CHAPTER 2

COTTON AND ITS TREATMENT

2.1 LITERATURE SURVEY

Cotton fibres contain \( \alpha \)-cellulose (88.0-96.5\%) (Goldwaith and Guthrie, 1954). The non-cellulosics are located either on the outer layers (cuticle and primary cell wall) or inside the lumens of the fibres whereas the secondary cell wall is purely cellulose. The specific chemical composition of cotton fibres vary by their varieties, growing environments (soil, water, temperature, pest, etc.,) The non cellulosics include proteins (1.0-1.9\%), waxes (0.4-1.2\%) inorganics (0.7-1.6\%) and other substances (0.5-8\%) primary cell walls contains less than 30\% cellulose, non-cellulosic polymers, neutral sugars utopic acid and various proteins. Degree of polymerization (Dp) in the primary wall ranges between 2000 and 6000 and the distributions are broadened. The secondary wall of the cotton fibre is nearly 100\% cellulose and Dp is about 1400 and the molecular weight distribution is more uniform.

2.1.1 Chemical Aspects of Cellulose

Cotton cellulose is highly crystalline and oriented. \( \alpha \)-cellulose is distinct in its long and rigid molecular structure. The \( \beta \)-1, 4-D(+) glucopyranose building blocks in long cellulose chains are linked by 1,4 glycosidic bonds. The steric effects prevent the free rotation of the an-hydro gluco-pyranose C-O-C link. Each anhydroglucose contains three hydroxyl groups, one primary on C-6 and two secondary on C-2 and C-3. The hydrogen
bonding due to the hydroxyl groups improves the rigidity of the cellulose structure. The length and fineness of the fibres are determined in the early stages of cell growth and development.

Textile finishing is the term used for a series of processes to which all scoured, bleached, dyed and printed fabrics are subjected before they are put on the market. Fabric finishing is necessary to achieve minimum care properties, pleat retention and minimum shrinkage. The finishing formulation depends on the nature of the fibres and fabric namely woven or knitted, blend percentage of the fibres and end use of the fabric.

Technical performance of such fabrics should be of very high standard as they are very expensive. Any textile material containing cotton fibre, however, needs to be extensively processed to remove the natural added impurity. These treatments are given using selected enzymes and solvents. These technologies are now a days named as “Bio Technology” and “Solvent Technology”.

Bio technology can be defined as the application of scientific and engineering principles in the processing of textile materials by biological agents to provide goods and services. Industrial applications of enzyme form an important branch of bio-technology. It is controlled hydrolysis of cellulose fibres, by the group of enzymes in order to improve surface appearance.

2.2 CELLULASE TREATMENT OF COTTON YARNS

2.2.1 Enzymes

The term enzymes is derived from the Greek word “enzymes” which means “in the cells of percents”, Enzymes are present in living organisms and structurally they resemble proteins of varying complexity,
based on chains of amino acids linked by peptide linkages. Each enzyme is different from other enzyme and the difference is due to

- Particular amino acid present.
- The order in which amino acids are linked.
- The presence or absence of metal ions
- The conformation of a structure as a whole.

2.2.2 Enzyme Preparation

In the present context, the term "enzyme preparation" is intended to mean either a Regular enzymatic fermentation product, possibly isolated and purified, from a single species of a microorganism, such preparation usually comprising a number of different enzymatic activities; or a mixture of mono component enzymes, preferably enzymes derived from bacterial or fungal species by using Regular recombinant techniques, which enzymes have been fermented and possibly isolated and purified separately and which may originate from different species, preferably fungal or bacterial species; or the fermentation product of a microorganism which acts as a host cell for expression of a recombinant polymethyl galacturonase, but which microorganism simultaneously produces other enzymes, e.g. pectin lyses, petites lyses, proteases, or celluloses, being naturally occurring fermentation products of the microorganism, i.e. the enzyme complex regularly produced by the corresponding naturally occurring microorganism.

2.2.3 Enzymatic Hydrolysis of Cellulose Substrates

Cellulase enzyme complexes usually consist of 3 major types of high-molecular weight proteins that synergistically catalyze the break-down of a cellulose substrate at the β-glycoside bond. Exo-type cellulases cause chain scission from the non-reducing chain end and Endo-type cellulases
attack at random, both producing smaller chain fragments. \(\beta\)-Glycosidase breaks down cellobiose and very short fragments to the final product glucose. The hydrolysis products of each reaction step have a controlling (inhibiting) effect on the activity of the respective enzymes.

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 also occur in the accessible amorphous areas of large pores and at crystallite surfaces.

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.

2.2.4 Size and Diffusibility of Cellulolytic Enzymes in Relation to the Capillary Structure of Cotton

The capillary structure of cellulose relative to the size and diffusivity of each cellulolytic enzyme is the most significant structural feature. Enzymatic degradation of cellulose requires that the celluloses diffuse from the micro-organism producing them to accessible molecular surfaces within the cellulose material. This accessible surface is defined by the size, shape and surface properties of microscopic and submicroscopic capillaries within cellulose matrix in relation the size, shape and diffusibility of the cellulolytic enzyme molecules themselves. The capillaries of water swollen cotton fibre were found to be around 30-75° A. The average dimension of the cellulose molecule is reported to be around 59° A. For this reason, cellulolytic enzymes are likely to be physically excluded from all but the largest cell wall capillaries. These capillaries must be enlarged to render them accessible to the enzymes.

2.2.5 Degree of Crystallinity

The influence of degree of crystallinity on the susceptibility of cellulose to enzymatic hydrolysis has been reported widely in the literature. The cellulolytic enzymes degrade the more readily the accessible amorphous regions of regenerated cellulose, but were unable to attack the less accessible crystalline portions. With the depletion of the highly accessible amorphous
material, the substrate becomes more crystalline, thereby offering an increased resistance to further hydrolysis.

2.2.6 Extraneous Matter

Cellulose hydrolysis by enzymes is also dependent on the type of extraneous matter the cellulose is associated with. In case of raw cotton, non-cellulose components make up for at least 10% of the total composition. The wax present in the outer layer of raw cotton prevents the action of enzyme, similar to resistance offered to other dyes and chemicals. Therefore, the fibre or fabrics used in bio-polishing is usually pre-treated to remove the non-cellulose components.

