility of cotton scouring with enzymes, to see if cotton could be made hydrophilic in a reasonable time. Extracellular enzymes involved in the degradation of the plant cell wall's outer layer during the invasion of the plant, excreted by phyto-pathogenic fungi and by bacteria have been considered as candidates.

Different enzymes like pectinases such as lyases (EC 4.2.2.2); polygalacturonase endo acting type (EC 3.2.1.15) and polygalacturonase exo acting type (EC 3.2.1.67), proteases (EC 3.4.21-25), cellulases such as endoglucanases (EC 3.3.1.4); cellobiohydrolases (EC 3.2.1.91), xylanases (EC 3.2.1.8), lipases (EC 3.1.1.3) and recently cutinases (EC 3.1.1.74) have been examined to degrade and subsequently remove the natural component present in the outer layer of cotton fibres (Lin & Hsieh 2001; Buchert 2000; Etters 1994; Cavaco-Paulo et al 1996, Csiszar et al 2001; Degani et al 2002).

The scheme essentially contains the impregnation of cotton fabric with one or more enzymes in presence or absence of surfactants and chelators, followed by a high temperature rinsing step. The enzyme incubation time used, was up to 24 hours depending on other process conditions and the density of the fabric.

Lipases, were found to be less effective in fulfilling this task (Buchert 2000). Proteases were found to be efficient to improve whiteness rather than hydrophilicity (Lin & Hsieh 2001). Cellulases were the only enzymes reported to improve the wettability efficiently when applied without any other treatment or in combination with other enzymes. However, cellulase also causes a decrease in fibre strength and hence a decrease in fabric quality (Cavaco-Paulo et al 1996,1998; Csiszar et al 2001; Hartzell & Hsieh 1998; Lenting et al 2001; Li & Hardin 1998; Pere et al 2001). The best results have been obtained by alkaline pectinases or pectinases in combination with cellulase. Especially bacterial alkaline pectinase, a pectate lyase (EC 4.2.2.2) has been proven to be effective

(Buchert & Pere 2000; Etters et al 1999). Hardin & Li (1991) postulated that pectin acts as cement in the primary wall of cotton fibres. After enzymatic destabilisation of a pectin structure, the different components present in the primary wall layer can be removed easily in subsequent rinsing steps. A proper interpretation of the enzymatic action on cotton fibres on a molecular basis was not possible because of the lack of structural knowledge of cotton fibre and grey cotton fabric.

Cellulase, Acidic pectinase, Alkaline pectinase, Lipase, Protease, Hemicellulase or any combinations of the above enzymes were used. Enzyme incubation was carried out for 1 - 24 hours at 95°C for >15 minutes followed by rinsing with water.

A typical adopted approach in the past towards enzymatic scouring process of cotton fabrics by Hardin & Li 1997; Lin & Hsieh 2001; Buchert & Pere 2000; Etters et al 1999; Lenting et al 2002; Throtman 2001; Hartzell & Hsieh 1998; Li & Hardin 1998; Pere et al 2001 are presented. From the literature, it can be concluded that enzymatic scouring of cotton fibre is possible (Hardin & Li 1997; Lin & Hsieh 2001; Buchert & Pere 2000; Etters et al 1999; Lenting et al 2002; Throtman 2001; Hartzell & Hsieh 1998; Li & Hardin 1998; Pere et al 2001). However, it still faces several problems such as longer incubation time with enzymes, non-uniformity of enzyme treatment and sometimes a lack of fundamental knowledge to explain the obtained results. The potential advantages that can make enzymatic scouring commercially attractive include better quality (texture and tensile strength), less waste water, energy savings and compatibility with other processes, machinery and materials.

