Chapter 1

INTRODUCTION

1.1. General Introduction

In recent years, composites made of natural fibres have received increasing attention in light of the growing environmental awareness. Also because of their low density, good mechanical performance, unlimited availability and problem-free disposal, natural fibres offer a real alternative to the technical reinforcing fibres presently available. Natural fibres can compete with glass fibres especially with respect to the specific strength and specific stiffness.

Composites were a need in the evolution of engineering materials because by a combination of materials it is possible to overcome, for instance, brittleness and poor processability of stiff and hard polymers. The developments in composite material after meeting the challenges of aerospace sector have cascaded down for catering to domestic and industrial applications. Composites, the wonder material with light weight, high strength-to-weight ratio and stiffness properties have come a long way in replacing the conventional materials like metals, wood etc. The material scientists all over the world focused their attention on natural composites reinforced with jute, sisal, coir, pineapple etc. primarily to cut down the cost of raw materials.

The relative importance of the structural materials most commonly used, ie. metals, polymers, composites, and ceramics, to various societies throughout history has fluctuated. Ashby presents a chronological variation of the relative importance of each group from 10,000 B.C. and extrapolates their importance through the year 2020. The information contained in Ashby's article has been partially reproduced in Figure 1.1. The importance of composites has
experienced steady growth since about 1960 and is projected to continue to increase through the next several decades.

**Figure 1.1. Relative importance of material development through history**


The fibre-reinforced plastics market is estimated at almost 1.04 million metric tonnes (2.3 billion lbs) in 2002, and is expected to increase by 15% in volume by 2007. These figures are forecast in a study released from Business Communications Co, Inc, *Composites: Resins, Fillers, Reinforcements, Natural Fibers and Nanocomposites* (report number RP-178). According to the report, the market for fibre-reinforced plastics will grow at an average annual growth rate (AAGR) of 3.0% through the next five years, increasing to 1.2 million tonnes per year by 2007.

A composite material is defined [1-2] as any substance which is made by physically combining two or more materials differing in composition or form to produce a multiphase material which possesses superior properties that are not obtainable with any of the constituent materials acting alone. These constituents remain bonded together but retain their identity and properties. The constituent that is continuous and is often but not always, present in the greater quantity in the composite is termed the *matrix* [3]. The second constituent is referred to as the *reinforcement*, as it enhances or reinforces the mechanical properties of the
In principle, any isotropic material can be reinforced; the reinforcing material is usually stiffer, stronger or tougher than the matrix and there has to be a good adhesion between the components. At least one of the dimensions of the reinforcement is small, say less than 500μm and sometimes only of the order of a micron. The geometry of the reinforced phase is one of the major parameters in determining the effectiveness of the reinforcement. In other words, the mechanical properties of composites are function of the shape and dimensions of the reinforcement.

![Figure 1.2. Formation of composite material](image)

Although composite materials are widely perceived as being a modern development, composites have in fact been around for over 5000 years—since the construction of Babylon with bitumen reinforced with straw and horse hair. Indeed, composites can theoretically be called the oldest engineering concept, as nature has been exploiting them since the dawn of time. Modern and ancient applications all make use of the fact that composites can possess enhanced strength, stiffness and fracture toughness whilst not exhibiting an increase in weight.

Composites prepared from plastic materials with fibre reinforcement are called fibre-reinforced plastics (FRP). Fibres can be either discontinuous (chopped) or continuous. In FRP, the polymer or plastics possessing the properties like durability and easy modality is combined with reinforcements like synthetic or natural fibres having characteristics like light weight, non-corrosiveness, adequate strength, stiffness and load bearing capacities. The combination of these properties provides synergism to the composite making it
more suitable for the desired end users. The unprecedented growth of FRP nowadays is due to their great versatility and high performance [4,5].