2.2.7 Structure of Enzymes

Enzymes are proteins which consist of one or more polypeptide chains. Each polypeptide is a chain of amino acid linked together by peptide bonds. A different gene code for each polypeptide determines the sequence of amino acids of the polypeptide. Polypeptide chains fold up when synthesized to form a unique three-dimensional shape (conformation), determined by their amino acid sequences. Multiple weak interactions stabilize the conformation of polypeptides and factors (such as pH, heat and chemicals) that disrupt these interactions distort the polypeptide’s conformation. Enzymes lose their functional activity when their three-dimensional conformation is distorted in this manner, through enzyme de-maturation. This demonstrates a clear dependence of enzyme functioning upon protein structure. Microbial enzymes vary in length from 100 to 500 amino acids and typically have a molecular weight ranging from 25,000 to 50,000 da.
2.2.8 Properties of the Enzymes

2.2.8.1 Accelerate reactions

Enzymes increase the rate of a particular reaction, by lowering the activation energy of the reaction by forming an intermediate enzyme-substrate complex, which alters the energy of the substrate such that it can be readily converted into the product. The enzyme itself is unaltered at the end of the reaction, thus acting as a catalyst. Enzymes do not alter the equilibrium positions of the reactions they catalyze. If in the conversion of the substrate (A) to the product (B) the concentration of B is two times greater than that of A when equilibrium is reached in the absence of enzyme, then the same ratio of B is produced when the enzyme is present.

2.2.8.2 Specificity

Most enzymes have a high degree of specificity and will catalyze a reaction with only one or a few substrates. There are exceptions and some proteases have a fairly low specificity to protein substrates. However, one particular enzyme will only catalyze a specific type of reaction. This property is the basis of a method of classification of enzymes.

2.2.9 Mild Operating Conditions

In contrast to chemical catalysts, most enzymes operate under mild temperature and pH conditions. They have a maximum activity at an optimum temperature, which is often the temperature within the cell media from which the enzyme is derived. For extra-cellular enzymes of a particular organism or those secreted by a microorganism the optimum temperature may be that of the environment in which the enzyme normally operates. The reaction rate increases with increasing temperature until the optimum temperature is reached, after which the enzyme activity decreases rapidly. This is the point
when the enzymes become permanently deactivated by denaturation. Temperature below the optimum range decreases the enzyme activity without damaging the protein structure. Enzymes also have an optimum pH and its activity decreases sharply on both sides of the optimum range. Since they are protein molecules, enzymes can be denatured by extremes of pH and temperature and excessive stirring. An increase in temperature or pH is commonly used in the industry to terminate the enzyme reaction.

2.3 FACTORS AFFECTING ENZYME ACTIVITY

2.3.1 Temperature

As in most chemical reactions, the rate of an enzyme-catalyzed reaction increases as the temperature is raised. A 10° C rise in temperature will increase the activity of most enzymes by 50 to 100%. Variations in reaction temperature as small as 1 or 2 degrees may introduce changes of 10 to 20% in the results. In the case of enzymatic reactions, this is complicated by the fact that many enzymes are adversely affected by high temperatures. The reaction rate increases with temperature to a maximum level, then abruptly declines with a further increase in temperature. Over a period of time, enzymes will be deactivated at even moderate temperatures. Storage of enzymes at 5° C or below is generally the most suitable. The shelf life of enzymes under these conditions is about a year.

2.3.2 Effects of pH

Enzymes are affected by changes in pH. The most favourable pH value, the point where the enzyme is most active is known as the optimum pH. Extremely high or low pH values generally result in complete loss of activity for most enzymes. pH is also a factor in the stability of enzymes. As with activity, for each enzyme there is also a region of pH optimal stability. In addition to temperature and pH, there are other factors such as ionic strength
which can affect the enzymatic reaction. Each of these physical and chemical parameters must be considered and optimized in order for an enzymatic reaction to be accurate and reproducible.

2.3.3 Enzyme Concentration

Enzyme concentration has a significant effect on the reaction. For a constant amount of substrate present in the solution, the higher the amount of enzymes present in the solution, the higher is the reaction rate. In order to study the effect of increasing the enzyme concentration upon the reaction rate, the substrate must be present in an excess amount; i.e., the reaction must be independent of the substrate concentration. Any change in the amount of product formed over a specified period of time will be dependent upon the level of enzyme present. However, for a certain amount of substrate there should be a limiting enzyme concentration after which there is no significant effect in the product formation. Moreover, the amount of product formed also is important as cellobiose, one of the products formed as a result of action of cellulose on cotton acts as an inhibitor to further enzyme action.

2.3.4 Substrate Concentration

It has been shown experimentally that if the amount of the enzyme is kept constant and the substrate concentration is then gradually increased, the reaction velocity will increase until it reaches a maximum. After this point, increases in substrate concentration will not increase the kinetics of the reaction. It is theorized that when this maximum velocity had been reached, the entire available enzyme has been converted to enzyme substrate complex.
2.3.5 Effects of Inhibitors on Enzyme Activity

Enzyme inhibitors are substances which alter the catalytic action of the enzyme and consequently slow down, or in some cases, stop catalysis. There are three common types of enzyme inhibition - competitive, non-competitive and substrate inhibition. Most theories concerning inhibition mechanisms are based on the existence of the enzyme-substrate complex, competitive inhibition to convert to ES, the enzyme substrate complex if substrate and a substance resembling the substrate are added to the enzyme. A theory called the "lock-key theory" of enzyme catalysts can be used to explain why inhibition occurs. Non-competitive inhibitors are considered to be substances which, when added to the enzyme, alter the enzyme in a way that it cannot accept the substrate. Substrate inhibition will sometimes occur when excessive amounts of substrate are present. Additional amounts of substrate added to the reaction mixture after a certain point actually decrease the reaction rate. This is thought to be due to the fact that there are so many substrate molecules competing for the active sites on the enzyme surfaces that they block the sites and prevent any other substrate molecules from occupying them. This causes the reaction rate to drop since all the enzymes present are not being used.

2.4 CELLULASE

Cellulase refers to a group of enzymes that contribute to the degradation of cellulose to glucose. They are natural catalysts for the modification of cellulose materials. The multicomponent enzyme system can be classified as:

a. Endoglucanases (EG, EC 3.2.1.4)

b. Exoglucanases or celllobiohydrolases (CBH, EC 3.2.1.19)

c.  β-glycosidase or cello biases (EC 3.2.1.21)
The cellulases used in textiles are of fungal or bacterial origin. The fungal enzymes are secreted from the *Trichoderma* species and *Humicola insolents*. The fungal cellulytic systems usually consist of several exo- and endoglucanases and one or two β-glycosidase. The number of components secreted depends on the fungus which it is derived from. The cellulolytic system from trichoderma species consists of two exoglucanases, at least four endoglucanases and one β-glycosidase. Most bacterial systems produce only endoglucanases. Among the bacterial cellulose systems, the most extensively studied system is that of *C.thermaocellum*. This bacterium produces a very active cellulose in the form of compels termed as cellulose, which degrades the crystalline cellulose in the presence of Ca\(^2+\) and a reducing agent. The cellulose consists of several endoglucanases and at least three exoglucanases. The activity of these systems towards crystalline cellulose is highly dependent on the reducing agent and calcium ions.