1.1.7 Definition and Research Strategy

Several attempts were made to develop enzyme technology for cotton scouring. Still this process faces several problems like a need for long incubation time, high enzyme doses, sometimes non-uniform enzyme action, uneven dyeing behaviour, high temperature water treatment before enzyme incubation and overall slow process speeds (Hardin & Li 1997; Lin & Hsieh 2001; Buchert & Pere 2000; Etters et al 1999; Lenting et al 2002; Throtman 2001; Hartzell & Hsieh 1998; Li & Hardin 1998; Pere et al 2001). A rational approach is necessary to design a new efficient enzymatic scouring process. Several aspects such as the specificity of enzymes, the complexity of the substrate (cotton fibre) and mass transfer, need to be considered for a successful and efficient enzymatic scouring process. A systematic approach will lead to the design of a new cotton scouring process in which the selected enzymes are efficiently used to remove specific unwanted components to achieve hydrophilic fabric.

The aim of this research is to study the potential of enzyme technology to design an efficient and fast low-temperature scouring process for grey cotton yarns. In other words, the aim is to obtain a hydrophilic cellulosic yarn surface, which is well accessible for chemicals that are used in textile treatment steps like bleaching and dyeing.

1.1.8 Cotton yarns

The textile industry is undoubtedly one of the oldest and the largest industries in the world. Even though numerous types of fabrics made from different materials are manufactured for multiple use across the world, the most common and universal fabric is cotton. There are two technologies available to spin the yarn, first and the foremost is Ring Spun and second is

Open End. With the development in technology, and changing need of people world over different types of cotton yarns like 100% cotton compact yarn, 100% organic cotton yarns, 100% cotton mercerized yarns etc. have been developed which are used to manufacture a wide variety of cotton fabrics and clothing. Landmark International is one such leading supplier of 100% cotton yarns which deals in high end and high quality yarns used to manufacture clothing and made-ups. The process of making fabric from raw cotton is a long one and consists of various stages. Mostly ring spun yarns are used for producing fine quality clothing, bed linens, bed sheets, bed spreads, pillow covers etc., while open end yarns are used for manufacturing denim wear, towels, etc This is similar to treating different diseases with different medicines. Like a wrong medicine can prove hazardous for the heath of a patient, in a similar way a wrong choice of yarn will result in the creation of the wrong type of fabric or clothing.

The basic difference between the yarns is their count. Different counts are used to make different type of fabrics. In some cases, the cotton yarn is blended with some other yarn in different ratios to provide different effects like shining or to lend more elasticity to the yarn. It is the yarn count and the twisting mode of the yarn that actually determines the overall strength and look of the manufactured fabric. 100% cotton compact yarn and 100% cotton mercerized yarns have less hairiness and the fabric made from these is of fine quality and is used for manufacturing luxury clothing and bedding.

Yarn trading is a fast growing industry and for achieving success in this field it is vital to first become familiar with the wide variety and types of yarns that are available.

1.2 MOTIVATION AND OBJECTIVES

A considerable amount of work on the effect of enzymatic treatment on the properties of textile yarns and fabrics has been reported. What appears to be less emphasized is the effect of cellulase on the properties of regular and compact yarns. These yarns differ in structure and properties and a study of the response of these to cellulase treatment will shed considerable light on the way that fabrics containing these yarns needs to be processed in wet finishing. The precaution that should be taken during wet processing will be helpful as a result of this study.

Environmentally friendly polymer composites obtained from natural bio-derived reinforcements have received considerable attention during the recent past due to cost effectiveness and increased environmental awareness (Bledzki Faruk et al 2006, Panthapulakkal Sain 2007). Several bio-based fibres such as wood, sisal, jute, flax, abaca, banana, oil palm, pineapple leaf, and bamboo have been studied as reinforcements for polymers (Saheb Jog 1999). Among natural fibres (NF), wood was the most extensively and more frequently used reinforcement for polymers. However, due to expensive manufacturing process of wood fibres, inexpensive and sustainable alternatives such as agricultural waste have attracted considerable interest. Wheat straw is one of such agro- derived materials with applications in polymer composites (Hornsby Hinrichsen et al 1997b, Panthapulakkal Sain 2006). In general, the term natural fibre is used to designate materials (used as fibre or filler in composites) that are derived from plant tissue containing cellulose fibres on the cell wall.