![Figure 1.3. Tailored composite (Laminar)](image)

In recent years, polymer composites containing vegetable fibres have received considerable attention both in the literature and industry. The interest in natural fibre reinforced polymer composites is growing rapidly due to the high performance in mechanical properties, significant processing advantages, low cost and low density. Natural fibres are renewable resources in many developing countries of the world; they are cheaper, pose no health hazards and finally, provide a solution to environmental pollution by finding new uses for waste materials. Furthermore, natural fibre reinforced polymer composites form a new class of materials, which seem to have good potential in the future as a substitute for scarce wood and wood based materials in structural applications. The structure, properties and applications of various composites have been investigated worldwide by several researchers [6-12]

1.2. Classification of Composites

Composites can be classified in different ways depending on

a. The size of the constituents-macro (>10^{-6}m), micro (10^{-8}-10^{-6}m) and nano (10^{-8}-10^{-9}m)

b. The occurrence of the composites-natural, synthetic
c. The form of their structural components- fibrous (composed of fibres in a matrix), laminar (composed of layers of materials-Fig. 1.3) and particulate (composed of particles in a matrix).

d. The matrix material- metal (MMC), ceramics (CMC), polymer (PMC)

Fibrous composite can be subdivided into - continuous fibre (large aspect ratio), discontinuous (short) fibre (low aspect ratio) and hybrid (combination of more than one type of fibre)

![Fibre reinforced composites diagram](image)

Schematic representation of fibrous composites is given in Figure 1.4.

![Figure 1.4. Schematic representation of fibrous composites.](image)
The particulate class can be further subdivided into flake (flat flakes in a matrix) or skeletal (composed of a continuous skeletal matrix filled by a second material).

Composites in which the reinforcements are discontinuous fibres or whiskers can be produced so that the reinforcements have either random or biased orientation. Material systems composed of discontinuous reinforcements are considered single layer composites. The discontinuities can produce a material response that is anisotropic, but in many instances the random reinforcements produce nearly isotropic composites. Continuous fibre composites can be either single layer or multilayered. The single layer continuous fibre composites can be either unidirectional or woven, and multilayered composites are generally referred to as laminates. The material response of a continuous fibre composite is generally orthotropic. Schematics of both types of fibrous composites are shown in Figure 1.4.

A particulate composite is characterized as being composed of particles suspended in a matrix. Particles can have virtually any shape, size or configuration. There are two subclasses of particulates: flake and filled skeletal: A flake composite is generally composed of flakes with large ratios of platform area to thickness, suspended in a matrix material. A filled/skeletal composite is composed of a continuous skeletal matrix filled by a second material (Figure 1.5).

Figure 1.5. Schematic representation of particulate composites.
1.3. Role of matrix materials in composites

In a composite the matrix is required to fulfil the following functions:

- To bind together the fibres by virtue of its cohesive and adhesive characteristics
- To protect them from environments and handling.
- To disperse the fibres and maintain the desired fibre orientation and spacing.
- To transfer stresses to the fibres by adhesion and/or friction across the fibre-matrix interface when the composite is under load, and thus to avoid any catastrophic propagation of cracks and subsequent failure of the composites.
- To be chemically and thermally compatible with the reinforcing fibres.
- To be compatible with the manufacturing methods which are available to fabricate the desired composite components.

The matrices are of three types. They are:

1.3.1. Thermoset polymer matrices

Thermosetting polymers or thermosets are resins which change irreversibly under the influence of heat into an infusible and insoluble material by the formation of covalently cross-linked, thermally stable networks. Such polymers are prepared in two stages. The first step is the formation of long chain molecules, which are capable of further reaction with each other. The second stage is the application of heat and/or the addition of curatives, which causes a reaction to occur between the chains, thus producing a complex cross-linked polymer. Sometimes irradiation is employed to achieve cross-linking [13]. Important thermosetting resins are unsaturated polyesters, epoxy resins, alkyds, vinyl esters and allyl resins, phenolics, amino plastics, urethanes, silicones, furfural etc. [14]
The thermosetting category is dominated by polyester resins which accounts for 88% of this category and 74% of all matrix resins. Epoxy resins (5% of the total) come next, followed by other phenolic resins (7% of the total). The popularity of polyester resins is due to their ease of handling, good curing properties and for the fact that they are the cheapest among all the thermoset resins.

The structure of epoxy resin and unsaturated polyester resin are given below.

1.3.1.1. Epoxy resins

Epoxy resins are characterized by the presence of more than one 1, 2- epoxide groups per molecule. It has the general structure shown below.