### 2.4.1 Fabric Softening

It has been long known that repeated washing of cotton-containing textiles causes harshness in the fabric that is related to physical damage of the cellulose material. As a result, otherwise highly structured regions of cellulose fibres become amorphous and micro-fibrillar material protrudes from the smooth fibre. Due to the removal of micro-fibrils, the texture and the grip of fabrics can be improved. The origin of pilling is based on mechanical damage by wearing and washing a textile. Pilling changes the look of the surface of the fabric and at the same time can result in a different perception of colour, based on different light diffraction. Pilling can be removed using cellulases that attack the attachment site of the pilling to the fabric. The pills become weaker after some cellulase hydrolysis and they are removed by mechanical agitation from the fabric.
2.4.2 Colour Revival

Cellulose based fabrics, such as cotton, rayon, flax and others often develop a reduction in colour brightness. The effect is caused by disordered structures of the cellulase fibrils caused by mechanical and chemical damage by washing and wearing. The brightness of colours can be revived by means of cellulases. The effect can be seen best with dark coloured textiles. Cellulases that show this effect are able to remove damaged fibril parts and micro fibrils. The effect originally was described for fungal enzymes for H.insolens, Fusarium oxysporum, Sporotrichum pulverulentum and Trichoderma reesei.

2.4.3 Ageing Effect

Ageing effects are obtained mainly with EG or EG rich cellulose mixtures. The dyed yarns on the denim fabric after enzymatic action with sequential or simultaneous mechanical agitation release the “trapped dye” in the bath. This produces areas of high contrast of blue color. The fibrillation produced during the ageing process is a result of the simultaneous action of cellulases and mechanical agitation. Therefore, the ageing look is produced with less aggressive action when compared to previously used pumice stones.

2.4.4 Cleansing Effect

Recently published results indicate that enzymes, mainly cellulases and several non-cellulolytic enzymes (lipases, proteases, and pectinases) may be used effectively in the cleaning processes of cotton. Raw cotton contains approximately 10% of non-cellulases depending upon the variety. These impurities are mainly located in the outer layers of the fibre in the cuticle and the primary wall. Traditional cleaning procedure involves scouring with sodium hydroxide solution. Cellulase treatment prior to the alkaline scouring
process has shown to enhance both the removal and degradation of seed coat fragment impurities of cotton fabrics.

The effects of fabric softening, anti-pilling and colour revival are all based on an identical mechanism achieved by cellulases having a high degree of avicelase activity and a certain capacity of cellulase binding. Thus, even when stated separately, the effects can be differentiated only on the basis of the difference in perception and difference in the textile material that are suitable to demonstrate the effect. The use of enzymes is not restricted to the above stated applications. Different enzymes such as proteases, lipases, have been used.

2.5 COMPACT YARN SPINNING SYSTEMS

In regular ring spinning, the zone between the nipline of the delivery rollers and the twisted end of the yarn is called the spinning triangle. This is the most critical part of the ring spinning system. In this zone, the fibre assembly does not have any twist. The edge fibres play out from this zone and make little or no contribution to the yarn tenacity.

In compact spinning, the spinning triangles is eliminated and almost all the fibres are incorporated into the yarn structure under the same tension. This results in significant advantages such as improved tenacity, yarn abrasion resistance and lowest yarn hairiness. There are different compact spinning systems which work on pneumatic and mechanical principles. Suessen Elite, Rieter comfor spin and Zinser Air-com Tex Frobel belong to the former while Rocos compact spinning belongs to the latter category.
2.6 WEIBULL DISTRIBUTION

2.6.1 Design and Development of Weibull Distribution

Weibull modeling is used to model extreme values such as failure times and fracture strength. The variability in yarns materials is studied by Weibull modeling. The scale and shape parameters of the distribution function $F(x,b,c)$ are estimated from the values obtained.

2.6.2 Weibull Modulus

There is a need to measure the yarn strength within the range of intended use. Due to the effects that may be present the mechanical tests may vary significantly depending on the size and population of these defects. Weibull distribution is widely used to study the magnitude of scatter. The basic Weibull distribution is a plot between random variables $x$ and its cumulative probability $F(x)$. The two parameter form of the Weibull distribution is expressed as follows.

$$F(x) = 1 - e^{-\left(\frac{x}{x_0}\right)^\beta}$$

(2.1)

Where $F(x)$ is the fraction of specimens that fail at or below a given value of $x$ (e.g. a measured tensile strength) $x_0$ is a characteristics value of $x$ at which 63% of the population of the specimens have failed (also known as alpha ($\alpha$) – characteristic life) and $\ln$ is the Weibull modulus (also known as beta ($\beta$) – shape parameter which is a constant that characterises the spread of the failure data with respect to the $x$ axis. A high Weibull modulus is desirable since it indicates an increased homogeneity, less spread and more predictable failure behaviour.
In respect of mechanical tests, the equation can be rewritten as follows.

\[ P(\sigma)_p = 1 - e^{-\frac{\sigma}{\bar{\sigma}}} \]  \hspace{1cm} (2.2)

Where \( P \) is probability of and \( \sigma \) is the strength. Linear regression is used to determine the model parameters where \( m \) is not simply the slope of the graph:

\[ L \ln \left[ \ln \left( \frac{1}{1 - p(\sigma)} \right) \right] = m \ln(\sigma) - \ln(\sigma) \]  \hspace{1cm} (2.3)

Since \( \sigma \) is simply obtained from the experimental results, the most important parameter is the plotting positions given as \( P(\sigma) \). The strength values (\( \sigma \)) are arranged from low to high and each has to be assigned to a probability of failure based on its ranking. There are several probability estimators available in the literature. These probability estimators can all be written in the form

\[ P = \frac{i - a}{n + b} \]  \hspace{1cm} (2.4)

Where \( i \) is the rank of data point in the sample in ascending order, \( n \) represents the sample size and \( a \) and \( b \) are generic coefficients such that \( 0 \leq a \leq 0.5 \) and \( 0 \leq b \leq 1 \). The common probability estimators found in the literature are provided in Table 2.1.
Table 2.1 probability estimators reported in the literature

