Chapter 1
INTRODUCTION

Abstract

This chapter deals with a review of the literature on the various aspects of natural fibre composites and composites in general. Composite materials are replacing conventional materials in several applications, because of their high specific strength and ease of processing. Natural fibres based on plant fibres are finding application as potential reinforcement in polymeric matrices. The various fields of application of natural fibres have been touched upon. Physical structure of plant fibres along with their various properties have been discussed in detail. The wide spectrum of application of natural fibre composites have also been dealt with. The mechanics and properties of short fibre, hybrid fibre and textile fibre reinforced composites have been carefully reviewed. The newly developed processing techniques for composite manufacturing, like resin transfer moulding, vacuum infusion etc. have been discussed. Very new developments such as nano composite and green composites have also been incorporated.

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Introduction

1.1. Composites

A composite is a heterogeneous material created by the synthetic assembly of two or more components, selected filler or reinforcing agent and a compatible matrix binder, in order to obtain specific characteristics and properties [1]. The components of a composite do not dissolve or otherwise merge completely with each other, but nevertheless do act in concert. The components as well as the interface can be physically identified and it is the behaviour and the properties of the interface that generally control the properties of the composite. The properties of the composite cannot be achieved by any of the components acting alone.

Composites can be classified on the basis of the form of their structural components: fibrous (composed of fibres in a matrix), laminar (composed of layers of materials), and particulate (composed of particles in a matrix). The particulate class can be further sub divided into flake (flat flakes in a matrix) or skeletal (composed of a continuous skeletal matrix filled by a second material). In general, the reinforcing agent can be fibrous, powdered, spherical, crystalline, or whiskered, and either an organic, inorganic, metallic or ceramic material. Typical resins include polyester, phenolic, epoxy, silicones, alkyd, melamine, polyamide, fluorocarbon, polycarbonate, acrylic, acetal, polypropylene, polyethylene and polystyrene.
Composites, the wonder materials with light-weight, high strength-to-weight ratio and stiffness properties, have come a long way from their inception in replacing conventional materials like metals, woods etc. [2].

Fibre reinforced composites (FRC) contain reinforcements having lengths much higher than their cross-sectional dimensions. Fibres are the load-carrying members, while the surrounding matrix keeps them in the desired location and orientation. Further, the matrix acts as a load transfer medium and protects the fibres from environmental damage due to elevated temperature and humidity. Fibre reinforced composites have a low specific gravity and high strength-weight and modulus-weight ratios, which have tremendous potential, and consequently possess a distinct advantage over conventional materials. Today, fibre reinforced composites have emerged as a major class of structural materials with an increasing application in weight-critical components for industry, particularly the aerospace, marine, and automotive sectors. Fibre reinforced plastic (FRP) composites form a major class of composites. The versatility, strength and non-corrosive properties of plastics in combination with fibres have helped establish this class of composites as a potential and viable alternative in several applications.

1.2. Fibres, Matrices and Composites

1.2.1. Advanced fibres

A great majority of materials are stronger and stiffer in the fibrous form than as bulk material. A high fibre aspect ratio permits a very effective transfer of load via the matrix material to the fibres, thus taking advantage of their
excellent properties. Therefore, fibres are very effective and attractive reinforcement materials. Reinforcing fibres used in advanced composites are: glass fibres, carbon and graphite fibres, aramid fibres, boron fibres etc.

1.2.2. Glass fibres

Glass fibres are the most common of all reinforcing fibres for polymer matrix composites. Glass fibres are amorphous solids. Chemically, glass is primarily composed of silica (SiO₂) backbone in the form of \((-\text{SiO}_4\)\)ₙ tetrahedral. Modifier ions are added for their contribution to glass properties and manufacturing capability.

1.2.3. Carbon and graphite fibres

Graphite fibres are the predominant high-strength, high-modulus reinforcement used in the fabrication of high-performance resin-matrix composites. The term 'graphite fibre' is used to describe fibres that have a carbon content in excess of 99% whereas the term 'carbon fibre' describes fibres that have a carbon content of 80-95%. The carbon content is a function of the heat treatment temperature.

1.2.4. Aramid fibres

The aramid-fibre-forming polymers, that is the aromatic polyamides, are believed to be made of solution–polycondensation of diamines and diacid halides at low temperatures. Tensile strength and modulus are substantially higher and fibre elongation is significantly lower for Kevlar fibres than for other organic fibres. Kevlar fibres have poor characteristics in compression, with
compressive strength being only one-eighth of the tensile strength. This is a result of the anisotropic structure, which permits the relative ease of local yielding, buckling, and kinking of the fibre in compression.

1.2.5. Boron fibres

Boron filaments are produced by the chemical vapour deposition, from the reduction of boron trichloride (BCl₃) with hydrogen, on a tungsten or carbon monofilament substrate. Currently boron filaments are produced with diameters of 100, 140 and 200μm, in descending order of production quantity; however, both smaller and larger diameter fibres have been produced in experimental quantities.

1.2.6. Other high-performance fibres

The need for reinforcing fibres in high temperature applications has led to the development of ceramic fibres. The ceramic fibres combine high strength and elastic modulus with high-temperature capability and, in general, freedom from environmental attack. Alumina fibres and silicon carbide fibres are among the important ceramic fibres. Alumina and SiC fibres are suitable for reinforcing metal matrices in which carbon and boron fibres exhibit adverse reactivities. In addition, alumina has an inherent resistance to oxidation that is desirable in applications such as gas turbine blades.

1.3. Plant Fibre

With the exception of synthetic polymers, most economically important products, such as paper, cordage (cords and rope) and textiles, are derived from
plant fibres. Fibres are elongated cells with tapering ends and very thick, heavily lignified cell walls. The lumen or cavity inside mature, dead fibre cells is very small when viewed in cross section. Figure 1.1 shows the longitudinal cross section of a fibre cell.

![Cell Wall](image)

**Figure 1.1: Longitudinal section and cross section of a fibre cell**


Plant fibres vary widely in chemical composition, structure and dimension, and originate from different parts of the plant. Many varieties of plant fibre exist, such as hairs (cotton, kapok), fibre sheaf of dicotylic plants or vessel sheaf of monocotylic plants (e.g. flax, hemp, jute and ramie) and hard fibres (sisal, henequen and coir). Based on the part of the plant from which they are obtained, plant fibres are classified as cotton (seed fibres), ramie, jute, banana and flax (bast fibres) and sisal and abaca (leaf fibres).

A recent report on the ongoing research and development of prolific bast fibre crops, noted for the strength of their fibre bundles, revealed that these materials hold strong potential [3], particularly in applications demanding substantial strength. They have excellent heat and sound insulating properties, good chemical reactivity for processing and even a built-in pesticide system, given their anti-microbial and anti-mildew properties [4]. Germany has been the driving force behind the use of composites, accounting for more than two-
thirds of the European production of natural fibre composites, with the car manufacturers Mercedes (Daimler/Chrysler), BMW, and Audi/Volkswagen leading the way. Following the introduction of jute-based door panels in the Mercedes E class five years ago, fibre consumption in the German car industry has soared from 4,000 tons in 1996 to 15,500 tons in 1999 and is predicted to double over the next five years. The door trim panels for the Daimler/Chrysler Sebring convertible are made from Eco-Cor, a bio-composite plastic made of 25% hemp, 25% kenaf and 50% polypropylene. The blend is formulated for fire-resistance and is "self-extinguishing". Not only are plant-based fibres usually cheaper to process and more environmentally friendly than glass-fibre and plastic alternatives, which are tricky to dispose of, they often have superior technical properties. They are less prone to splintering and save weight by as much as 30%, improving fuel consumption. With market prices of 30-35p/kg, compared to 85-90p/kg for plastics or pounds 5.50/kg for fibreglass, natural fibre composites present a cheaper alternative that can also be recycled. Plant fibres have been used in other applications as well; ingenious production methods have made it possible to process agricultural waste into wood board. Its uses range from back panels for cupboards to kitchen cabinet doors to laminate flooring [5]. Such plant fibres also have the advantage of a very reactive surface chemistry and a high work of fracture of over 104kJ/m².

Table 1.1 contains the world production of certain commercially important fibre sources. Bast fibres or some of the 'hard' leaf fibres are extracted from stems (or leaves) after a process called retting [6]. Various aerobic
Table 1.1 Commercially important fibre sources

<table>
<thead>
<tr>
<th>Fibre source</th>
<th>Species</th>
<th>World production ($10^3$ tonnes)</th>
<th>Origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood</td>
<td>(&gt;10,000 species)</td>
<td>1,750,000</td>
<td>Stem</td>
</tr>
<tr>
<td>Bamboo</td>
<td>(&gt;1250 species)</td>
<td>10,000</td>
<td>Stem</td>
</tr>
<tr>
<td>Cotton lint</td>
<td>Gossypium sp.</td>
<td>18,450</td>
<td>Fruit</td>
</tr>
<tr>
<td>Jute</td>
<td>Corchorus</td>
<td>2,300</td>
<td>Stem</td>
</tr>
<tr>
<td>Kenaf</td>
<td>Hibiscus cannabinus</td>
<td>970</td>
<td>Stem</td>
</tr>
<tr>
<td>Flax</td>
<td>Linum usitatissimum</td>
<td>830</td>
<td>Stem</td>
</tr>
<tr>
<td>Sisal</td>
<td>Agave sisilana</td>
<td>378</td>
<td>Leaf</td>
</tr>
<tr>
<td>Roselle</td>
<td>Hibiscus sabdariffa</td>
<td>250</td>
<td>Stem</td>
</tr>
<tr>
<td>Hemp</td>
<td>Cannabis sativa</td>
<td>214</td>
<td>Stem</td>
</tr>
<tr>
<td>Coir</td>
<td>Cocos nucifera</td>
<td>100</td>
<td>Fruit</td>
</tr>
<tr>
<td>Ramie</td>
<td>Boehmeria nivea</td>
<td>100</td>
<td>Stem</td>
</tr>
<tr>
<td>Abaca</td>
<td>Musa textiles</td>
<td>70</td>
<td>Leaf</td>
</tr>
<tr>
<td>Sunhemp</td>
<td>Crotolaria juncea</td>
<td>70</td>
<td>Stem</td>
</tr>
</tbody>
</table>


bacteria develop on and in the stems at the beginning of the ret, and persist until all the air is driven out and all the oxygen consumed. Eventually, anaerobic bacteria, especially *Clostridium*, bring about the gradual decomposition of the pectin material forming the middle lamella of the cell wall, so that the fibre bundles are released from the tissues around them. The bark is removed from the retted stems and beaten until the fibre bundles are separated from phloem,
cortex and epidermal tissues [7]. Important natural resources used in obtaining fibres are Hemp, Kenaf [8], Coir [9], oil palm fibre [10], and pineapple leaf fibre[11]. Table 1.2 contains the properties of some natural fibres.