Natural fibre polymer composites have found applications in construction, transportation and packaging sectors. Despite their relative low cost, improved mechanical properties, light weight, recyclability and environmentally friendliness of composites with natural fibres, poor resistance to water absorption restricts their use in many structural and out-doors applications. The poor resistance of those composites to water absorption is due to hydrophilic nature of natural fibres (Marcovich, Reboredo et al 1998). The hydrophilicity of natural fibre also leads to incompatibility with hydrophobic polymer matrix and hence reduces the interfacial interaction between natural fibre and polymer. Several research attempts have been made in order to improve interfacial interaction between natural fibres and polymer matrices. Most of the studies in this area have focused on reducing the hydrophilic nature of the natural fibres through various physical or chemical modifications (Arbelaiz Fernández et al 2005).

Incorporation of coupling agents enhanced the interfacial interaction between natural fibre and polymer matrix and also resistance for water absorption (Panthapulakkal Sain et al 2005). Surface modification of natural fibres with organo-silane compounds are used to improve the interfacial interaction between the fibre and polymer matrix and hence improved mechanical properties. Hybridization of the composites formulation by using a natural fibre and another fibre with good resistance to water absorption seemed to be an interesting alternative. Glass fibre is one of the most studied materials along with natural fibres such as hemp, sisal, bamboo and oil palm fruit bunch fibre to enhance the resistance for water absorption and mechanical properties of composites (Thwe Liao 2002)

Wheat straw is a relatively inexpensive agricultural by-product since wheat is planted primarily for food. In Ontario, wheat straw can be used for animal bedding or mushroom composting. Many farmers believe that the straw should be left in the field to improve the soil quality and reduce the use of fertilizers. Although this hypothesis could have economic impact on the supply of wheat grain or straw, no conclusive study at the present moment is available in the literature.

Organo-clays have been known as good reinforcements or functional fillers in polymers (Ray, Okamoto 2003). When organo-clays are used as reinforcements for polymers, the composite resulted may be either a Regular microcomposite or a nanocomposite. The type of composite formed depends on the type of polymer and the method used for preparation. Nanocomposites are obtained when the layered structures of clays are exfoliated and the Regular composites are obtained when clay particles are either clumped together or poorly intercalated by the polymer.

1.2.1 Natural Fibres in Composites

In comparison with synthetic polymeric materials supplied by the petrochemical industry, natural polymeric materials such as plant fibres are extremely abundant because of their renewable characteristics. It has been reported that the annual production of plant fibres as a result of photosynthesis is as high as $2x10^9$tonnes. More importantly, the biodegradability of natural polymers guarantees that their disposal would not cause environmental pollution. Therefore, many materials scientists have started to investigate the possibility of the partial replacement of synthetic polymers by natural ones in the next few years, in the hope of solving the worsening energy crisis and various ecological problems.

Plant fibres consist mainly of cellulose, hemicellulose and lignin. Due to the high degree of crystallinity of cellulose compared to hemicelluloses and lignin and the three-dimensional net structure of lignin, plant fibres cannot be processed into various products like thermoplastic polymers. This is a major drawback that hinders their large-scale application in modern industry. It is encouraging that recent research in this area has shown that wood can be converted into thermally formable materials by suitable chemical modification such as cyanoethylation, benzoylation and carboxylation reactions, which have traditionally been used for the modification of cellulose.