<table>
<thead>
<tr>
<th>A</th>
<th>b</th>
<th>References estimators</th>
<th>Names</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0</td>
<td>( \frac{1-0.5}{n} )</td>
<td>Hazen</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>( \frac{i}{n+1} )</td>
<td>Mean</td>
</tr>
<tr>
<td>0.3</td>
<td>0.4</td>
<td>( \frac{i-0.3}{N+0.4} )</td>
<td>Benard</td>
</tr>
<tr>
<td>0.3175</td>
<td>1.6375</td>
<td>( 1-\frac{3}{8}[N+1.6375] )</td>
<td>Weibull</td>
</tr>
<tr>
<td>0.5</td>
<td>0.25</td>
<td>( \frac{i-0.3175}{N+0.25} )</td>
<td>Filliben</td>
</tr>
<tr>
<td>0.44</td>
<td>0.12</td>
<td>( \frac{i-0.5}{N+0.12} )</td>
<td>Blom</td>
</tr>
<tr>
<td>0.375</td>
<td>0.25</td>
<td>( \frac{i-0.44}{N+0.25} )</td>
<td>Gringoten</td>
</tr>
</tbody>
</table>

From equation, the average value of \( \sigma \) can be calculated.

\[
\sigma \approx \sigma_0 \left[ \frac{L}{L_0} \right]^{\frac{1}{m}} \left[ 1 + \frac{1}{m} \right]
\]  
(2.5)

Where \( L_0 \) is the reference length, \( L \) is the yarn length.

From equation (2.6) the average value of \( \sigma_2 \) at gauge length \( L_2 \) can be calculated from \( \sigma_1 \) at gauge length of \( L_1 \).

\[
\sigma_2 = \sigma_1 \left[ \frac{L_2}{L_1} \right]^{\frac{1}{m}}
\]  
(2.6)
2.6.3 Effect of Gauge Length and Strain Rate on Yarn Properties

Several workers (Balasubramanian & Salhotra, 1985; Kaushik et al 1989; Anindya Ghosh(2003); Singh & Sengupta(1977); Bharani & Mahendra Gowda (2012) have made useful contributions to this area. Surprisingly, with the exception of the work of Anindya Ghosh(2003), none of other authors have applied Weibull modelling. Oxenham et al (1992) have looked at the tensile properties of ring and OE friction spun yarns at a wide range of gauge length ranging from 1mm to 100mm. They observed that the tenacity of the ring spun yarns showed a sharp drop as the gauge length increased from 1mm to 40mm (which is approximately the fibre length) and it appears to be fairly constant on further increase of gauge length. While the tenacity of OE friction spun yarns drops sharply as gauge length increased from 1 to 20 mm(which is almost equal to the fibre extent in the yarn), it continued to reduce as gauge length increased further.

Realf et al (1991) looked at the tensile failure of ring, rotor and air-jet spun yarns at gauge length above and below the mean staple length while at short gauge length yarn failure was predominantly due to fibre breakage at longer gauge length, it was found to be the result of combined slippage and breakage of fibres, The balance between slippage and breakage of fibres was shown to vary with yarn structure. The slippage was seen to be more predominant in the failure of air jet yarn, especially at longer gauge length. The strength obtained at very short gauge lengths was shown to differ considerably from that predicted based on the weakest link theory and the authors concluded that this deviation of predicted values serve as proof of a change in failure mechanisms at very short gauge length.

The study of tensile properties of yarns at different gauge lengths and strains rates is important because in processes such as winding, warping, sizing and weaving, the stresses that are imposed on the yarn are different.
Realising this fact many have carried out work on tensile properties at different gauge lengths and strain rates. Moreover, Realf et al (1991) have found that yarn strength measured at shorter gauge length has a better correlation with fabric strength rather than that tested with standard gauge length. The work of Balasubramanian & Salhotra (1985) was confined to ring and rotor yarns upto an extension of 1000mm/min. No significant literature is available on the tensile failure of Regular and compact yarns in untreated and treated states at different gauge length strain rates. During the time of Midgley (1926), Peirce (1926) and Meredith (1950), these yarns namely Regular and compact which are considered in this study were not available. Chattopadhyay (1999) reported on the influence of strain rate on the characteristics of the load-elongation curves of ring spun and air jet spun yarns.

2.7 HYBRID FIBRE REINFORCED POLYPROPYLENE COMPOSITES

2.7.1 Natural Fibre

It has been estimated that there are at least 1000 types of plants that produce usable fibres or fibre bundles. However, the numbers that are currently grown, specifically for fibre production are relatively small. Natural fibres are obtained from different parts of the plants, to name a few, for example, jute, ramie, flax, kenaf and hemp are obtained from the stem; sisal, banana and pineapple from the leaf; cotton and kapok from seed; coir from the fruit, etcetera. Figure 2.1 shows the classification of natural fibres which can be considered as reinforcement of fillers in polymers.
Figure 2.1 Classification of natural fibres which can be used as reinforcement or fillers in polymers

Cotton fibre possesses good mechanical properties and can be harvested from renewable resources. Recently, composites using sisal fibre as reinforcements have attracted considerable attention. One of the key issues for cotton fibre composites is concerned with the weak fibre–matrix interface. Bisanda studied the treatment of sisal fibres using sodium hydroxide solution. The treated cotton fibre/epoxy composites showed improvements in the compressive strength and water resistance. It was suggested that the removal of the intracrystalline and intercrystalline lignin and other surface waxy substances by alkali, substantially increased the mechanical and chemical bonding. In Table 2.2 are presented the chemical composition of plant fibres.

Figure 2.2 illustrates the chemical structure of glucose materials.
Table 2.2 Percentage chemical composition of plant fibres

<table>
<thead>
<tr>
<th>Material</th>
<th>Cellulose</th>
<th>Hemicellulose</th>
<th>Lignin</th>
<th>Pectin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flax</td>
<td>81</td>
<td>14</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Jute</td>
<td>72</td>
<td>13</td>
<td>13</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Hemp</td>
<td>74</td>
<td>18</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>Sisal</td>
<td>73</td>
<td>13</td>
<td>11</td>
<td>1</td>
</tr>
<tr>
<td>Cotton</td>
<td>92</td>
<td>6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ramie</td>
<td>76</td>
<td>15</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Wood</td>
<td>45</td>
<td>23</td>
<td>27</td>
<td>-</td>
</tr>
<tr>
<td>Coir</td>
<td>43</td>
<td>&lt;1</td>
<td>45</td>
<td>4</td>
</tr>
<tr>
<td>Straw</td>
<td>40</td>
<td>28</td>
<td>17</td>
<td>8</td>
</tr>
</tbody>
</table>

Figure 2.2 The chemical structure of glucose showing the carbon numbers and two glucose to form cellobiose

2.7.2 Properties of Natural Fibre

Natural fibres have always found wide applications from the time they gained commercial recognition. Their versatility is based on the following desirable material properties:

- Plant fibres are renewable raw materials and their availability is more or less unlimited.
- Very good mechanical properties, especially tensile strength. In relation to its weight, the best bast fibres attain strength similar to that of kevlar.
- Very good heat, acoustic and electrical insulating properties.
- Combustibility: products can be disposed of through burning at the end of their useful service lives and energy can simultaneously be generated.