Table 1.2 Properties of some natural fibres

<table>
<thead>
<tr>
<th>Fibrous Material</th>
<th>Density (g/cm³)</th>
<th>Length (mm)</th>
<th>Diameter (μm)</th>
<th>L/D Ratio</th>
<th>Tensile Strengths (Psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fibre</td>
<td>Bundle</td>
<td>Range</td>
<td>Avg</td>
<td>Range</td>
</tr>
<tr>
<td>Flax</td>
<td>1.51</td>
<td>1.2</td>
<td>10 - 65</td>
<td>32</td>
<td>10 - 25</td>
</tr>
<tr>
<td>Kenaf (Bast)</td>
<td>-</td>
<td>1.2</td>
<td>1.4 - 5</td>
<td>2.6</td>
<td>14 - 23</td>
</tr>
<tr>
<td>Kenaf (Core)</td>
<td>0.31</td>
<td>-</td>
<td>0.4 - 1.1</td>
<td>0.6</td>
<td>18 - 37</td>
</tr>
<tr>
<td>Hemp</td>
<td>1.48</td>
<td>1.2</td>
<td>7 - 55</td>
<td>25</td>
<td>13 - 30</td>
</tr>
<tr>
<td>S.Y. Pine</td>
<td>0.51</td>
<td>-</td>
<td>2.7 - 4.6</td>
<td>3.7</td>
<td>32 - 43</td>
</tr>
<tr>
<td>D. Fir</td>
<td>0.48</td>
<td>-</td>
<td>2.7 - 4.6</td>
<td>3.7</td>
<td>32 - 43</td>
</tr>
<tr>
<td>Aspen</td>
<td>0.39</td>
<td>-</td>
<td>0.7 - 1.6</td>
<td>1.2</td>
<td>20 - 30</td>
</tr>
</tbody>
</table>

(Sources: Wood Handbook; Danforth International; W.S.U., WMEL; Columbus, Institute of Natural Fibres, U.S.D.A., A.R.S.; The BioComposite Centre (1996))

1.3.1. Chemical structure and applications

The essential component of all plant fibres is cellulose. The term cellulose was first used by Payen [12] in 1838. Since then it has been generally accepted that cellulose is a linear condensation polymer consisting of D-anhydroglucopyranose units, joined together by β-1-4-glycosidic bonds. The Haworth projection formula for cellulose is given in Figure 1.2.
In another sense, cellulose can be considered as a polyacetal of glucose. Terminal hydroxyl groups are present at both ends of the cellulose chain molecule. However, these groups are quite different in nature. The C (1) hydroxyl at one end of the molecule is an aldehyde hydrate group with reducing activity and originates from the formation of the pyranose ring through an intermolecular hemiacetal reaction. In contrast to this, the C (4) hydroxyl on the other end of the chain is an alcoholic hydroxyl and is non-reducing. The chemical character of the cellulose molecule is determined by the sensitivity of the β-glucosidic linkages, between the glucose repeating units, to hydrolytic attack, and by the presence of three reactive hydroxyl groups, one primary and two secondary, in each of the base units. These reactive hydroxyl groups are able to undergo etherification and esterification reactions. The main cause for the relative stiffness and rigidity of the cellulose molecule is the intramolecular hydrogen bonding, which is reflected in its high viscosity in solution, its high tendency to crystallise, and the ability to form fibrillar strands. The β-glucosidic linkage further favours the chain stiffness.
The molecular structure of cellulose is responsible for its supramolecular structure and this, in turn, determines many of its physical and chemical properties. In the fully extended molecule, their mean planes are at an angle of 180° to each other and orient adjacent chain units. The mechanical properties of natural fibres also depend on the cellulose type, because each type of cellulose has its own cell geometry and the geometrical conditions determine the mechanical properties. The crystal structure of natural and regenerated cellulose is known as cellulose I and II respectively. In cellulose I the chains within the unit cell are in parallel configuration [13], while they have an antiparallel configuration [14] in cellulose II. In addition to the cellulose component, natural fibres contain hemicellulose, which consists of a group of polysaccharides that remain associated with the cellulose after lignin has been removed. The hemicelluloses differ from cellulose, in that they contain several sugar units whereas cellulose contains only glucopyranose units. Hemicellulose also exhibits considerable chain branching whereas cellulose is strictly linear. The degree of polymerisation of native cellulose is also ten to one hundred times higher than that of hemicelluloses. Unlike cellulose, the constituents of hemicelluloses differ from plant to plant [15]. Lignins, complex hydrocarbons, with aliphatic and aromatic components, are the other constituents of plant fibres. Lignin is an aromatic biopolymer, an integral cell constituent in all vascular plants including the herbaceous varieties. It is built up by oxidative coupling of three major C6-C3 (phenylpropanoid) units, namely, syringyl alcohol, guaiacyl alcohol, and p-coumaryl alcohol, which form a random structure in a tri-dimensional network inside the cell walls [16]. The major inter-unit linkage is an aryl-aryl
ether type. Besides the 20 different types of bonds present within the lignin itself, lignin seems to be particularly associated with the hemicellulosic polysaccharides\[17\]. Their chief monomer units are various ring-substituted phenyl propane, linked together in ways which are not fully understood. Lignin forms the matrix sheet around the fibres that hold the natural structure together. The mechanical properties of lignin, however, are lower than that of cellulose \[18\]. In addition to these, pectin and waxes make up parts of the fibre \[19\].

Natural fibres, as a substitute for glass fibre in composite components, have gained interest in the last decade, especially in the housing sector \[20\]. The moderate mechanical properties of natural fibres prevent them from being used in high-performance applications (e.g. where carbon reinforced composites would be utilised), but for many reasons they can compete with glass fibre. Low specific weight, which results in a higher specific strength and stiffness than those of glass, is a benefit. The use of renewable natural fibres contributes to sustainable development. The range of products in the automobile industry based on natural fibres, is based on polyester and PP and fibres like flax, hemp or sisal. The interior parts of the Mercedes A-200 made by Natural Mat Thermoplastic is shown in Figure1.3. The use of natural fibres in the automobile industry has grown rapidly over the last 5 years.

Natural fibres enjoy the right potential for utilisation in composites due to their adequate tensile strength and good specific modulus, thus ensuring a value-added application avenue. The maximum tensile, impact and flexural
strengths for natural fibre composites reported so far are 104.0 MPa (jute-epoxy), 22.0 kJ/m² (jute-polyester) and 64.0 MPa (banana-polyester) respectively.

Figure 1.3 The interior parts of the Mercedes A-200 made by natural mat thermoplastic


Plant-based composites have been widely used in construction; the ancient Egyptians used straw to reinforce clay walls. Again, during the sixties, glass fibres in combination with tough rigid resins were produced on a large scale. In 1908, the first composite materials were applied for the fabrication of large quantities of sheets, tubes and pipes for electronic purposes, paper or cotton were used to reinforce sheets made of phenol or MF resins. In 1896, aeroplane seats and fuel tanks were made of natural fibre with a small content of polymeric binders [21]. Plant fibres were left in the lurch, with the advent of more durable construction materials. Now, they are being recognised as a valuable alternative for the composites industry. Material scientists all over the world focus their attention on natural composites reinforced with jute, sisal, coir, pineapple etc., primarily to cut down on the cost of raw materials.
1.4. Cellulose Micro Fibrils

Cellulose is found not to be uniformly crystalline. However, the ordered regions are extensively distributed throughout the material and these regions are called crystallites. The threadlike entity which arises from the linear association of these components, is called the microfibril. It forms the basic structural unit of the plant cell wall. These micro-fibrils are found to be 10-30 nm wide, less than this in width, indefinitely long containing 2-30,000 cellulose molecules in cross section. Their structure consists of predominantly crystalline cellulose core.


These are covered with a sheath of para-crystalline polyglucosan material surrounded by hemicelluloses [22]. In most natural fibres, these microfibrils orient themselves at an angle to the fibre axis called the microfibril angle. The ultimate mechanical properties of natural fibres are found to be dependent on the microfibrillar angle. Gassan et al. [23] have done calculations on the elastic properties of natural fibres. Cellulose exists in the plant cell wall in the form of thin threads with an indefinite length. Such threads are cellulose microfibrils, playing an important role in the chemical, physical, and mechanical
properties of plant fibres and wood. Microscopists and crystallographers' studies have shown the green algae Valonia to be excellent material for the ultra-structural study of the cellulose microfibril [24]. A discrepancy in the size of the crystalline regions of cellulose, obtained by X-ray diffractometry and electron microscopy, led to differing concepts on the molecular organisation of micro-fibrils. Frey-Wyssling [25] regarded the microfibril itself as being made up of a number of crystallites, each of which was separated by a para-crystalline region and later termed “elementary fibril”. The term ‘elementary fibril’ is therefore applied to the smallest cellulosic strand. Electron micrograph studies of the disintegrated micro-fibrils, showing the crystalline nature of cellulose micro-fibrils (Magnfn 100nm) taken by diffraction contrast in the bright field mode, are given in Figure1.4. Reports on the characterisation and the make-up of the elementary fibrils and on their association while establishing the fibre structure-usually called fibrillar or fringed fibril structure- are there in the literature [26]. According to this concept, the elementary fibril is formed by the association of many cellulose molecules, which are linked together in repeating lengths along their chains. In this way, a strand of elementary crystallites is held together by parts of the long molecules reaching from one crystallite to the next, through less ordered inter-linking regions. Molecular transition from one crystallite strand to an adjacent one is possible, in principle. Apparently, in natural fibres this occurs only to a minor extent, whereas in man-made cellulosic fibres such molecular transitions occur more frequently.
The internal cohesion within the elementary fibrils is established by the transition of the long cellulose chain molecules from crystallite to crystallite. The coherence of the fibrils in their secondary aggregation is given either by hydrogen bonds at close contact points or by diverging molecules. Access into this structure is given by large voids formed by the imperfect axial orientation of the fibrillar aggregates, interspaces of nanometer dimensions between the fibrils in the fibrillar aggregations, and by the less ordered inter-linking regions between the crystallites within the elementary fibrils. Dufresne [27] has reported on whiskers obtained from a variety of natural and living sources. Cellulose micro-fibrils and cellulose whisker suspension were obtained from sugar beet root and from tunicin. Typical electron micrographs obtained from dilute suspensions of sugar beet are shown in Figure 1.5. Individual micro-fibrils are almost 5nm in width while their length is of a much higher value, leading to a practically infinite aspect ratio of this filler. They can be used as a reinforcing phase in a polymer matrix.
1.5. **Physical Structure of Plant Fibres**

A single fibre of all plant based natural fibres consists of several cells. These cells are formed out of cellulose-based crystalline micro-fibrils, which are connected to a complete layer by amorphous lignin and hemicellulose. Multiples of such cellulose-lignin-hemicellulose layers in one primary and three secondary cell walls, stick together to form a multiple layer composite. The fibre strength increases with increasing cellulose content and decreasing spiral angle with respect to fibre axis.