1.2.2 Scouring with Solvents

Solvent scouring appears to be an alternative to the aqueous scouring and is particularly suitable for polyester or woollen fabrics. Solvent processing has been developed due to the reduced water pollution, reduced energy consumption and costs apart from an effective removal of the impurities. Solvent scouring gives excellent results in terms of uniformity, reproducibility and high absorbency (Rouette 2001; Karmakar 1999; Menachem 1998; Stephen 1957). The most widely used solvents for textile processing are the chlorinated hydrocarbons, e.g. tetrachloroethylene (perchloroethylene), trichloroethylene and 1,1,1-trichloroethane (Williams 1968). Usually stabilisers and booster solvents are added during the process to stabilise the solvent and to make the process more efficient. The use of a detergent is also reported for enhancing the detergency of the scouring process. Examples of such solvent detergents are mono-ethanolamine, alkyl-benzene sulphonate, alkyl poly-glycol ether and alkyl pyridine chloride (Kurz 1969). The use of solvent scouring is limited because of the increasing governmental and environmental restrictions. Several drawbacks are associated with the solvent scouring. Only waxes are removed by this method and therefore some form of alkaline scouring is still required (Vigo 1997). Most of the scouring solvents are flammable and/or carcinogenic in nature. Moreover, there is the need of the system to recover the solvent from the fabric after processing. This is why solvents have very limited applications for cotton scouring.

Cotton holds its place as a textile material due to its excellent properties such as higher water absorbency, hydrophilic character coupled with high fibre tenacity, easy care, rapid moisture absorption and desorption which led to the development of a wide variety of characteristic textiles ranging from apparel fabrics to house hold furnishings to artists canvas. Cotton fibre contains approximately 90% cellulose and various noncellulosics such as waxes, fats, pectins and colouring matter. Surface waxes are natural lubricating agents in yarn spinning and fabric weaving, but they are hydrophobic in nature and are responsible for nonwetting behaviour of cotton by water and impedes efficient and uniform dyeing and finishing. These noncellulosic substances have been traditionally removed by alkaline scouring. The industrial scouring process consists of alkaline treatment in the presence of wetting and sequestering agents. Alkaline scouring also imparts the hydrophilic character and permeability necessary for subsequent processing, improves fabric wettability but causes fabric shrinkage and increase in fabric thickness (Hsieh et al 1996). Treating cotton substrates with hydrogen peroxide under boiling conditions in alkaline medium is another step for dyeing textiles. However several environmental issues are associated with Regular alkaline scouring which requires large quantities of water and energy and generates huge amount of highly alkaline water effluent (Rossner 1993). Enzyme treatment of textiles, typically in the form of cotton fabric, has been introduced in textile wet processes as a new means of enhancing cotton wettability under mild reaction conditions while there is a great interest in enzymatic pretreatments such as desizing and scouring(Lange 1997; Li & Hardin 1997; Buschle – Diller et al 2001; Patni et al 2004; Wakida et al; Cava Co – Paulo 2001; Jin & Maekawa 2001; Kang & Kin 2001; Samanta et al 2005; Mori et al 1999 Mecloskey & Jump 2005; Doshi & Shelke 2001), biopolishing is currently the major textile application. Enzymatic treatments of cellulose fibres are widely used for producing specific finishing effects on cotton. The effects of enzyme treatment on fibre, dyeing properties are also being extensively studied (Buschle – Diller & Traore 1998; Cava Co – Paulo & Almeidal 2001 Koo et al 1994. Among all, the enzymes cellulases are widely used for biopolishing as they have the capability to modify cellulosic fibres in a controlled and desired manner. Even though cellulases were introduced only a decade ago, they have gained industrial acceptance for finishing of cellulosic fabrics to achieve a variety of effects including enhancement of fabric surface appearance and softening of denim garments without or with low environmental impacts (Wadham 1994; Blanchard et al 2000; Cortez et al 2002; Bohringer & Rupp 2002; Nicolai & Nechwatal 2002; Paulo 2001). They have become the third largest group of enzymes used and also their worth has proved in textiles as its advantages include improved elasticity, hydrophilicity, and dye affinity. In the initial stages of the hydrolysis, cellulases primarily act on fibre surfaces due to their large size. Simultaneously, considerable mechanical action is usually involved in industrial applications by the use of jets or tumblers for the enzymatic treatment. Mechanical action during the treatment in the initial stages helps enzyme adsorption and desorption processes as well as aids the removal of enzymatically loosened material from fibre surfaces, leaving the fibres very smooth. Due to this polishing effect, some weight loss is observed, which however does not yet indicate any fibre damage. Only with prolonged treatment duration, does degradation occur in the accessible amorphous areas of large pores and at crystallite surfaces.