- Biodegradability: as a result of their tendency to absorb water, natural fibres will biodegrade under certain circumstances through the actions of fungi and bacteria.

- The abrasive nature of natural fibre is much lower compared to that of glass fibre, which leads to advantages in regard to technical, material recycling or processing of composite materials in general.

- Reactivity: the hydroxyl groups present in the cell wall constituents not only provide sites for water absorption but are also available for chemical modification (e.g. introduce dimensional stability, durability or improved oil/heavy metal absorption properties).

The properties described above show that there should be an increasing role for plant fibre based products in the future. The drawbacks of natural fibres are listed below:

- Lower strength properties, particularly their impact strength and poor fire resistance.

- Variability in quality, depending on unpredictable influences such as weather.

- Moisture absorption, which causes swelling of the fibres.

- Restricted maximum processing temperature.

- Lower durability, fibre treatments can improve this considerably.
Dimensional stability, as a consequence of the hygroscopicity of the fibres, products and material based on plant fibres are not dimensionally stable under changing moisture conditions. Eichhorn (2001) reported that there is a variability of mechanical properties that one can obtain for natural fibres such as flax and hemp when compared to Regular reinforcements such as glass and aramid fibres. In terms of strength and modulus, typical values are summarized in Table 2.3. It can be seen that the natural fibres compared reasonably well with glass (given their low density), but are not as strong as both aramid and carbon fibres.

Table 2.3 Mechanical properties of natural fibres.

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Density (g/cm³)</th>
<th>Elongation at break (%)</th>
<th>Tensile strength (MPa)</th>
<th>Young’s modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cotton</td>
<td>1.5 - 1.6</td>
<td>7.0 - 8.0</td>
<td>287 - 597</td>
<td>5.5 - 12.6</td>
</tr>
<tr>
<td>Jute</td>
<td>1.3</td>
<td>1.5 - 1.8</td>
<td>393 - 773</td>
<td>26.5</td>
</tr>
<tr>
<td>Flax</td>
<td>1.5</td>
<td>2.7 - 3.2</td>
<td>345 - 1035</td>
<td>27.6</td>
</tr>
<tr>
<td>Hemp</td>
<td>-</td>
<td>1.6</td>
<td>690</td>
<td>-</td>
</tr>
<tr>
<td>Ramie</td>
<td>-</td>
<td>3.6 - 3.8</td>
<td>400 - 938</td>
<td>61.4 - 128</td>
</tr>
<tr>
<td>Sisal</td>
<td>1.5</td>
<td>2.0 - 2.5</td>
<td>511 - 635</td>
<td>9.4 - 22.0</td>
</tr>
<tr>
<td>Coir</td>
<td>1.2</td>
<td>30.0</td>
<td>175</td>
<td>4.0 - 6.0</td>
</tr>
<tr>
<td>Viscose (cord)</td>
<td>-</td>
<td>11.4</td>
<td>593</td>
<td>11.0</td>
</tr>
<tr>
<td>Soft wood Kraft</td>
<td>1.5</td>
<td>-</td>
<td>1000</td>
<td>40.0</td>
</tr>
<tr>
<td>E-glass</td>
<td>2.5</td>
<td>2.5</td>
<td>2000 - 3500</td>
<td>70.0</td>
</tr>
<tr>
<td>S-glass</td>
<td>2.5</td>
<td>2.8</td>
<td>4570</td>
<td>86.0</td>
</tr>
<tr>
<td>Aramid (normal)</td>
<td>1.4</td>
<td>3.3 - 3.7</td>
<td>3000 - 3150</td>
<td>63.0 - 67.0</td>
</tr>
<tr>
<td>Carbon</td>
<td>1.4</td>
<td>1.4 - 1.8</td>
<td>4000</td>
<td>230.0 - 240.0</td>
</tr>
<tr>
<td>(standard)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.8 SISAL FIBRE

Sisal fibre is one of the most widely used natural fibres and is very easily cultivated. Sisal fibre is a hard fibre extracted from the leaves of the sisal plant (Agavesisalana). The processing methods for extracting sisal fibres have been described by (Chand et al, 1988; Mukherjee and Satyanarayana, 1984; Gassan, J & Bledki, AK 1997). The methods include
(1) Retting followed by scraping and

(2) Mechanical means using decorticators.

The major studies on sisal fibres carried out during this 10-year period can be broadly divided into the following topics:

- Properties of sisal fibres.
- Interface properties between sisal fibre and matrix.
- Properties of sisal-fibre-reinforced composites with thermoplastics (polyethylene, polypropylene, polystyrene, PVC, etc.), thermosets (epoxy, polyester, etc.), rubber (natural rubber, styrene-butadiene rubber, etc.), gypsum and cement.
- The effects of processing methods, fibre length, fibre orientation, fibre-volume fraction and fibre-surface treatment on the mechanical and physical properties of sisal-fibre-reinforced composites have been studied.
- Sisal/glass-fibre-reinforced hybrid composites.

It can be seen that research interest has changed from the fibre itself to sisal-fibre-reinforced composites and hybrid composites. The study of interface between sisal fibre and matrix, however, remains an important topic.

2.8.1 Properties of Sisal Fibre

The structure and properties of natural fibres depend on their source, age, etc. The tensile properties of sisal fibre are not uniform along its length. The fibre becomes stronger and stiffer at mid-span and the tip has moderate properties. Table 2.4 shows the properties of sisal fibres as reported
by different researchers. Note that except for the structure and properties of
the natural fibre itself, experimental conditions such as fibre length, test
speed, etc., all have some effects on the properties of natural fibres.

Mukherjee & Satyanarayana (1984) studied the effects of fibre
diameter, test length and test speed on the tensile strength, initial modulus and
percent elongation at the break of sisal fibres. They concluded that no
significant variation of mechanical properties with change in fibre diameter
was observed.