1.5.1. **Fibrillar structure**

Light microscopy has shown that fibrous substrates are built from fibrillar elements. These fibrillar elements are termed macro-fibrils and micro-fibrils. The elementary micro-fibrils are formed by the association of many cellulose molecules, which are linked together in repeating lengths, along their chains.

1.5.2. **Cell wall structure of native cellulose**

The architecture of both man-made and native cellulose is based on elementary fibrils. The primary wall is only a few tenths of a micron thick and contains only approximately 5% of the cellulose matter constituting the fibre. It consists mainly of pectins and waxes, besides cellulose.

1.6. **Determination of Degree of Crystallinity**

X-ray diffraction techniques give the most direct results, although their interpretation and evaluation is still under discussion and widely based on convenience. On the basis of the two-phase fringe-micellar structure, Hermans and
Weidinger [28] derived a theory on the proportionality of the intensity or amplitude of scattering from the amorphous and crystalline phases of cellulose. The respective crystallinities are based on certain expressions.

1.7. Microfibril Angle Measurements

Wood fibres are a composite sheath of several layers; the primary, $S_1$, $S_2$, and $S_3$, of which the $S_2$ is the thickest and gives rise to the thickness of the fibre [29]. The measurement of the microfibrillar angle of the cellulose in the $S_2$ layers of the cell walls of soft wood is an essential step in the process of understanding the elastic, creep, and strength properties of a particular wood specimen. A widely used technique for the measurement of the micro-fibril was developed by Cave [30]. Specimens with a vertical orientation of their cell axes are irradiated in a direction perpendicular to one set of cell walls and (002) diffractions from the cellulose fibres are recorded. It is not easy to extract a value for the micro-fibril angle from the diffraction pattern because the diffractions from the individual fibres overlap. Drawing tangents to the extreme edges of the total intensity distribution round the diffraction circle has been suggested as a solution. Figure 1.6 a and b shows the irradiation geometry for a cell with four sets of fibres a, b, c and d. The figure shows the location of the eight diffraction spots for $M = 45^\circ$ and $\alpha = 45^\circ$. 
1.6. Diffraction from a single cellulose fibre. b. wide angle diffraction pattern from a set of parallel cellulose fibres with $M = 45^\circ$ and $\alpha = 45^\circ$
(Reprinted: Eichhorn et al., J. Mater. Sci. 36, 2107-2133, (2001))

1.8. Thermal Stability of Natural Fibres

Natural fibres are complex mixtures of organic materials and, as a result, thermal treatment leads to a variety of physical and chemical changes. The limited thermal stability of natural fibres is one of their major drawbacks. The first degradation occurs at a temperature above 180°C. The thermal degradation of cellulose-based fibres is greatly influenced by their structure and chemical composition [31]. Gassan and Bledzki [32] studied the thermal degradation of jute and flax fibres at temperatures below 170 and 210°C for a maximum of 120 minutes. It was found that temperatures below 170°C only slightly affect the fibre properties, while temperatures above 170°C significantly dropped the tenacity and degree of polymerisation. Because of chain scissions, a slight
increase in degree of crystallinity was observed. Chemical modification was found to improve the thermal stability of the composites. Baiardo et al. [33] studied the surface chemical modification and its effect on the thermal stability of flax fibres. It was found that the chemically modified fibres showed a satisfactory thermal stability at processing temperatures for potential composites.

### Table 1.3 The mechanical properties of various natural fibres

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Density (g/cm³)</th>
<th>Tensile Strength (MPa)</th>
<th>Modulus (Gpa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jute</td>
<td>1.3</td>
<td>393-773</td>
<td>26.5</td>
</tr>
<tr>
<td>Sisal</td>
<td>1.5</td>
<td>468</td>
<td>22</td>
</tr>
<tr>
<td>Flax</td>
<td>1.5</td>
<td>344</td>
<td>27</td>
</tr>
<tr>
<td>Pineapple</td>
<td>1.56</td>
<td>172</td>
<td>62</td>
</tr>
<tr>
<td>Banana</td>
<td>1.3</td>
<td>750</td>
<td>29-32</td>
</tr>
<tr>
<td>OilPalm</td>
<td>1.55</td>
<td>100-400</td>
<td>1-9</td>
</tr>
<tr>
<td>Sunhemp</td>
<td>1.07</td>
<td>389</td>
<td>35</td>
</tr>
<tr>
<td>E- glass</td>
<td>2.54</td>
<td>3400</td>
<td>72</td>
</tr>
<tr>
<td>Coir</td>
<td>1.2</td>
<td>175</td>
<td>4.0-6.0</td>
</tr>
<tr>
<td>Ramie</td>
<td>-</td>
<td>400-938</td>
<td>61.4-128</td>
</tr>
</tbody>
</table>

(Reprinted: Saheb and Jog, Advances in Polymer Technology, 18, 4, 351-363 (1999))

The physical and mechanical properties of a few natural fibres are shown in Table 1.3.

### 1.9. Matrix Materials

Since fibres cannot transmit loads from one to the other, they have limited use in engineering applications. When they are embedded in a matrix material to form a composite, the matrix serves to bind the fibres together, transfer loads to the fibres, and protect them against environmental attack and damage due to handling. The matrix has a strong influence on several
mechanical properties of the composite such as transverse modulus and strength, shear properties and properties in compression. Physical and chemical characteristics of the matrix such as melting or curing temperature, viscosity, and reactivity with fibres influence the choice of fabrication process. The matrix material for a composite system is selected, keeping in view all of the above factors. Commonly used matrix materials include polymers, metals, and ceramics.

1.9.1. Polymers

Polymers are the most widely used matrix material for fibre composites. Their chief advantages are low cost, easy processability, good chemical resistance and low specific gravity. On the other hand, low strength, low modulus and low operating temperatures limit their use. They are also degraded by prolonged exposure to ultraviolet light as well as some solvents.

a) Thermosetting and thermoplastic polymers

According to their structure and behaviour, polymers can be classified as thermoplastics or thermosets. The polymers that soften or melt on heating are called thermoplastic polymers, and consist of linear or branched-chain molecules having strong intramolecular bonds but weak intermolecular bonds. Melting and solidification of these polymers are reversible and they can be reshaped by application of heat and pressure. They are either semicrystalline or amorphous in structure. Examples include polyethylene, polystyrene, nylons, polycarbonate, polyacetals, polyamide-imide, polyether-ether ketone, and polysulfone polyphenylene sulfide and polyether imide. Thermosetting plastics have cross-linked or network structures with covalent bonds between all molecules. They do not
soften but decompose on heating. Once solidified by cross-linking process, they cannot be reshaped. Common examples of thermosetting polymers include epoxies, polyesters, phenolics, ureas, melamine, silicone and polyimides.

b) Polyester resin

A polyester resin is an unsaturated (reactive) polyester solid dissolved in a polymerisable monomer. Unsaturated polyesters are long chain, linear polymers containing a number of carbon double bonds. They are made by a condensation reaction between a glycol and an unsaturated dibasic acid (maleic or fumaric). A polymerisable monomer such as styrene, which also contains carbon double bonds, acts as a cross linking agent by bridging adjacent polyester molecules at their unsaturation points. The monomer also acts as a diluent, reduces viscosity, and makes it easier to process. The curing or cross linking process is initiated by adding a small quantity of a catalyst such as organic peroxide or an aliphatic azo compound. Since there is no by-product of the reaction, the curing is done at room temperature or elevated temperature with or without application of pressure. The structure of typical polyester made from maleic acid and diethylene glycol is shown below:

\[
\begin{align*}
\text{Maleic acid} & \quad \text{Diethylene glycol} \\
\text{Polyester} & \quad \text{Polyester}
\end{align*}
\]

The length of the molecule or degree of polymerisation may vary. The resin will generally be a solid but is dissolved in a monomer such as styrene. The solution viscosity can be controlled by the percent styrene and is generally quite fluid. The conversion from liquid to solid occurs through the use of a free radical initiator or curing agent. The styrene monomer cross-links or reacts with the double bond in the polyester backbone above, to form a network polymer as shown:

The curing process does not produce any by-product and is accompanied by shrinkage as well as temperature increase. The ability to modify or tailor the chemical structure of polyesters through processing techniques and raw material selection, make them versatile.

c) Epoxy resin

Epoxy resins are organic liquids of low molecular weight containing a number of epoxide groups, which are three-membered rings with one oxygen and two carbon atoms. The most common process for producing epoxies is the reaction of epichlorohydrin with bisphenol-A amino or acid compounds, and
cross-linking is obtained by introducing chemicals that react with the epoxy and hydroxy groups between the adjacent chains. The chemical reaction to form epoxy resin pre-polymer is as shown.

\[
2[\text{CH}_2=\text{CHCH}_2\text{Cl}] + \text{HO-CH}_3 \xrightarrow{\text{Curing Agent}} \text{CH}_2=\text{CHCH}_2\text{O} \left[ \text{HO-CH}_3 \right] \xrightarrow{\text{Curing Agent}} \text{CH}_2=\text{CHCH}_2\text{O} + 2\text{HCl}
\]

Epoxy systems, like polyesters, can be cured at room temperature, but quite often heat is added to accelerate and improve curing. The choice of the curing agent dictates whether a room temperature or elevated temperature cure is required.

1.10. Interface Modification

The quality of the fibre/matrix interface is important in the application of natural fibres as reinforcement in plastics. The interphase is called the heart of the composite and the composite properties depend on the interphase. The schematic representation of the composite interphase is shown in Figure 1.7. Both physical and chemical methods can be used for the modification of the interface. The physical methods used for surface modification involve methods such as stretching [34], calendering [35], thermo treatment [36], and production of hybrid yarns [37]. These methods do not change the chemical composition of the fibre. However, they change the structural and surface properties of the fibre and thereby influence the mechanical bonding to polymers.
Electric discharge (corona, cold plasma) is another way of physical treatment. Corona treatment is one of the most interesting techniques used for surface oxidation and activation. Plasma treatment is evidently a progressive oxidation of the surface. This process changes the surface energy of the cellulose fibres \[38\]. An increase in the polar component of the free surface energy was reported, mainly due to the increasing content of carboxyl and hydroxyl groups. Sakata et al. \[39\] reported on the oxidation of hydrophilic constituents of the surface of different types of wood through corona treatments. In the case of wood fibres, surface activation increases the number of aldehyde groups. Gassan and Gutowski treated tossa jute fibres by corona discharge and ultra violet rays to improve the properties of natural fibre epoxy composites \[40\]. Corona-treated fibres exhibited significantly higher polar components of the free surface energy with increasing treatment energy output. It was observed that at optimum treatment conditions, an increase of about 30% in the composite flexural strength was observed. The same effects are achieved with cold plasma treatment. Depending on the nature and the type of gases used, a variety of surface modifications can be achieved. Electric discharge methods are known to be very effective for non-active
polymer substrates such as polystyrene, polyethylene, polypropylene, etc. [41]. Khan et al. [42] studied the effect of gamma irradiation and UV radiations on the mechanical properties of jute composites. Jute yarn treated with MMA+MeOH solutions were used for irradiation. In gamma radiation, polymer loading of MMA (methyl methacrylate) onto jute increased quite substantially; however, the strength of the composite decreases sharply after 15% polymer loading. The tensile strength of the UV-cured jute yarn composite was found to increase with an increase of grafting level, in contrast to the behaviour observed with gamma-irradiated jute composite samples. Figure 1.8 shows the polymer loading values of the jute yarn samples irradiated with 10kGy at 5kGy/h. It was further found that the tensile strength of the composite samples could be further enhanced by the incorporation of certain additives and co-additives into MMA+MeOH solutions.