Cross-linking is achieved by introducing curatives that react with epoxy and hydroxyl groups situated on adjacent chains. Epoxy resins can be cured at room temperature but quite often heat is applied to accelerate and improve curing. Hardeners include anhydrides (acids), amines, polyamides, dicyandiamide etc. Where mechanical properties and temperature tolerance of unsaturated polyesters are no longer suffice, epoxies are often used due to their significant superiority in these respects. Significance of epoxies are low viscosity, low shrinkage and the fact that they adhere well to the reinforcement fibres make them a unique matrix. The major drawbacks of epoxies are high price, toxicity and complex processing requirements, which often include elevated temperature and consolidation pressure, thus translating into costly manufacturing operations.

1.3.1.2. Unsaturated Polyester resin (UPR)

A large number of thermoset resins are commercially available and these can be classified into alkyds, unsaturated polyesters, vinyl esters, allyl
resins etc. It has been reported that USP represents about 70% of the total use while the other thermoset and thermoplastics evenly share the remaining part.

General-purpose (GP) grade USP is prepared by the condensation of propylene glycol with a mixture of maleic anhydride and phthalic anhydride. The condensate is then dissolved in an unsaturated co-reactant diluent, styrene to get a resin formulation. It has the following typical structure.

When cross-linking is initiated with the help of a catalyst and an accelerator, styrene facilitates cross-linking at the sites of unsaturation in the polyester chains. The saturated acid reduces the number of cross-linking sites and consequently the cross-link density and brittleness of the cured resin. Since cross-linking occurs via free radical addition mechanism across the double bonds in the polyester chain and the reactive diluent, no volatiles are given off during cure.

In addition to the above-mentioned thermosets, there are several other thermoset matrices used in composite applications. Some of them are: Polyurethanes, Aminoplasts, silicones etc.

1.3.2. Thermoplastic matrices

Thermoplastic matrices were developed to provide cheaper alternative to thermosets and to improve the upper use temperature of polymer matrix composites. Thermoplastics readily flow under stress at elevated temperatures, so allowing them to be fabricated into the required component, and become solid and retain their shape when cooled to room temperature [3]. These polymers may be repeatedly heated, fabricated and cooled and consequently scrap may be recycled. Unlike thermosets, thermoplastics are
not cross-linked, and can therefore melt. They derive their strength and stiffness from the inherent properties of the monomer units and the very high molecular weight. They are semi crystalline or amorphous in nature. Thermoplastics have superior toughness to thermosets. Some of the thermoplastic polymers in common use are: Polyethylene (PE), Polypropylene (PP), Polyamides (PA), Poly(ethylene terephthalate) (PET), poly (butylene terephthalate) (PBT), poly (ether ketone) (PEK), poly (ether ether ketone) (PEEK), polysulphone (PSU), polyether sulphone (PES) and poly(arylsulphone) (PAS), poly (ether imide) (PEI) and poly (amide imide) (PAI), Poly(phenylene sulphone) PPS.

1.3.3. Elastomers

These are macromolecular materials that return rapidly to their initial dimension and shape (approximately) at room temperature, after substantial deformation by a weak stress and subsequent release of the stress. Rubber is a versatile and adaptable material that has been successfully used as matrix for composite preparation. There are different types of rubbers including Natural rubber (NR) which is a high molecular weight polymer of isoprene in which essentially all the isoprenes have the cis 1-4 configuration and a variety of synthetic rubbers like Styrene butadiene rubber (SBR), Polybutadiene rubber (BR), nitrile-butadiene rubber (NBR), Ethylene propylene co polymer (EPM), Ethylene propylene diene monomers (EPDM), Poly isoprene rubber (IR), Butyl rubber (IIR) etc.

1.4. Reinforcements used in composites

The structural load applied to the composite is primarily carried by the reinforcement. Thus the strength and stiffness of the composite is mainly determined by the reinforcement. Composite reinforcement may be in the form of fibres, particles or whiskers. Particles have no preferred directions and are mainly a means to improve properties or lower the cost of isotropic material. The aspect ratio (length to diameter ratio) of the particles is of the order of unity and
dimension that range from that of a fibre diameter to several millimeters. Whiskers have aspect ratios of order 1000 and diameter of order 0.1-1μm. Whiskers are pure single crystals manufactured through chemical vapour deposition and thus have preferred directions. Whiskers are more or less randomly arranged in the matrix, whisker reinforced composites are likely to be considered as macroscopically isotropic. Reinforcements are of two types-synthetic and natural.