Table 2.4 Properties of sisal fibres reported by different researchers

<table>
<thead>
<tr>
<th>Density (kg/m³)</th>
<th>Moisture content (%)</th>
<th>Tensile strength (MPa)</th>
<th>Tensile Modulus (GPa)</th>
<th>Maximum strain (%)</th>
<th>Diameter (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1450</td>
<td>11</td>
<td>604</td>
<td>9.4-15.8</td>
<td></td>
<td>50-200</td>
</tr>
<tr>
<td>1450</td>
<td>-</td>
<td>530-640</td>
<td>9.4-22</td>
<td>3-7</td>
<td>50-300</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>347</td>
<td>14</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>1030</td>
<td>-</td>
<td>500-600</td>
<td>16-21</td>
<td>3.6-5.1</td>
<td>-</td>
</tr>
<tr>
<td>1410</td>
<td>-</td>
<td>400-700</td>
<td>9-20</td>
<td>5-14</td>
<td>100-300</td>
</tr>
<tr>
<td>1400</td>
<td>-</td>
<td>450-700</td>
<td>7-13</td>
<td>4-9</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>530-630</td>
<td>17-22</td>
<td>3.64-5.12</td>
<td>100-300</td>
</tr>
<tr>
<td>1450</td>
<td>-</td>
<td>450-700</td>
<td>7-13</td>
<td>4-9</td>
<td>-</td>
</tr>
</tbody>
</table>

However, the tensile strength and percent elongation at the break
decrease while Young's modulus increases with fibre length.

For electrical applications, the dielectric properties of sisal fibre at
different temperature and frequency have also been studied (Yang, 1995).
Increase of frequency decreases the dielectric constant $\delta$ value, while increase of temperature increases $\delta$ at all frequencies.

Yang et al (1996) used IR, X-ray diffraction and TG to study the effect of thermal treatment on the chemical structure and crystallinity of sisal fibres. They concluded that the IR spectrum did not change below 200°C treatment while density and crystallinity increased.

2.8.2 Surface Treatment of Sisal Fibre

Several investigators have studied the surface morphology, mechanical and degradation properties of the treated fibres. Yang et al (1996) studied the relationship of surface modification and tensile properties of sisal fibres. Their modification methods include: alkali treatment, H$_2$SO$_4$ treatment, conjoint H$_2$SO$_4$ and alkali treatment, benzol/alcohol dewax treatment, acetylated treatment, thermal treatment, alkali-thermal treatment and thermal-alkali treatment. The results are summarised in Table 2.5. To improve the moisture-resistance, Chand et al (1989) acetylated sisal fibre and studied its tensile strength. It was shown that acetylation could reduce the moisture content. However, the tensile strength of acetylated sisal fibre was reduced, caused by the loss of the hemicellulose in the fibre during acetylation.

Surface modification of sisal fibre using coupling agents was also studied by Singh et al (1996). The effects of these coupling agents on the moisture content in sisal fibre are discussed. It is clear that moisture absorption of surface-treated fibres has been reduced significantly by providing hydrophobicity to the surface via long-chain hydrocarbon attachment. In addition, these coupling agents penetrate the cell wall through surface pores and deposit in the inter-fibrillar regions and on the surface, restricting further ingress of moisture.
Table 2.5 Effect of treatment methods on tensile properties of sisal fibres

<table>
<thead>
<tr>
<th>Treatment methods</th>
<th>Tensile strength (g/tex)</th>
<th>Tensile modulus (x10³ g/tex)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>30.7</td>
<td>1.18</td>
<td>2.5</td>
</tr>
<tr>
<td>Benzol/alcohol</td>
<td>38.8</td>
<td>0.99</td>
<td>3.7</td>
</tr>
<tr>
<td>Acetic acid + alkali</td>
<td>9.3</td>
<td>0.39</td>
<td>2.6</td>
</tr>
<tr>
<td>Alkali</td>
<td>31.7</td>
<td>0.53</td>
<td>7.5</td>
</tr>
<tr>
<td>Acetylated</td>
<td>33.2</td>
<td>0.35</td>
<td>8.3</td>
</tr>
<tr>
<td>Thermal</td>
<td>42.0</td>
<td>1.22</td>
<td>3.5</td>
</tr>
<tr>
<td>Alkali-thermal</td>
<td>27.6</td>
<td>0.70</td>
<td>4.7</td>
</tr>
<tr>
<td>Thermal-alkali</td>
<td>25.7</td>
<td>0.71</td>
<td>4.4</td>
</tr>
</tbody>
</table>

2.9 SURFACE MODIFICATION OF NATURAL FIBRES

Some of the disadvantages and limitations of natural fibres, when used as reinforced for composites, are related to the lack of proper interfacial adhesion, poor resistance to moisture absorption, limited processing temperature to about 200°C, and low dimensional stability (shrinkage, swelling). The fibre/matrix interface plays an important role in the physical and mechanical properties of composites. To improve the interfacial properties, natural fibres are subjected to chemical treatments. Research on “a cost effective” modification to natural fibres is necessary, since the main market attention of natural fibres prior to their use in composite materials is also needed to facilitate fibre dispersion and induce bond formation between the fibre and the polymer matrix.
2.9.1 Chemical Treatments

Chemical modifications of natural fibres aimed at improving the adhesion with a polymer matrix were investigated by a number of researchers. However, different chemicals were used and very limited papers took a partial review on the mechanism and utilization of chemical treatments in fibre reinforced composites.

2.9.1.1 Mercerization

Alkaline treatment or mercerization is one of the most used chemical treatments of natural fibres when used to reinforce thermoplastics and thermosets. The important modification done by alkaline treatment is the disruption of hydrogen bonding in the network structure, thereby increasing surface roughness. This treatment removes a certain amount of lignin, wax and oils covering the external surface of the fibre cell wall, depolymerises cellulose and exposes the short length crystallites. Thus, alkaline processing directly influences the cellulose fibril, the degree of polymerization and the extraction of lignin and hemicelluloses compounds.