Figure 1.8 Polymer loading with MMA in the presence of different additives
Mercerisation of natural fibres is another method used, especially with cotton textiles. In addition to the physical methods, there are chemical methods employed to modify the fibre surfaces. Strongly polar cellulose fibres are inherently incompatible with hydrophobic polymers [43]. There are several mechanisms of coupling in materials [44]. Coupling agents help in eliminating weak boundary layers, produce a tough flexible layer, and develop a highly cross-linked interphase region with a modulus intermediate between the substrate and the polymer. In addition, coupling agents improve the wetting between polymer and substrate. Coupling agents form covalent bonds with both materials and also alter the acidity of the substrate surface. The coupling agents are all based on silane/titanate/zirconate etc. Most of the coupling agents have a hydrolysable alkoxy group and a functional organic group. The development of a definitive theory for the mechanism of bonding by coupling agents in composites is a complex problem. Concepts like the morphology of the interphase, acid-base reactions at the interface, surface energy, and wetting phenomena are all to be considered.

The surface energy of the fibres is closely related to the hydrophilicity of the fibre. In the case of natural fibres, an important aspect is the lowering of the hydrophilicity. Modification of wood-cellulose fibres with stearic acid was found to hydrophobize the surface and improve their dispersion in polypropylene [45]. Jute reinforced unsaturated polyester resin composites, on treatment with polyvinylacetate, was found to have improved mechanical properties and moisture repellence [46]. Optimal conditions of mercerization, when used on natural fibres, ensures the improvement of their tensile properties [47]. Ray et al. [48] studied the effect of alkali treatment on the mechanical properties...
of vinyl ester resin matrix composites reinforced with alkali-treated jute fibre. It was observed that treatment of jute fibres with 5% NaOH for varying periods of time showed an overall improvement in properties both as fibres as well as reinforced composites. Ray and Sarkar [49] studied the changes occurring on the surface of jute fibres treated with alkali of different concentration. They observed an improvement in tenacity and modulus of the fibres by about 45% and 79% respectively. They attributed the improvement in mechanical properties to the reduction of linear density of the fibre after treatment. Figure 1.9 shows the X-ray diffractogram of raw and 8-h alkali-treated jute fibres. In addition, a weight loss of 9.63% was observed during a 2-hour treatment, with a drop in hemicellulose content from 22 to 12.9%. X-ray diffractograms showed an increase in the crystallinity of the fibres after 6 hours of treatment.

![X-ray diffractogram of raw and 8-h alkali treated jute fibres](image)

**Figure 1.9 X-ray diffractogram of raw and 8-h alkali treated jute fibres**  

Alkalisation of plant fibres has been found to change the surface topography of the fibres and their crystallographic structure. Reports in literature on alkalisation of natural fibres have observed the subsequent changes in the
surface morphology and an increase in the availability of the hydroxyl groups [50]. Rout et al. [51] have reported on the scanning electron microscopy studies of the alkali-treated coir fibres. Figure 1.10 shows the SEM of the 10% alkali treated coir fibres, with a magnification of 500.

![Figure 1.10 SEM of the 10% alkali treated coir fibres, with a magnification of 500](Reprinted: Rout et al., J. Appl. Polym. Sci., 79,1169-1177, (2001))

In addition, SEM of the 8.56% MMA-grafted coir fibres is also shown. All the pictures show that PMMA grafts have been deposited on the intercellular gaps and on the surface of the unit cells. Figure 1.11 shows the SEM of the 8.56% MMA grafted coir fibres.

![Figure 1.11 SEM of the 8.56% MMA grafted coir fibres(X500)](Reprinted: Rout et al., J. Appl. Polym. Sci., 79,1169-1177, (2001))
These changes have been reported to result in improved adhesion, surface tension, wetting ability and compatibility with polymeric matrices [52]. Bismarck et al. [53] studied the influence of alkali treatment on the electrokinetic properties of coir and sisal fibre. The influence of fibre surface modifications on the thermal and electrokinetic properties of coir and sisal fibres has been investigated. It was observed that alkali treatment of the fibres caused a reversal in \( \zeta \)-potential for the modified fibres. The \( \zeta \)-potential decay depends on the degree of hydrophilicity of the investigated fibres. Figure 1.12 shows the pH dependence of the zeta potential curves of the various modified sisal fibres. Bismarck et al. [54] reported on the characterisation of modified jute fibres using zeta potential measurements.

![Figure 1.12](image)

Figure 1.12 \( \zeta \)-Potential-time dependence of unmodified and modified sisal fibres measured in 1mMKCl

(Reprinted: Bismarck et al., Green Chemistry, 3,100-107, (2001))

Alkali treatment has been proved to be an effective method for fibre modification from as early as 1935 [55]. It has been reported that on treatment with alkali, some of the wax components at the fibre surface are saponified and
thereby removed from the fibre surface [56]. Increased fibre/matrix adhesion as a result of improved surface area and increase in the availability of the hydroxyl groups have also been reported as a result of alkali treatment [57]. The effect of alkali treatment on the wetting ability and coherence of sisal-epoxy composites has been examined by Bisanda [58]. Treatment of sisal in 0.5N solution of sodium hydroxide resulted into more rigid composites with lower porosity and hence higher density. The density of the composites produced using untreated sisal fibre and mercerized fibre was determined and is displayed in Figure 1.13. Generally, the density of untreated fibre composites did not appear to be influenced by the volume fraction of fibres. On the other hand, for mercerized fibres, there was some slight increase in the density of the composites as the fibre volume fraction was increased.

![Figure 1.13 The density of sisal-epoxy composites](Reprinted: Bisanda E. T. N., Applied Comp. Mater., 7, 331-339, (2000))

The treatment has been shown to improve adhesion characteristics due to improved work of adhesion because it increases the surface tension and surface roughness. Ray et al. [59] studied the impact fatigue behaviour of vinyl ester resin matrix composites reinforced with alkali treated jute fibres. Longer
alkali treatment removed the hemicelluloses and improved the crystallinity and was found to give better fibre dispersion. The flexural strength properties of the composite made from treated fibre were also found to be superior. Alkalisation of natural fibres, have been reported to be effective in increasing the fibre/matrix adhesion by the creation of high fibre surface area required for the optimisation of the fibre/resin reinforcement. The modification has been found to develop changes in the surface morphology and increase in the hydroxyl groups. These changes ultimately will effectively result in improved surface tension, wetting ability, swelling, adhesion and compatibility with polymeric materials [57]. Calado and Barreto [60] reported on the effect of surface treatment on the surface and morphology of coir fibres. The treatment was done to reduce the number of hydroxyl group on the surface of the fibres. Reduction in the number of hydroxyl groups will reduce the polarity and improve the compatibility with common thermosetting matrices. The scheme of reaction followed by them is shown in Figure 1.14.

![Scheme of interaction of the sulfonation reaction between lignin and sodium sulfite](image)

**Figure 1.14** Scheme of interaction of the sulfonation reaction between lignin and sodium sulfite  
The chemical treatment involved the removal of lignin from the surface of the fibres, roughening their surface. The untreated fibres have an outer surface layer, which is completely removed by the treatment. This layer is full of randomly distributed organic material, as shown at higher magnification in Figure 1.15.b. Upon the removal of this outer layer, a rougher but more ordered structure is revealed. The ordered white dots found on the surface of the treated fibres can be seen in Figure 1.15.b and were identified as silica rich material.

Chemical modification through graft co-polymerisation provides a potential route for significantly altering their physical and mechanical properties. Chemical grafting involves attaching to the surface of the fibre, a suitable polymer with a solubility parameter similar to that of the polymer matrix, which acts as an interfacial agent and improves the bonding between the fibre and the matrix. Graft co-polymerisation of vinyl monomers such as methyl methacrylate, acrylamide, and acrylonitrile onto cellulose, cellulose derivatives and lignocellulosic fibres has been well established and extensively studied over the past few decades [61]. Escamilla et al. [62] have found that the compatibility
between fibre and matrices can be improved by grafting a matrix compatible polymer on to the fibre surface. Initiation by free radicals is one of the most common methods used for the grafting of vinylic monomers on to cellulose. In this reaction, oxidation of the anhydroglucose units occur along the cellulosic chains and macrocellulosic radicals are generated on the surface of the fibre. These reactions were found to modify the surface of henequen fibres and these reactions modify the properties of the fibre. The initiator concentration, however, was found to affect the tensile strength and modulus of the fibres. Increased initiator concentration increases the crystallinity and decreases the tensile strength of the composite. When cellulose fibres are impregnated with a butyl benzyl phthalate plasticised poly vinyl chloride dispersion, excellent partitions can be obtained in polystyrene. This significantly lowers the viscosity of the solvent and results in co-solvent action for both PS and PVC [63]. Mohanty et al. [64] have reported grafting of acrylonitrile on jute to improve the thermal stability of the fibre and the resulting composite. Impregnation with monomer followed by its polymerisation has also been one of the most common methods used for the treatment of fibres. Samal and co-workers [65] have reviewed various methods of graft co-polymerisation onto cellulose fibres. Graft co-polymerisation on to cellulose takes place through an initiation reaction involving attack by macrocellulosic radicals on the monomer to be grafted. The generation of the macrocellulosic radicals is accomplished by a variety of methods such as a) diazotization, b) chain transfer reactions c) redox reactions d) photochemical initiation and e) radiation induced synthesis. Botaro and Gandini [66] reported on the treatment of various cellulosic substrates with
isocyanates bearing an alkenyl function in a non-swelling medium. These reactions introduced a small but significant number of polymerisable moieties at the surface of the cellulose. Free radical polymerisation of styrene or methyl methacrylate was carried out in the presence of these modified cellulosics. It was shown that the alkenyl functions appended on to their surface took part in the chain growth giving a continuous path of covalent bonds between the solid substrate and the polymeric matrix. The surface properties were characterised based on IGC (Inverse Gas Chromatography). The typical diagrams in which the excellent linearity related to alkane probes which provide a reliable source for calculating the dispersive contribution to the surface energy of AV before and after treatment with TMI is shown in Figure 1.16. Figure 1.17 shows the IGC plot of the unmodified AV.