As the efficiency of cellulase action on solid substrate is known to be related to the specific surface area (Grethlein 1985) it could be expected that the accessibility of cotton for enzymatic modification would increase in the following order: fabric<yarn<fibre (Jaakko pere 2001).

This process can eventually lead to significant fibre deterioration, indicated by a high weight and strength loss. Cracks in fibril direction as well as extensive surface peeling occur as indicators of this effect which is additionally overlaid by the effect of pure mechanical abrasion during the treatment. Cellulases are strictly substrate-specific in their action. Any change in the structure or accessibility of the substrate can have a considerable influence on the course of the hydrolysis reaction. Since the enzymatic treatment is often performed prior or subsequent to dyeing and finishing, it is very important to study the interaction of enzymes with compounds used for this process. Radhakrishnaiah et al (2008) have conducted studies in which, the effect of enzymatic treatment on the low stress mechanical behaviour of 100% cotton yarns produced from ring, rotor and friction spinning systems has been studied. Tyagi et al (2009, 2009a) have conducted studies on mechanical and surface properties of cotton ring and OE rotor yarns.

As far as it is known, a considerable amount of work has been done on finishing of cellulosic textile materials using enzymes. However, the yarns having different structural aspects have not been examined so far following these treatments. The new types of yarns such as regular and compact when treated with enzymes are likely to have different effects. The response of these yarns to enzymatic treatment in terms of weight loss, shrinkage, tensile strength, bending and wicking has been examined in this work. This will provide some guidelines in understanding the problems involved in wet processing of them.

The potential of natural fibre–based composites using cellulose, wood, jute, kenaf, hemp, sisal, pineapple, coir, etc., as reinforcing fibres in a thermosetting resin matrix has received considerable attention from scientists all over the world. Composites, based on thermoplastic resins, are now becoming popular due to their processing advantages. Among all natural fibres, sisal fibre (SF)–based thermoplastic polymer matrix composites have widely been used because of their low cost, good specific properties, environmental friendliness, and ease of processing. Hybridization of two different fibres has proved to be an effective method to design materials suited for various requirements. Research work on lignocellulosic fibre composites showed that their properties can effectively be utilized in hybrid composites. Hybridization of natural fibre with stronger and more corrosion-resistant synthetic fibres, e.g., glass fibre or carbon fibre, can improve the stiffness, strength, as well as moisture-resistance behavior of natural fibre–based composites. When using a hybrid composite that contains two or more types of different fibres, the desirable properties of one fibre could complement the undesirable properties of the other. As a consequence, a balance in performance and cost could be achieved through proper material design. (Alagirusamy 2004, Samal et al 2008 and Nayak &Mohanty 2010) The main economic advantage of natural fibres may be found in their local availability. Automotive applications of natural fibre composites have proven themselves very well, especially in the German automotive industries, but for the moment mainly with the fibres that are grown in Northern parts of Europe being flax and hemp.

Some sisal is used in some technologies where fast impregnation is required, like the Polyurethane Reaction Injection Moulding (RIM) techniques used for interior parts like door upholstery. Sisal has a less dense character than flax, thus providing a good resin flow. A 50 percent-50 percent hybrid mat of flax and sisal is an often used semi-finished material.

The development and characterization of polymer-clay nanocomposites have been a subject of rising interest in the recent years. Polymer-layered silicate (PLS) nanocomposites exhibit outstanding properties that are synergistically derived from the organic and inorganic components. The enhanced properties are presumably due to the synergistic effects of nanoscale fillers within the polymer. The delamination and dispersion of clays in the polymeric matrix are the key to design nanocomposites. In the ideal conditions, the delamination of the original clay structures, as well as the polymer intercalation in the clay can be achieved. Nanoparticles can significantly improve the stiffness, heat distortion temperature (HDT), dimensional stability, gas barrier properties, electrical conductivity and flame retardancy of polymer with only a 0.1–10 vol.% addition of dispersed nanophase. These performance improvements largely depend upon the spatial distribution, arrangement of intercalating polymer chains and interfacial interaction between the silicate layers and the polymer. (Samal et al 2008, Lu et al 2009 and Rahman et al 2012)

The focus of this study is on the modification of cotton yarns by cellulose hydrolysis. This topic is selected because of the considerable importance of cotton yarns which are largely used in apparel production. Improving the comfort of cotton fabrics will be the major selling point of apparel fabrics. This chapter outlines the importance of the study and provides a brief scope.