2.9.1.2 Silane treatment

Silane is a chemical compound with chemical formula SiH₄. Silane coupling agents may reduce the number of cellulose hydroxyl groups in the fibre matrix interface. Silane coupling agents were also found to be effective in modifying natural-fibre matrix interface and increasing interfacial strength. It was verified that the interaction between the silane coupling agent modified fibre and the matrix was much stronger than that of alkaline treatment, which led to composites with higher tensile strength from silane-treated than alkaline-treated fibre. Thermal stability of the composite was also improved after silane treatment.
2.9.1.3 Acetylation treatment

Acetylation means introducing an acetyl functional group (CH$_3$COO$^-$) into an organic compound. Acetylation of natural fibres is a well known esterification method causing plasticization of cellulosic fibres. Acetylation can reduce the hydroscopic nature of natural fibres and increase the dimensional stability of composites. It was reported that acetylated natural fibre reinforced polyester composites exhibited higher bio-resistance and less tensile strength loss compared to composites with silane treated fibre in biological tests.

2.9.1.4 Benzoylation treatment

Benzoylation is an important transformation in organic synthesis. Benzoyl chloride is most often used in fibre treatment. Benzoyl chloride includes benzoyl (C$_6$H$_5$C=0) which is attributed to decrease hydrophilic nature of the treated fibre and improved interaction with the hydrophobic polymer matrix. Benzoylation of fibre improves fibre matrix adhesion, thereby considerably increasing the strength of the composites, decreasing its water absorption and improving its thermal stability (Kaushik et al 2010).

2.9.1.5 Enzyme treatment (ref.2.2.1)

2.9.2 Other Chemical Treatments

Several other interface modification methods were reported in literature. Isocyanate treatment on natural fibres was carried out by few researchers. An isocyanate is a compound containing the isocyanate functional group (N=C=O), which is highly susceptible to reaction with the hydroxyl groups of cellulose and lignin in fibres. Isocyanate is reported to work as a coupling agent used in fibre reinforced composites.
Another effective method of surface chemical modification of natural fibres in graft copolymerization, optimized vinyl grafted natural fibres, consisting of the orderly arrangement of graft moieties; act as compatible reinforcing fibres with several resin systems to obtaining better fibre-matrix adhesion of the resulting biocomposites.

Permanganate treatment also improves the bonding at the fibre-polymer interface. Tensile strength values of the composite showed a marginal increase with permanganate treatment.

Maleated coupling agents are widely used to strengthen composites containing fillers and fibre reinforcements.

Benzoyl peroxide (BP, \((\text{C}_6\text{H}_5\text{CO})_2\text{O}_2\)) and dicumyl peroxide (DCP, \((\text{C}_6\text{H}_5\text{C(CH}_3_2\text{O})_2\)) are chemicals in the organic peroxide family that are used in natural fibre surface modifications. As a result of peroxide treatment, the hydrophilicity of the fibres decreased and the tensile properties increased.

2.9.3 Physical Treatment

Plasma treatment is an effective method to modify the surface of natural polymers without changing bulk properties. The plasma discharge can be generated by either corona treatment or cold plasma treatment. Both methods are considered as a plasma treatment. Pre-treatment of wool fabric with low temperature plasma as an eco-friendly process was tested in a reactor tube of the radio frequency plasma system. This treatment resulted in improvement in fabric hydrophilicity and wettability and created new active sites along with the improved initial dyeing rate.
The mechanical properties of the plant fibre/novolac (Fu et al 2001) composites were also increased with Maleic anhydride(MA) treatment. Thomas and co-workers have studied the effect of sisal fibre surface treatment for polyethylene and polypropylene matrix composites. In this study, the injection moulding of cotton fibre-reinforced polypropylene will be investigated.

The weak cotton fibre/PP interface issue will be improved by PP maleation, i.e., melt blending of maleic-anhydride-grafted-PP (MAPP) with PP homopolymer. The resulting properties of the maleated and nonmaleated composites will be evaluated and compared.

2.10 Nanoclay

Montmorillonite is a very soft phyllosilicate group of minerals that typically form in microscopic crystals, forming clay. It is named after Montmorillon in France. Montmorillonite, (Dho & Cho 1998) a member of the smectite family, i.e 2:1 clay, meaning that it has 2 tetrahedral sheets sandwiching a central octahedral sheet. The particles are plate-shaped with an average diameter of approximately one micrometre. Members of this group include saponite. Montmorillonite is the main constituent of the volcanic ash weathering product, bentonite. The water content of montmorillonite is variable and it increases greatly in volume when it absorbs water. Chemically it is hydrated sodium calcium aluminium magnesium silicate hydroxide

\[(\text{Na, Ca})_{0.33}(\text{Al, Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}\].

Potassium, iron and other cations are common substitutes; the exact ratio of cations varies with the source. It often occurs intermixed with chlorite, muscovite, illite, cookeite, and kaolinite (Chiu et al 2004).
2.10.1 Structure of Nanoclay

Silica is the dominant constituent of the montmorillonite clays, with alumina being essential. The chemical structure of montmorillonite clays is illustrated in Fig. 2.3, showing its sheet structure consisting of layers containing the tetrahedral silicate layer and the octahedral alumina layer. The tetrahedral silicate layer consists of $\text{SiO}_2^-$ groups linked together to form a hexagonal network of the repeating units of composition Silica. The alumina layer consists of two sheets of closely packed oxygen or hydroxyls, between which octahedrally coordinated aluminum atoms are embedded in such a position that they are equidistant from six oxygen or hydroxyls. The two tetrahedral layers sandwich the octahedral layer, sharing their apex oxygen with the latter. These three layers form one clay sheet that has a thickness of 0.96 nm. The chemical formula of the montmorillonite clay is $\text{Na}_{1/3}(\text{Al}_{5/3}\text{Mg}_{1/3})\text{Si}_4\text{O}_{10}(\text{OH})_2$. In its natural state Na$^+$ cation resides on the MMT clay surface.

![Chemical structure of montmorillonite nanoclays](image)

**Figure 2.3** Chemical structure of montmorillonite nanoclays
2.10.2 Physical and Chemical Properties of Clay Nanoparticles

The clay known as montmorillonite consists of platelets with an inner octahedral layer sandwiched between two silicate tetrahedral layers. The octahedral layer may be thought of as an aluminium oxide sheet where some of the aluminium atoms have been replaced with magnesium; the difference in valences of Al and Mg creates negative charges distributed within the plane of the platelets that are balanced by positive counter ions, typically sodium ions, located between the platelets or in the galleries. In its natural state, this clay exists as stacks of many platelets. Hydration of the sodium ions causes the galleries to expand and the clay to swell; indeed, these platelets can be fully dispersed in water. The sodium ions can be exchanged with organic cations, such as those from an ammonium salt, to form an organoclay. The ammonium cation may have hydrocarbon tails and other groups attached and is referred to as a “surfactant” owing to its amphiphilic nature. The extent of the negative charge of the clay is characterized by the cation exchange capacity, i.e., CEC. The X-ray d-spacing of completely dry sodium montmorillonite 0.96 nm while the platelet itself is about 0.94 nm thick. When the sodium is replaced with much larger organic surfactants, the gallery expands and the X-ray d-spacing may increase by as much as 2 to 3-fold. While the thickness of montmorillonite platelets is a well-defined crystallographic dimension, the lateral dimensions of the platelets are not. They depend on how the platelets grew from solution in the geological process that formed them. Many authors grossly exaggerate the lateral size with dimensions quoted of the order of microns or even tens of microns. A commonly used montmorillonite was accurately characterized recently by depositing platelets on a mica surface from a very dilute suspension and then the lateral dimensions were measured by atomic force microscopy. Since the platelets are not uniform or regular in lateral size or shape, the platelet area, $A$, was measured and its square-root was normalized by platelet thickness, $t$, to calculate an “aspect ratio”. 