![IGC plots for microcrystalline cellulose Avicell (AV) modified by TMI (3-isopropenyl-α, αα-dimethylbenzyl isocyanate)](image)

Figure 1.16 IGC plots for microcrystalline cellulose Avicell (AV) modified by TMI (3-isopropenyl-α, αα-dimethylbenzyl isocyanate)

Gellerstedt and Gatenholm [67] reported on the chemical modification of fibres with succinic anhydride. Fibres with various amounts of carboxylic acid functionalities as determined with FTIR and conductometric titration were prepared by chemical modification of high bleached kraft pulp (CP) and chemical thermomechanical pulp (CTMP) with succinic anhydride. The degree of modification was found to be dependent on the reaction time and the type of fibre used. ESCA characterisation of the fibres indicated that the carboxylic acid functionalities are predominantly introduced at the fibre surface.

The wettability in water, measured as contact angle of the succinylated fibres was significantly improved by modification. The reactions occurring between fibre components and succinic anhydride are schematically shown in Figure 1.18. Figure 1.19 illustrates changes in the chemical composition of the fibre surfaces at various treatment times. For CP fibres, the intensity of the C4 peaks increases with reaction time during the first 12 hour of treatment and
then decreases. The C1 contribution is difficult to evaluate, since it is composed of carbon signals originating from the succinic moiety as well as non-cellulose that might be extracted during the modification process. The relative intensity of the C4 peak for CTMP pulp is higher than for CP at the lower reaction times and does not decrease with increased reaction time. The C1 peak, which becomes a major peak, is composed of non-carbohydrates and carbon signals from succinic moieties.

It decreases at longer reaction times, however, which can possibly be due to mass loss caused by solubilisation of derived non-cellulosic materials.

Figure 1.18 Possible reactions occurring when succinylating lignocellulosic fibres
(Reprinted: F. Gellerstedt and P. Gatenholm, Cellulose, 6,103-121, (1999))
Figure 1.19 The ESCA deconvolution spectra of the C1s signal for the succinylated fibres

(Reprinted: F. Gellerstedt and P. Gatenholm, Cellulose, 6, 103-121, (1999))

1.10.1. Interfacial characterisation

The ultimate mechanical properties of fibre reinforced polymeric composites depend not only on the properties of the fibres and the matrix, but also on the fibre/matrix interface [68].

While characterising the mechanical properties of the resin and the fibre is simple, measuring the interfacial shear strength is not so straightforward. A number of experimental methods have been developed to characterise fibre/matrix adhesion based on micro-mechanical analysis [69]. The most common techniques used for Inter Facial Shear Strength (IFSS) measurement are the
micro bond test [70], the single fibre pull out test [71] and the single fibre fragmentation test [72].

The microbond technique, a modification of the single-fibre-pullout, involves depositing a micro-bead of the matrix onto a fibre [73]. The fibre with the micro-bead is then mounted in a micro-vise blade and the fibre is pulled out. The average IFSS, $\tau$, is given by

$$\tau = \frac{F}{\pi d l}$$

where $F$ is the load needed to debond the fibre from the micro-bead, and $d$ and $l$ are the diameter and the embedded length of the fibre, respectively. It is assumed that the shear stress along the interface is uniform.

The Single Fibre Fragmentation (SFF) technique involves embedding a single fibre along the centreline of a dog-bone-shaped specimen of matrix material [74]. The specimen is then strained along the fibre axis. The shear in the resin exerts a tensile stress on the fibre. At some stress, the fibre fractures at its weakest point. With increasing specimen strain, the fibre fractures repeatedly at different locations. No additional breaks, however, can occur when the fragments become so short that the shear transfer along the length of the broken fibre can no longer make the tensile strength higher to cause additional fractures. This fragment length at the end of the test is known as the critical length, $l_c$. The average IFSS, $\tau$, is then calculated using the force balance equation as follows:

$$\tau = \frac{d \sigma_f}{2 l_c}$$

where $d$ is the fibre diameter and $\sigma_f$ is the fibre failure strength at the critical length $l_c$. 

Prepared by BeeHive Digital Concepts Cochin for Mahatma Gandhi University Kottayam
The ratio $l_c/d$ is called the critical aspect ratio. Several refinements to equation (1.2) have been suggested based on better models developed by other researchers. The tensile stresses generated in the fibre in the shear lag model mentioned above have been validated using Raman spectroscopy [75].

1.10.2. Interphase thickness and properties

In polymer matrix composites, the interphase between the reinforcing phase and the bulk phase is paramount to the overall performance of the composite as a structural material. This interphase is now thought to be a distinct, three-dimensional phase surrounding the reinforcing phase called the interphase. It is not a distinct phase, as the interphase does not have a clear boundary. It is more accurately viewed as a transition region that possesses neither the properties of the fibre nor of the matrix. The interphase has been reported to have distinct properties by researchers [76]. The developments of atomic force microscope and nanoindentation devices have facilitated the investigation of the interphase. The primary methods for measuring the interphase characteristics have been AFM force modulation and various forms of nanoindentation. Force modulation involves moving the atomic force microscope tip across a sample in contact mode while the force between the tip and the sample is modulated using a piezoelectric element in the tip holder [77]. To probe soft materials such as polymers, the tapping mode AFM is advantageous. In tapping mode, the AFM tip is oscillated at its resonant frequency and the tip briefly and lightly impacts the sample surface during each
oscillatory cycle. The tip sample interactions are much less damaging than in force modulation or nanoindentation.

1.11. Fabrication of Composites

The fabrication and shaping of composites into finished products often combines the formation of the material itself during the fabrication process. The formation of the composite involves the combination of the matrix and fibre such that the matrix impregnates, surrounds, and wets the fibres. The important processing methods for thermosetting polymers involve Hand lay-up, Bag moulding process, Filament winding, Pultrusion, Bulk moulding, Sheet moulding, Resin Transfer moulding etc.

1.11.1. Hand Lay-up

The hand lay-up technique is the oldest, simplest and most commonly used method for the manufacture of both small and large reinforced products. A flat surface, a cavity or a positive shaped mould, made from wood, metal, plastics, or a combination of these materials may be used. Fibre reinforcements and resin are placed manually against the mould surface. The layers of materials placed against the mould control thickness.

1.11.2. Bag moulding process

Bag moulding is one of the oldest and most versatile of the processes used in manufacturing composite parts. The lamina are laid up in a mould and resin is spread or coated, covered with a flexible diaphragm or bag and cured with heat and pressure. After the required curing cycle, the materials become an
integrated moulded part shaped to the desired configuration. The general process of bag moulding can be divided into three basic moulding methods: pressure bag, vacuum bag, and autoclave. Vacuum bag and autoclave methods are used to produce most bag-moulded parts. Their main advantages are that the tooling is relatively inexpensive and the basic curing equipment can be used for the unlimited variety of shaped parts. The disadvantage of the pressure bag system is that the tooling is relatively expensive because it is combined with the curing pressure system and can be used only for the specific part for which it is designed.

1.11.3. Filament winding

Filament winding is a technique used for the manufacture of surfaces of revolution such as pipes, tubes, cylinders, and spheres and is frequently used for the construction of large tanks and pipe work for the chemical industry. High-speed precise lay down of continuous reinforcement in predescribed patterns is the basis of the filament winding method. Continuous reinforcements in the form of roving are fed from a multiplicity of creels. A creel is a metallic shelf holding roving packages at desired intervals and designed for pulling roving from the inside of the package.

1.11.4. Pultrusion

Pultrusion is an automated process for manufacturing composite materials into continuous, constant-cross-section profiles. This technique has some similarities to aluminium extrusion or thermoplastic extrusion. In pultrusion, however, the product is pulled from the die rather than forced out by pressure. A large number of profiles such as rods, tubes and various structural shapes can be
produced using appropriate dies. Profiles may have high strength and stiffness in the length direction, with fibre content as high as 60-65% by volume.

1.11.5. Preformed moulding compounds

A large number of reinforced thermosetting resin products are made by matched die moulding processes such as hot-press compression moulding, injection moulding and transfer moulding. Matched-die moulding can be a wet process but it is most convenient to use a preformed moulding compound or premix to which all necessary ingredients have been added. This enables faster production rates to be achieved. Moulding compounds can be divided into three broad categories: dough moulding, sheet moulding and prepregs.

1.11.6. Dough moulding compounds

It consists of dough like or putty like mixture of a resin, fibre reinforcement and filler to which pigments and other materials may be added.

1.11.7. Sheet moulding compounds

These compounds are produced as flat sheets and are invariably based on unsaturated polyester resin systems reinforced with chopped glass fibres although carbon and/or aramid can also be used separately or as hybrids.

1.11.8. Prepregs

This is the short form for preimpregnated fibre-reinforced plastics. Prepregs consist of roving, woven fabric, and continuous unidirectional fibre reinforcement sheets, or random chopped-fibre sheets impregnated with a
partially cured resin system. These differ from sheet moulding compounds in those thickening agents and additives.

All the processes mentioned are either slow or therefore suitable only for low volume production, or are restricted to the manufacture of parts with only very simple geometries. In addition the processes are labour intensive and the parts produced have only relatively low volume fraction (typically 20-40%) and can vary widely in mechanical performance. Tool turnaround times are also slow.

A process that has received considerable attention in recent years is resin transfer moulding. RTM is a closed mould, low pressure, two-step process [78].

1.11.9. Resin transfer moulding (RTM)

RTM is unique in that it permits the manufacture of high performance composite parts of essentially unrestricted geometry with fast turn around times. The first step in RTM involves the manufacture of a dry reinforcement preform by processes such as knitting, weaving and stitching. The preform is placed in the mould and the mould is closed. The second step is impregnation of the preform with a thermoset liquid resin, which is injected into the mould through one or more appropriately located openings. The resin is introduced into the mould by an applied pressure difference created by an external source of elevated pressure such as gravity feed or, more usually, a pressure vessel. The air inside the closed mould cavity is displaced by the advancing resin front and escapes through the vents located at the high points or the last areas of the mould to fill. During the infiltration process, the resin wets out the reinforcement and polymerises. Once the composite
develops sufficient green strength it can be removed from the tool and post cured [79].

1.11.10. Newer developments using thermosets

SMC and DMC are both characterised by supplying a prepared reinforced mix to the mould. One of the disadvantages is that the reinforcement may not be oriented in the most effective way; ‘resin-rich’ regions develop in thin sections and laying up blanks in the mould can be time consuming and not fully reproducible.

A series of processes has emerged in which the reinforcement is placed in the mould and the resin matrix is injected. These are called collectively Liquid Composite Moulding, LCM. At its simplest, this involves placing the glass (usually) in the mould in a prescribed pattern, followed by injection of resin.

Manual placement of glass is slow and skill-dependent, and preforms are widely used. The glass is prepared to shape in a separate operation, and is lightly bonded with a thermoplastic binder, which softens when warm to accommodate to the mould. It is simply dropped into place at the moulding stage.

Variations also exist in the resin injection details:

- RTM-resin transfer moulding, uses premixed resin; rather like a development of hand lay-up with a closed mould.
- VARI-vacuum assisted resin injection, the vacuum helping to speed up the fill rate. This resembles a lot the vacuum injection, but it is a bit quicker and less sophisticated. After fibre placement a basket with resin is poured
in the middle of the product, a rigid top mould is put on and at the edge of the set of moulds vacuum is applied. Successful replacement of glass fibres by natural fibre has meanwhile been achieved by researchers in Netherlands.