A rational approach is adopted to design a new efficient enzymatic scouring process. Several aspects were considered such as the specificity of enzymes, the complexity of the cotton fibre substrate and mass transfer.

Cellulose fibres have many advantages compared to synthetic fibres which make them attractive as reinforcements in composite materials. They come from an abundant and renewable resources at low cost which ensures a continuous fibre supply and a significant material cost saving to the plastics industry. Cellulose fibres, despite their low strength, can lead to composites with high specific properties because of their low densities.

Unlike brittle fibres, such as glass and carbon fibres, cellulose fibres are flexible and will not fracture when processed over sharp curvatures . This enables the fibres to maintain the desired aspect ratio for good performance. Their non-abrasive nature permits a high volume fraction of filling during processing, and this results in high mechanical properties without the usual machine wear problems associated with synthetic fibres especially glass and ceramic. Cellulose fibres are also non-toxic easy to handle and present no health problems like glass fibres that can cause skin irritations and respiratory diseases when the fibrous dust is inhaled. They offer a high ability for surface modification, are economical, require low amounts of energy for processing and are biodegradable. In terms of socio-economic issues, the use of cellulose fibres as source of raw materials is beneficial (Mat Taib et al 2006). Despite the advantages mentioned above, use of cellulose fibres in thermoplastics has not been extensive. Possible reasons that contribute to unsatisfactory final properties of the composite include: (i) Limited thermal stability at typical melt processing temperatures of about $200^{o}C$. This limits the type of thermoplastic that can be used with the fibres. (ii) Poor dispersion characteristics in the non - polar, olefinic thermoplastic melt due to strong hydrogen forces between the fibres. (iii) Limited compatibility with many thermoplastic matrices due to their highly hydrophilic character. This results in poor mechanical properties of the composites produced. (iv) High moisture absorption of the fibres that can affect the dimensional stability of the composite and the interfacial bond strength; and (v) high biodegradability when exposed to the environment. This limits the service life of composites particularly in outdoor applications. There are many reports on the potential use and limitation of cellulose fibres as reinforcement in thermoplastics available in the literature. These studies show that the problems mentioned above are common, independent of the type and origin of the fibre employed. Other factors that may hamper increased use of cellulose fibres in plastics are problems and costs associated with the collection and storage which are not yet mechanized and standardized to produce fibres of high and uniform quality .

Cellulose fibres are not compatible, i.e., do not wet, with many thermoplastic matrices and this is also due to differences in polarity . Cellulose fibres are hydrophilic while most of the thermoplastics (polyolefins) are hydrophobic. This leads to the presence of voids or porosity , and to weak fibre-matrix interfaces and poor overall mechanical properties. There are several possible strategies for improving compatibility between cellulose and thermoplastic matrices, and the most extensively used methods are the use of coupling or compatibilization agents, and surface treatments of the fibres. Coupling agents such as isocyanates and silanes modify the fibre-matrix interface by forming a bridge of chemical bonds between the two components. This results in improved fibre-matrix adhesion, which is reflected in the mechanical properties of the composite produced. The reinforcement caused by short fibres, including cellulose fibres, in the thermoplastic matrix is governed by the following parameters: i) fibre dispersion, ii) fibre-matrix adhesion, iii) fibre aspect ratio, iv) fibre orientation, and v) fibre volume fraction. Studies to understand the influence of these factors on cellulose-based composites have been carried out and reported in the literature by many investigators such as Gatenholm (1993) and Kokta (1991).