2.10.3 **Organic Treatment of Nanoclay**

Because layered silicates are hydrophilic materials, they must be made organophilic (hydrophobic) to become compatible with most host polymers that are hydrophobic polymers. Without organic treatment, layer silicates will only disperse and phase separate in the presence of very polar polymers. Organic treatment is typically accomplished via ion exchange between inorganic alkali cations on the clay surface with the desired organic cation. The organic treatment, at the interface between inorganic silicate and organic polymer, is a vital part of the polymer nanocomposite, and therefore, it must be tailored to synthetic conditions. Synthetic methods for polymer nanocomposites preparation include solvent mixing, in-situ polymerization, and melt compounding. One of the most "industry friendly" methods of making polymer nanocomposites is the use of melt compounding. The polymer and organically treated clay are heated to the melting point of the polymer, and the two are mixed together using compounding equipment such as an extruder or a mixing head. There are several types of clay surface treatments, which are listed below:

Quaternary ammonium salts based on textile antistatic agents alkyl imidazoles provide improved thermal stability. Coupling and tethering agents, reactive diluents can be functional amino compounds. Others consist of cation types containing phosphorous ionic compound.

2.10.4 **Dispersing of Nanoclays in Polymer Matrix**

Achieving exfoliation of organo montmorillonite in various polymer continuous phases is a function of the surface treatment of the MMT clays and the mixing efficiency of the dispersing apparatus or equipment. For hydrophilic nanoclay such as SCP's.
Cloisite Na\textsuperscript{+}, it is recommended that it be dissolved in either water using high-shear mixing or to add Cloisite Na\textsuperscript{+} directly into a water soluble, aqueous polymer solution. The recommended equipment is as follows: high-shear mixer or 3 roll mill for liquid resins, Brabender mixer for viscous resins, or twin-screw extruder for solid resins.

Depending on the physical state of the polymer, one can incorporate the clay into the polymer by solution blending, melt blending, or in-situ polymerization processes to form polymer-clay nanocomposites. Polymer-clay nanocomposites can be classified morphologically into (a) Unmixed (b) Intercalated and (c) Exfoliated (delaminated) states, as shown in Figure 2.4

![Figure 2.4](image)

**Figure 2.4** (a) Unmixed (b) Intercalated and (c) Exfoliated (delaminated) states of nanocomposites

The most desirable morphological state for the polymer-clay nanocomposites is exfoliation, followed by intercalation. The processing
challenge of nanoclay is to disperse the 8-(o,m particles into > 1 million platelets using the proper processing technique and conditions.

In order to make the nanocomposite with the most improved in properties, an exfoliated structure is required. The greatest dispersity of clay and interfacial interaction of clay platelets with polymer can be obtained in the exfoliated structure. Proper hydrophobicity of clay and compatibility between organically modified clay and polymer are critical factors in nanocomposite formation “Li (2001)”. Additionally, large interlayer spacing in clay and interaction ability between clay and polymer are the other factors which are considered in the development of exfoliated nanostructures.

Properties that can be improved with the addition of clay include

- Physical properties; modulus, dimensional stability, etc.
- Barrier properties; reduced gas permeability to oxygen and carbondioxide.
- Chemical resistance.
- Flame retardance and slow smoke emission.
- Optical clarity increased over that of Regular filler.
- Increased heat distortion temperature.

2.10.5 Miscibility/Thermodynamics of Nanocomposite Formation

Similarly to polymer blends, any mixture of polymer and layered silicate does not necessarily lead to a nanocomposite. In most the incompatibility of the hydrophobic polymer and the hydrophilic silicate leads to phase separation similar to that of macroscopically filled systems. In contrast, by using surface-modifıed silicates, as noted earlier, one can fine-
tune their surface energy and render them miscible (or compatible) with different polymers. The approach is based on a chemical (rather than a mechanical) driving force which leads to nanoscopic dispersion.

Nanocomposites are formed if the free energy change, $\Delta G$, of the process is negative. The change in free energy is composed of an enthalpic term, $\Delta H$, due to the intermolecular interactions and an entropic term, $\Delta S$, associated with the configurational changes of the constituents, and $\Delta G = \Delta H - T \Delta S$, where $T$ is the temperature. The entropy change of the organically modified inorganic component is calculated using a modified Flory–Huggins lattice model in which the occupation of the lattice is weighted to simulate the preferred orientations of the organic modifier (tethered chains) in the presence of two impenetrable surfaces (silicate layers). The confinement of the polymer chains is similarly approximated using a self-consistent field treatment of a random-flight polymer between two surfaces. For the enthalpic term a modified mean-field, site-fraction approach where the number of contacts per lattice site is replaced by an interaction area per lattice site is being used. This approach makes it possible to express the interaction parameter as energy per area and may be approximated by interfacial or surface energies.

Using this model we find that the entropy loss associated with the polymer confinement is approximately compensated for an entropy gain associated with the increased conformational freedom of the surfactant molecules as the gallery distance increases due to the polymer intercalation. Therefore, enthalpy determines whether or not polymer intercalation will take place. As the polymer–silicate interactions become stronger, first intercalated and then delaminated nanocomposites are predicted, in agreement with the experiment. Figure 2.5 illustrates the In-situ intercalation of polymer nanocomposites.
2.11 Summary

From the foregoing, it is clear that a considerable amount of work has been done on the cellulase treatment of cotton yarns and on the effect of gauge length on the yarn characteristics. What appears to be less emphasised are the cellulase treatment applied to different yarn structures and the characteristics of hybrid composites made from treated cotton fibres and nanoclays. This work examines these aspects in depth.