- SRIM-structural resin injection moulding uses a preplaced reinforcement or preform and injects a resin system which mixes in a mixing head on the way into the mould.

- RRIM-reinforced resin injection moulding mixes the resin on the way into the mould.

1.12. Short Fibre Reinforced Thermosets

A discontinuous fibre composite is one that contains relatively short discrete lengths of the fibre dispersed within the matrix. The fibres may be aligned in one direction but are more usually in a random, or semi random configuration. Unlike continuous fibre composites, the mechanical behaviour of short fibre reinforced thermo sets is often dominated by complex stress distributions due to the fibre discontinuity, in particular the stress concentration at the fibre ends. A number of different approaches have been used to predict the mechanical properties of short fibre thermo sets, including modification of the ‘rule of mixture’ theory originally developed for continuous fibre composites, and the probabilistic theory. When an external load is applied to the composite, the fibres are loaded as a result of stress transfer from the matrix to the fibre across the fibre/matrix interface. The degree of reinforcement that may be attained is a function of the fibre fraction \((V_f)\), the fibre orientation distribution
(FOD), the fibre length distribution (FLD) and the efficiency of stress transfer at the interface. In general the reinforcement is more effective when $V_f$ is high, the fibres are long, the fibres are aligned in the principal stress direction and the interface is strong.

There are two well accepted but simplistic, models for stress transfer [80]. Cox models the composite as a pair of concentric cylinders. The representative element used in the Cox analysis is shown in Figure 1.20.

The central cylinder represents the fibre and the annular outer region, the matrix. The ratio of the diameters ($r/R$) is adjusted to the required $V_f$. Both fibre and matrix are assumed to be elastic and the cylindrical bond between them is considered to be perfect. It is also assumed that there is no stress transfer across the ends of the fibre. If, as is usually the case, the fibre is much stiffer than the matrix, an axial load applied to the system will tend to induce more strain in the matrix than in the fibre and leads to the development of shear stresses along the cylindrical interface. The tensile stress in the fibre rises from zero at the end of the fibre to a plateau region along the middle portion. The tensile (a) and shear (b) stress profiles in the fibre and the interface according to Cox model is shown in Figure 1.21.

![Figure 1.20](image)

**Figure 1.20** The representative element used in the Cox analysis. The inner cylinder represents the fibre and the outer annulus the matrix.

One shortcoming of the Cox approach is that a maximum shear stress is predicted at the end of the fibre; in fact, this is where the shear stress must be zero. The other problem is that the interface strength is not considered at all, as the model assumes a perfect bond and only elastic interactions.

The alternative model, due to Kelly and Tyson [81] is based on the concept of frictional stress transfer at the interface. It is considered that a constant shear stress is induced from the fibre ends; these results in a linear stress build up. The frictional stress may be regarded as the interface shear strength (τi); this concept is often used for the experimental estimation of interface shear strength by the fragmentation or pullout test.

In general, theoretical strength and stiffness are not achieved in real mouldings because of the complexities of load transfer. However, for longer fibres, the low strain properties approach those for continuous fibres with appropriate corrections for fibre orientation and length. Matrix cracking and fibre debonding contribute to non-linear stress-strain curves and the ultimate strength.

Figure 1.21(a) The tensile stress profiles in the fibre and interface according to the Cox model
The shear stress profiles in the fibre and interface according to the Cox model

The values used in the equations are typical of those for an E-glass fibre in an epoxy resin. The transfer length is of the order of 10 fibre diameters. The parameter $X/D$ is the distance from the end of the fibre in units of diameter.

1.13. Hybrid Composites

The incorporation of several different types of fibres into a single matrix leads to the development of hybrid fibre composites. In practice a combination of only two types of fibres would be the most useful [82]. A certain mechanical property, such as strength, modulus or fracture toughness of a hybrid system consisting of two single systems can be predicted by the rule of hybrid mixtures.

$$P_n = P_g V_g + P_c V_c$$

(1.3)

where $P_n$ is the property to be investigated, $P_g$ the corresponding property of the first system such as glass fibre/polypropylene and $P_c$ the corresponding property of the second system such as carbon fibre/polypropylene. $V_g$ and $V_c$ are
respectively, the relative hybrid volume fraction of the first system and the second system, and

\[ V_g + V_c = 1 \]  \hspace{1cm} (1.4)

A positive or negative hybrid effect is defined as a positive or negative deviation of a certain mechanical property from the rule of hybrid mixture.

The term hybrid effect has been used to describe the phenomenon of an apparent synergistic improvement in the properties of a composite containing two or more type of fibre [83]. The most common use of the term applies to the tensile strength of the composite, which may be higher than would be predicted from a simple application of the rule of mixtures. This is a positive hybrid effect. When fibre types of differing failure strains are mixed the result can be strength versus composition curve such as that shown in Figure 1.22 [84].

Assuming that the failure of the low strain fibre does not cause immediate failure of the high strain fibre, the total strength will be expected to decline initially to some minimum where the two fibres carry equal loads and rise thereafter. For fibre pairs where the tensile and compressive properties are very different the low strain fibre may be different for the two loading cases [85]. The hybrid stiffness, on the other hand, would be expected to follow a law of mixtures approach, at least up to the point where one fibre fails.

Two effects might be expected to change this general picture. The first is that if two fibres of very different thermal expansion properties are heat cured together, each fibre will carry a thermally induced strain different from that
which it would carry if it were used alone. This can affect properties in both fibre and resin dominated modes, and could lead to positive or negative deviations from the expected values. The second is that the strength values used to set up the basic strength/composition curve are measured on large specimens. If the fibres are finely intermingled the effective sample size of the lower strain to failure is very greatly reduced, leading to a higher effective strength for statistical reasons, and thus a higher strength and failure in the hybrids [86]. The hybrids may also have improved failure energy absorptions in these circumstances.

![Diagram of the strength of two-fibre hybrids](image.png)

**Figure 1.22 General form of the strength of two-fibre hybrids**

1.13.1. Components of hybrid composite materials

The selection of the Polymer Hybrid Composite Material Components (PHCM) relative to each specific case is determined by the purpose of hybridisation, requirements imposed on the material or the construction being designed. Since the reinforcing elements bear the main load in composite materials strengthened by continuous fibres, the problem of selecting the type of
compatible fillers and the level of their properties is of prime importance when designing and producing PHCM. From this point of view, the production of a reinforcement of high quality is one of the main trends in the field of perfection of PHCM properties. The successful use of PHCM is determined by the chemical, mechanical and physical stability of the fibre/matrix system. The role of the matrix in affording such stability is very important and diverse. The matrix provides the solidity of PHCM, its resistance to the action of environmental factors, the required level of operating temperatures and chemical resistance. The mechanical properties of the matrix mainly determine the level of shear and compression strength of PHCM, at loadings of the material in directions that differ from the direction of orientation of the fibres and contribute to the fatigue strength, torsional strength, creep, damping ability and the work of fracture.

1.13.2. Role of interface in production of hybrid composite materials

The interface is indefinite, to a certain extent, but it is an extremely important part of any laminated material. Its role is rather significant in hybrid composites, where the formation of boundary structures occurs under the action of many factors that sometimes exclude each other. The interface is the combination of regions where the matrix is bonded with the filler by chemical or mechanical means and with polymer layer adjoining the fibre. This polymer may have a more ordered structure and its properties may differ from the properties of the unfilled binder owing to, for example, selective adsorption of the binder components by the fibre or the catalytic effect of active centres of
different nature on the fibre surface on the chemical reactions in the process of binder hardening. The mechanical properties of the reinforcing fillers, the hybridisation effect obtained, the shear, compression and transverse tearing strength of PHCM, the fatigue characteristics of the material and its resistance to environmental action are realised in many respects and sometimes even completely by the interfacial interaction of the components.

Carbon and glass fibres are often used in the same polymeric resin matrix to form hybrids. Carbon fibres provide a strong, stiff and low-density reinforcement but is relatively expensive, while glass fibre is relatively cheap but its strength and stiffness are relatively low. The compression modulus of hybrid glass and carbon reinforced composites was reported to exhibit a negative hybrid effect [87].

The most important criteria for the effective use of polymer composite materials are their life, durability, crack propagation resistance etc. The multi functionality of the material is of prime importance: the combination of high elastic and strength properties with optimal thermo physical ones. The diverse and contradictory requirements for modern composite materials has brought to the forefront the very complex problem of developing new types of composite materials, in which a combination of reinforcing layers from two or more types of fibres is used. Polymer hybrid composite materials have found the widest application to the present time.
1.13.3. Calculation and design of hybrid composite materials

The combination of different reinforcing fibres in one material is a promising trend in the production of construction with high operation reliability and reduced mass. Three component materials can be manufactured by the principle of homogeneous mixtures, fibres of different type being evenly distributed in the primary filament. According to the second version, layers of reinforcing fillers of different nature are alternated in this or that order. The third version makes provision for production of a multicomponent combination filler manufacture of fabric, mat or sheets of veneer by using different filaments and fibre bundles. The principle of making homogeneous mixtures provides a more uniform distribution of stresses in the fibres and matrix as the plastic is loaded, but the fabrication of the primary filament or fibre bundle from different fibres can be extremely difficult because of substantial differences in their processability.

The use of polymer hybrid composites in construction also enables the solution of economic problems, which is of no small importance. An appreciable reduction of price of an article is possible without minimal or complete loss of quality. Hybrid composites are considered for tailoring materials of specific properties when one reinforcement alone is not enough to satisfy the end property. Using two different fibres and also two different resins can effect hybridisation. Several reports are there in the literature on the hybridisation of different synthetic fibres for preparing composite with improved strength and decreased cost. Park and Jang have done evaluation of
the impact behaviour of aramid fibre/glass fibre hybrid composites [88]. Hybridising natural fibres with glass fibres has been suggested by various researchers for obtaining composites with better strength and low water uptake. Investigations on lignocellulosic fibre composites have shown that the properties of the fibre can be better utilised in hybrid composites [56]. Mohan et al. [89] have reported that glass has got good reinforcement effect along with jute. Clark and Ansell [90] have reported improvement of various mechanical properties of jute-glass hybrid laminates with different arrangements of jute and glass in the laminate. Pavithran et al. [91] have studied the mechanical properties of coir-glass hybrid composites containing varying amounts of glass fibre. They have noticed a considerable enhancement in the mechanical properties by the incorporation of very small volume fraction of glass. Studies on sisal-glass in polyester have showed a linear increase in the work of fracture by varying the volume fraction of the glass at the core [92]. Attempts have been made in this laboratory to prepare hybrid composites of sisal and glass in polyethylene and oil palm empty fruit bunch fibre and glass in PF. It has been reported that addition of glass has improved the orientation characteristics and thereby the tensile strength of the composites [93]. A ratio of 0.26: 0.74 volume fractions of glass and oil palm fibre gave 23% improvement in the Izod impact strength of the composite. Better properties were given by intimately mixed hybrid composites [94]. Rout et al. [95] studied the effect of hybridisation on the water absorption behaviour of coir/polyester composites. The coir surface was modified and it was observed that surface modification along with hybridisation improved the flexural strength and reduced the water absorption of the composites. Environmental
ageing on the mechanical properties of bamboo-glass fibre reinforced polymer matrix hybrid composites have been studied by Thwe et al. [96]. It has been observed that after ageing in water for 1200 hours, reduction in tensile strength and modulus for the bamboo glass hybrid composites is nearly two times less than that of composites with bamboo alone. In other words, it has been observed that the durability of bamboo fibre reinforced polypropylene can be enhanced by hybridisation with small amount of glass fibre [96].