1.3 OBJECTIVES OF THE RESEARCH

This thesis aims to explore the modification of cotton yarns by cellulase hydrolysis. A scientific emphasis has been placed in the characterisation of the materials. From an application stand point, the process of enzymatic hydrolysis and its effects on the development of polypropylene hybrid composites for automotive industries will be explored. The specific aims are as follows:

a) To study the effect of cellulase enzyme on mechanical and surface properties of regular(R) and compact (C) cotton yarns.

b) To investigate the effects of gauge length on the tensile properties of regular and compact yarns both in untreated and treated forms and to model their strength by Weibull distribution.

c) To study the effect of cellulase enzyme in the hybrid fibre (cotton and sisal fibres) reinforced polypropylene composites.

d) To study the effect of cellulase enzyme in the hybrid fibre (cotton and sisal fibres) reinforced polypropylene nano composites.

In order to accomplish the set objectives, the following scope of works has been drawn.

- Two sets of regular(R) and compact(C) cotton yarns of 9.84 tex and 7.38 tex were pretreated and treated with cellulase enzyme and their properties like weight loss, wicking, tensile properties, elongation, shrinkage and minimum twist of cohesion and SEM were investigated.
- The various pretreated and enzyme treated yarns were subjected to strain rate of 5mm/min and 500mm/min with gauge lengths namely 254, 127, 76.2, 25.4, 12.7 mm to study the tensile strength at maximum load. The study of failure strain, load and stress was modelled by Weibull distribution.
- The blend of various percentage of the pretreated and cellulase treated cotton and sisal fibres with polypropylene was processed into composites using modular Haake PolyLab OS, an innovative torque rheometer.

- The blend of various percentage of the pretreated cotton and sisal fibres with polypropylene and nanoclay cloisite 25 A were also processed into composites.
- The blended composites so obtained have been characterised to evaluate their mechanical, surface and thermal properties.

1.4 ORGANISATION OF THE THESIS

Subsequent chapters of the thesis are briefly described in the following chapters.

Chapter 2: This Chapter includes a literature survey. It first introduces cotton and the pre-treatments applied on it and need for the treatment with cellulase enzyme, A brief introduction of the need for preparation of hybrid fibre reinforced polypropylene composites and nano composites is also provided.

Chapter 3: This Chapter contains a description of the experiments of this study and data analysis.

Chapter 4: This is the first of the Chapters describing the results of the experiments. This particular chapter discusses the effect of cellulase enzyme on the mechanical and surface properties of regular and compact yarns. The degrading property of cellulose by the enzyme is utilized in improving the surface properties by removing the protruding fibres from the surface of the yarn. In this work, the regular and compact yarns made out of same mixing were treated with cellulase enzyme with different levels of concentration and temperature. Measurement of the weight loss, specific flexural rigidity, wicking rate, work of rupture, shrinkage loss, tenacity, elongation and minimum twist of cohesion are reported for the two different yarns.

Chapter 5: This Chapter discusses the effect of gauge length and strain rate on the tensile properties of Regular and compact yarns before and after the enzyme treatment. The scale and shape factors of a series of yarns are presented and their implications are discussed. Prediction of tensile strength has been made by Weibull modelling.

Chapter 6: This Chapter outlines the results of the mechanical and thermal properties of hybrid fibres (sodium hydroxide and cellulase treated cotton and pre-treated sisal fibres (SF)) reinforced polypropylene composites. It covers the mechanical and thermal properties of the blends. In another case cellulase enzyme treated cotton and pre-treated sisal fibres were blended with polypropylene and PPgMA and the results of them are presented.

Chapter 7: This Chapter presents the mechanical and thermal properties of sodium hydroxide treated cotton and pretreated sisal fibres reinforced polypropylene nano composites containing nanoclay cloisite 25 A. They were characterized in terms of SEM, TGA, DSC and tensile properties.

Chapter 8: This Chapter outlines the main conclusions derived from the study. It also contains recommendations for further work.