Lignocellulosic fibres are finding application in polymer reinforcement because of desirable characteristics like high specific properties [97]. The matrix phase plays a crucial role in the performance of polymer composites. Both thermosets and, thermoplastics are attractive as matrix material in composites. Natural rubber is also used as matrix for natural fibres. In thermoset composites formulation is complex because a large number of components are involved such as base resin, curing agents, catalysts, flowing agents and hardeners. These composite materials are chemically cured to a highly cross-linked, three-dimensional network structure. These cross-linked structures are highly solvent resistant, tough and creep resistant. The fibre loading can be as high as 80% and because of the alignment of fibres; the enhancement in properties is remarkable.

Thermoplastics offer many advantages over thermoset polymers. One of the advantages of thermoplastic matrix composites is their low processing cost. Another is design flexibility and ease of moulding complex parts. Simple methods such as extrusion and injection moulding are used for processing of
these composites. In thermoplastics most of the work reported so far deals with polymers such as polyethylene, polypropylene, polystyrene, and polyvinyl chloride. This is because the processing temperature is restricted to temperatures below 200°C to avoid thermal degradation of the natural fibres. For thermoplastic composites, the dispersion of the fibres in the composite is also an important parameter to achieve consistency in the product. Thermoplastic composites are flexible and tough and exhibit good mechanical properties. However, the % loading is limited by the process ability of the composite. The fibre orientation in the composites is random and accordingly the property modification is not as high as is observed in thermo set composites.

Properties of the fibres, the aspect ratio of the fibres, and the fibre-matrix interface govern the properties of the composites. The surface adhesion between the fibre and the polymer plays an important role in the transmission of stress from matrix to the fibre and thus contributes towards the performance of the composite.

An important chemical modification is the chemical coupling. The fibre surface is treated with a compound that forms a bridge of chemical bonds between fibre and matrix. The coupling agents are tetra functional organometallic compounds based on silicon, titanium and zirconium and are commonly known as silane, zirconate or titanate coupling agents.
1.14. Natural Fibre Reinforced Polyester Composites

Sanadi et al. [21] studied the tensile and impact behaviour of polyester composites reinforced with sun hemp fibres. It was found that the tensile and impact strength of the composites increased with volume fraction of fibres. The composites also exhibited high toughness. All these enhancing properties can be attributed to high cellulose content (70-88%) and low micro fibrillar angle (9.8°) of sun hemp fibres. For jute/polyester composites, an increase in modulus and strength was reported up to a volume fraction of 0.6 followed by a decrease. Further increase in volume fraction resulted in a decrease in the properties, which was attributed to insufficient wetting of the fibre.

The reinforcing effect of coir fibre in polyester was studied by Satyanarayana et al. [99]. It was seen that the composites have low density and high electrical resistance and are likely to be suitable for use as electrical and acoustic insulators. The low strength of the composites was attributed to a lack of bonding between fibres and matrix. The mechanical properties of pineapple leaf fibre reinforced polyester composites were investigated by Uma Devi et al.[100]. Among various natural fibres, pineapple leaf fibres exhibit excellent mechanical properties due to the high cellulose content. These fibres are multicellular and lignocellulosic. Composites were also prepared after subjecting the fibres to alkali, silane and acetic anhydride treatment. They reported that the tensile strength and Young’s modulus of composites increased linearly with fibre weight fraction. The impact strength also showed the same trend. In the case of treated composites, the best properties were obtained for silane treated PALF.
(pineapple leaf fibre) composites. Hill and Khalil [101] determined the effect of environmental exposure on the properties of polyester matrix composites reinforced with acetylated coir fibres and oil palm empty fruit bunch fibres. A comparison of properties was made with silane and titanate treated fibre composites. It was seen that water sorption was substantially reduced and structural integrity maintained in contrast to composites in which no fibre treatment was used. Silane treatment of fibres was also found to give good protection to composites formed there from. Titanate treatment was not found to be as effective as silane. Ismail et al. [102] have reported on the effectiveness of the Silane 69 in improving the mechanical properties of bamboo fibre filled natural rubber composites.

Acetylation of the fibres is accompanied by cell wall swelling, due to the volume that the chemically bonded reagent occupies in the cell wall. When such a fibre is exposed to moisture there will be little additional swelling. Acetylation will also reduce the rate and extent of water uptake and improve the compatibility between the fibre and the matrix due to the improved hydrophobicity of the modified lignocellulosic. The mechanical property of jute fabric reinforced polyester composite was studied by Gowda et al. [103]. The composites were found to have better strength than wood composites though not as high as conventional composites. Since jute fibres are eco-friendly, non-toxic, non-health hazardous, low in cost and easily available the composite can be a good substitute for wood indoor applications. Jute/polyester composites are now found to be a commercial success. The lowering of the tensile strength upto 25% indicates their susceptibility to water absorption and shear failure.
Semsarzadeh [104] reported the effect of water absorption on the various jute fibre reinforced and filler filled polyester resins. In another important study, Markovich et al. [105] reported the moisture diffusion in polyester wood flour composites. Tobias and Ibarra [106] studied the effect of cure temperature on the flexural strength of polyester based composites. The flexural strength increased with increasing cure temperature and maximum strength was observed for abaca/polyester composites compared to banana/polyester and rice hull/polyester composites.

Pavithran et al. [107] examined the effect of hybridisation in polyester composites. It was found that impact performance of sisal/glass polyester composite was improved by using glass core sisal shell laminates.

The influence of adsorption behaviour of a silane coupling agent on interlaminar fracture in glass fibre fabric reinforced unsaturated polyester laminates was investigated by Suzuki et al. [108]. It was found that the amount of chemisorbed silane did not increase above a certain amount. On the other hand, the amount of physisorbed silane increased with increasing concentration of silane solution. Zhu et al. [109] carried out studies of banana fibre strands reinforced polyester composites. It was seen that the fracture toughness of composites was about 1.6 times greater than polyester matrix. Also, when the fibre length is continuous and at sufficiently high content, the banana fibre is seen to act as reinforcement in polyester matrix. Mishra et al.[110] studied the quality enhancement of pineapple leaf fibre through different surface modifications. Methods like dewaxing, alkali treatment, cyanoethylation and
grafting of acrylonitrile on to dewaxed PALF were all tried. The best improvement in tensile strength was observed in the case of 10% acrylo nitrile grafted PALF. Rout et al. [111] investigated the effect of the addition of surface modified coir fibres on the mechanical properties of polyester. Significant improvement in tensile properties was observed in the case of alkali treated composites whereas better flexural strength was observed in the case of bleached coir-polyester composites. Oksman [112] reported on the use of high quality flax fibre as reinforcement in epoxy resin using the RTM technique. This technique was proved to be suitable for natural fibres when high quality laminates are preferred. Singh et al. [113] studied sisal polyester composites and concluded that surface modification improves the properties of the composites. Aquino et al. [114] studied the mechanical properties of pissava fibre-resin matrix composites. The use of leftover pissava fibres as reinforcement in resin matrix composite materials was found to be very promising. He suggested that modified interphase prevents fibre/fibre contacts, hence removing the source of high stress concentration in the final composite. Sebe et al. [115] studied the properties of hemp fibre reinforced polyester composites prepared by the RTM technique. Chemical modification of the hemp fibres by the introduction of reactive vinyl groups at the fibre surface using methacrylic anhydride was found to increase the bonding between the fibre and the matrix.

1.15. Textile Composite

Polymers reinforced by woven fabrics are the most commonly used composites in structural applications such as aircraft, boats, reservoirs, pressure
vessels, etc. Woven fabrics offer many advantages in terms of manipulative requirements including dimensional stability, good conformability, and deep draw shapeability. Compared to unwoven, unidirectional composites, the woven fabric composites provide more balanced properties, higher impact resistance, easier handling and lower fabrication cost, particularly for parts with complex shape. The varieties of manufacturing methods have made textile composites cost-competitive with unidirectional laminated composites. Woven fabric composites provide more balanced properties in the fabric plane and higher impact resistance than UD (Unidirectional) composites, and the interlacing of yarns provides higher out of plane strength, which can take up the secondary loads due to load path eccentricities. A typical plain weave is represented as shown in Figure 1.23.

![Figure 1.23 Typical plain weave fabric](image)

In addition, it is easier to build thick laminates with woven fabrics than with UD laminates and the handling of woven fabrics is easier. This leads to a reduction in the labour and the manufacturing error involved in making thick laminates. Along with dimensional stability, WF (Woven Fabric) composites offer higher impact resistance and toughness compared to UD composites; however, these
advantages are obtained at the cost of in-plane stiffness and strength. Woven-fabric reinforcements are available in several forms as shown in Figure 1.24.

**PREFORM ARCHITECTURES**

![Various perform architectures](image)

**Figure 1.24 Various perform architectures**

The various weaving types can be identified by the repeating patterns in both the warp and weft directions. A number of other parameters are also involved in determining the fabric structure: weave, density of yarns in the fabric, fabric count, characteristics of warp and fill yarn, characteristics of fibres, and factors introduced during weaving, such as yarn crimp, etc. The increased interest in the use of natural fibre among researchers and technologists is well known. Attempts have been made by other researchers to use natural fibres in the woven form. Satyanarayana et al. [116] used cotton in the warp direction and banana in the weft direction to create fabrics, which could be used as reinforcement in plastics. Gowda et al. [117] carried out investigations on the mechanical properties of jute fabric reinforced polyester composites. Santulli et al. [118] carried out impact damage characterisation on jute reinforced composites. The type of defects that can occur in a textile composite
consists of the following, which is represented, in Figure 1.25 [119]. These include delaminations, intra bundle transverse cracks, fibre breaks, longitudinal splits etc.

![Figure 1.25](image1.png)

**Figure 1.25** The schematic representation of the type of defects that can occur in a textile composite


Figure 1.26 shows the unit cell of a 2D knitted fabric.

![Figure 1.26](image2.png)

**Figure 1.26** Unit cell of a 2D knitted fabric

(Reprinted: Scientific American on the web) (2001)

The need for increased damage tolerance, and decreased manufacturing costs for polymer composites has encouraged fundamental and applied research in advanced textiles, to be used as reinforcing fibre architecture for composites.
Work is ongoing in the field of long-term behaviour of knitted fabric composites, and the deformability of textile composites, especially knitted fabric composites, as these materials show superior drapeability [120].

1.16. Nanocomposites

Nanocomposites are defined as an interacting mixture of two phases, one of which is in the nanometer size range in at least one dimension. The name nanocomposite was first used by Rustum [121] to refer to the di-phasic xerogels and some products thereof to recognise and emphasise the fact that the products consisted of two or more phases each in nanometer scale. Nanocomposites are a class of materials that have gained much interest recently. Schematic representation of nano particles in polymer matrix is shown in Figure 1.27.

![Figure 1.27 Schematic representation of nanocomposite](Reprinted: S. Thomas and L. A. Pothen, Private communication)

The potential of producing materials with tailored physical and electronic properties at low cost are attractive for applications ranging from drug delivery to corrosion prevention. Polymer nanocomposites are a new class of engineering materials consisting of nanometer scale inorganic particles or
fillers dispersed in an organic polymer matrix. Compared to conventional filled polymers with micron-sized particles, they have superior specific strength and stiffness, good fire retardant and barrier properties. As such, they have found many potential applications in the automotive and packaging industries.

Nanocomposites exist in nature. Almost all, even moderately hard tissue is a nanocomposite of inorganic phases—principally CaCO$_3$ and appetite with various kinds of organic matrices. The hierarchical microstructure of human bones and seashells, sea urchins and abalone are all nature's cleverness in preparing nanocomposites.

Truly nanocomposite materials that are stable to about 400 to 700°C can be prepared by intercalating oxides or metal clusters of about 0.4 to 2.0nm in between 1.0nm layers of clays. Intercalation refers to the reversible insertion of molecules or compounds (guests) into a layered material (host) without destroying the host structure [122].

To fully understand the link between structure and performance, techniques are required that provide information on material properties at the nanometer scale. Scanning probe microscopy (SPM) with its various modes such as phase imaging, force modulation and pulsed force microscopy has emerged as an invaluable addition to other analytical techniques such as TEM, SEM, SIMS, Auger, and micro-indentation.

Polymers filled with nano-sized particles are ideal candidates for automotive applications because they have excellent stiffness and strength, high
heat distortion temperature, and good scratch resistance. The packaging industry will also find polymer nano-composite thin films extremely valuable due to their superb barrier properties. Lignocellulosic fillers also offer attractive properties, but are used only to a limited extent in industrial practice due to their inherent hydrophilic nature. An alternative way to overcome this restriction consists in obtaining both components (matrix and filler) dispersed in water. In this way, high performance composite materials can be processed with a good level of dispersion by taking advantage of the hierarchical structure of cellulose and using latex or a water-soluble polymer to form the matrix [123]. Cellulose micro fibrils can be found as intertwined micro fibrils in parenchyma cell wall. They can be extracted from the biomass by a chemical treatment leading to purified cellulose, followed by a mechanical treatment in order to obtain a homogeneous suspension due to the individualisation of the micro fibrils. The micro fibrils consist of monocrystalline cellulose domains with the micro fibril axis parallel to the cellulose chains. As they are devoid of chainfolding and contain only a small number of defects, each micro fibril can be considered as a string of polymer whiskers, linked along the micro fibril by amorphous domains, and having a modulus close to that of the perfect crystal of native cellulose. The amorphous regions act as structural defects and are responsible for the transverse cleavage of the micro fibrils into short monocrystals, or whiskers under acid hydrolysis. The effects of factors such as particle size of the latex and crystallinity of the matrix on the percolation phenomenon have also been studied [124].
1.17. Green Composites

Natural cellulose fibres have been used as reinforcement in biodegradable polymers such as poly (hydroxybutyrate-co-hydroxyvalerate) PHBV and polyester amide to make green composites, which are particularly attractive because of their fully degradable, compostable and environmentally friendly nature [125-127]. Interfacial shear strength of henequen fibre/PHBV composites has been studied and reported by Luo and Netravali [126]. Green composites made using pine apple leaf fibres and PHBV resin have been shown to possess mechanical properties comparable or better than some commonly used wood varieties. Mohanty et al. [128] have reported on the effect of chemical modification on the performance of biodegradable jute yarn-Biopol composites. Iannace et al. [129] studied the effect of processing conditions on dimensions of sisal fibres in thermoplastic biodegradable composites. They prepared composites based on treated and untreated sisal fibre and thermoplastic matrix using an internal batch mixer. Alkaline treatment increased the kinetics associated to the reduction of the fibre’s dimensions. Green composites are catching the attention of researchers all over the world due to environmental awareness and also for the utilisation of indigenous materials. Since natural fibres are cheap and biodegradable, the biodegradable composites from biofibre and biodegradable polymers will render a contribution in the 21st century due to serious environmental problem. Biodegradable polymers have offered scientists a possible solution to waste-disposal problems associated with traditional petroleum-derived plastics. Biodegradable polymers may be classed as: biosynthetic, semi-biosynthetic, and chemosynthetic type. Steinbuchel [130] has studied the use of biosynthetic,
thermoplastics and elastomers from renewable resources. Almost all biosynthetic polymers which are readily available from renewable resources are biodegradable within a reasonable time scale. Many semibiosynthetic and chemosynthetic polymers are also biodegradable if they contain chemical bonds, which occur in natural compounds. Thus biodegradability is not only a function of origin but also of chemical structure and degrading environments.

1.18. Purpose and Importance of the Work

1.18.1. Importance of banana fibre

A tribute to the tear and tensile strength of banana fibre are Japanese yen notes printed on paper based on the fibre banana, abaca. Abaca, *Musa textilis*, has long been used by rural people in the Philippines, the centre of origin of abaca, for making hard-wearing textiles, which they have woven from the fibres stripped from the pseudostem and colored using dyes from native plant leaves and roots.

The use of agricultural by-products helps us to achieve two environmentally friendly goals. First, it solves the problem of what to do with agricultural waste. Second, it helps alleviate a disposal problem inherent to the paper industry.

In the case of banana fibre, the banana stalk, isn't part of the fruit nor is it a permanent part of the tree. Typically, this banana stalk was casually disposed of into landfills and rivers where it would oxidise and harm the local ecology. Using ‘pinzotes’ as a secondary fibre source offers a solution to the thousands of tons that are left to rot and oxidise after each banana harvest.
About 230,000 tons of these banana stalks were disposed of yearly in Costa Rica alone. The banana stem contains fibre to the extent of approximately 4 per cent of its weight. Since there is a shortage of fibrous material for making paper, etc. in India, the banana stem fibre can be used economically. The banana fibre apart from serving as a very good base for making specialised products like plywood, craft papers, insulating papers, serves as an excellent source of strength. At present, the only use of banana fibres seems to be in the preparation of fancy bags and decorative articles, other than in the paper industry. At a time when natural fibres turn auto parts green, investigation of this abundantly available material which is currently under utilised will be the best way to meet the challenges facing the composite industry. In India approximately 1.5 million acres of land is cultivated with banana plantations which yield about $3 \times 10^5$ tons of fibre. Usage of banana fibres in the composite industry will boost the economy of banana cultivation, economy of the state and also open new job avenues for the rural people of the state.

1.18.2. Scope of the present work

The present work aims at investigating the prospect of using banana fibre as reinforcement in polyester matrix. Research work is going on with other natural fibres like jute, flax, hemp, kenaf etc. The factors, which affect the property of natural fibres is the cellulose content and the microfibrillar angle. Banana fibres have relatively high cellulose content and a low microfibrillar angle. Presently they are underutilised and if put to better use can improve the
economy of banana cultivation and can be used as a good candidate as reinforcement in polymeric and cement matrices.

1.19. Major Objectives

1.19.1. Chemical modification of the banana fibre surface for improved interaction with the polymer matrix

Natural fibres are known for their weak interaction with non-polar/less polar matrices. The polar natural fibre and non-polar polymer matrix end up in relatively weak bonding. This can be improved to an extent by varying the polarity of the fibre surface. Treatment with various chemical agents like silanes and alkali can be used effectively in order to change the surface polarity and thereby improve the fibre/matrix interaction. In view of this, cellulose fibre surface has been modified by silane and alkali treatments.

1.19.2. Characterisation of the modified fibre surface by techniques like zeta potential, solvatochromism and spectroscopic methods

Techniques like spectroscopy, zeta potential and solvatochromism have been used over the years to characterise modified fibre surface. An insight into chemical interaction that has occurred on the fibre surface can be obtained by techniques like FTIR. Changes in the polarity of a surface can be studied by techniques like solvatochromism. Carefully selected probe dyes, that were synthesized, found effective in measuring the polarity changes on polymer surfaces, can be easily used in the case of natural fibres as well.
1.19.3. Optimisation of the banana/glass fibre ratio and the layering pattern in the preparation of hybrid composites

This involves maintaining the lowest possible volume fraction of glass to make cost effective and high strength hybrid. Keeping the total volume fraction of the fibres constant, the banana fibre can be replaced gradually by glass fibres and mechanical/geometrical arrangement of glass and banana fibres have to be tried to find out the best hybrid configuration which gives the best properties including reduction in water uptake.

1.19.4. Design of textile composites from banana fibre and glass fibre

Woven fabric composites are widely used in laminated composites for engineering applications. Woven fabric composites have the advantage of easy mouldability and improved dimensional stability. Woven fabric of banana and glass with yarns of banana in the warp direction and bundles of banana and glass in the weft direction are used for the preparation of composites. The ultimate properties of the composite are determined by factors like weaving architecture, fibre volume fraction and the arrangement of the layers. Different layering patterns, fibre volume fraction and weaving architecture have to be tried to optimise the number of layers as well as the fibre volume fraction.

1.19.5. Macroscale examination of the composites to evaluate the fibre/matrix interactions

The mechanical properties of a composite are clear indications of the strength of the interface and thereby the fibre/matrix interaction. The fracture mechanism and the value of the strength characteristics point to the fibre/matrix
interaction. Therefore a comprehensive analysis of the macroscopic properties of the composite has to be undertaken.

1.19.6. Analysis of the dynamic mechanical properties of the composites

Fibre/matrix interaction in composites can be studied in detail based on the response of the material when subjected to dynamic mechanical analysis. The nature of the damping curves and the modulus curves can be good indications of the fibre/matrix interactions and the nature of the interface.

1.19.7. Stress relaxation behaviour of the composites

Long term behaviour of the composites can be obtained by studying the stress relaxation behaviour of the composites. Stress decay as a function of time is extremely important to predict the use of these composites for dynamic applications. Fibre/matrix interactions can also be analysed by stress relaxation experiments.

1.19.8. Water absorption behaviour of the composites

Water absorption is an extremely important characteristic of composites for applications where contact with moisture becomes essential. Addition of glass is found to reduce the water uptake of the composites because they are less hydrophilic than cellulose fibres. In applications where the composite comes in contact with moisture, the effect of the arrangement of the glass and banana on water absorption of the composite is also of extreme importance.
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