1.4.1. Synthetic fibres
1.4.1.1. Glass fibres

Glass fibre is the best known reinforcement in high performance composite applications due to its appealing combination of good properties and low cost. The major ingredient of glass fibre is silica which is mixed with varying amounts of other oxides. The different types of glass fibres commercially available are E and S glass. The letter ‘E’ stands for ‘electrical’ as the composition has a high electrical resistance and ‘S’ stands for strength.

1.4.1.2. Carbon fibres

Carbon fibres are commercially manufactured from three different precursors-rayon, polyacrylonitrile (PAN) and petroleum pitch. They are mainly used in aerospace industry due to its outstanding mechanical properties combined with low weight.

1.4.1.3. Aramid fibres

‘Aramid’ is a generic term for aromatic polyamide fibres. eg. Kevlar.

1.4.1.4. Polyolefins

The most common example of high strength polyolefin fibre is ultra high molecular weight polyethylene (UHMWPE). The potential applications of polyolefin fibres include ballistic protection and sporting goods.
Table 1.1. Mechanical properties of some mineral and synthetic fibres

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Sp. Gravity</th>
<th>Tensile strength (GPa)</th>
<th>Young’s Modulus (GPa)</th>
<th>Strain to Failure (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nylon 66</td>
<td>1.14</td>
<td>1.10</td>
<td>5.52</td>
<td>18</td>
</tr>
<tr>
<td>Kevlar 49</td>
<td>1.45</td>
<td>3.62</td>
<td>131</td>
<td>2.8</td>
</tr>
<tr>
<td>E-Glass</td>
<td>2.54</td>
<td>3.45</td>
<td>72.4</td>
<td>4.8</td>
</tr>
<tr>
<td>Carbon</td>
<td>1.76</td>
<td>3.20</td>
<td>86.9</td>
<td>1.4</td>
</tr>
<tr>
<td>Aramid</td>
<td>1.40</td>
<td>3.15</td>
<td>6.3-6.7</td>
<td>3.3-3.7</td>
</tr>
</tbody>
</table>

1.4.2. Natural fibres

These are one of the major renewable resource materials throughout the world. There are about 2000 species of useful fibre plants in various parts of the world and these are used for many applications. Jute, sisal, banana and coir, the major source of natural fibres, are grown in many parts of India. Some of them have aspect ratios >1000 and can be woven easily. Recent reports indicate that plant-based natural fibres can very well be used as reinforcement in polymer composites, replacing to some extent more expensive and non-renewable synthetic fibres such as glass.

Natural fibres are classified into three major types as animal fibres, vegetable fibres and mineral fibres. All animal fibres such as silk, wool and mohair are complex proteins. They are resistant to most organic acids and to certain powerful mineral acids. They constitute the fur or hair that serves as the protective epidermal covering of animals. Silk is an exception to this, which is extruded by the larvae of moths and insects and is used to spin their cocoons. It is the only filament that commonly reaches a length of more than 1000 m. Several silk filaments can be gathered to produce textile yarn and staple form is used to manufacture spin yarns. Naturally crimped wool fibres produce air trapping yarns that are used for insulating materials. An important class of naturally occurring mineral fibre is asbestos.
Natural fibres can be divided into three types- bast fibres, leaf fibres and seed hair fibres - based on their origin within the plant, as given below.

1.4.2.1. Bast fibres

Bast consists of a wood core surrounded by a stem. Within the stem, there are a number of fibre bundles, each containing individual fibre cells or filaments. The filaments are made of cellulose and hemicellulose, bonded together by a matrix, which can be lignin or pectin. The pectin surrounds the bundle thus holding them on to the stem. The pectin is removed during the retting process. This enables separation of the bundles from the rest of the stem (scutching). Stronger composites are obtained if the bundles are pre-treated in a way that removes the lignin between the cells. Boiling in alkali is one of the ways to separate cells. Bast fibres are usually grown in warm climates. e.g. Bagasse, flax, hemp, jute, kenaf, ramie.

a) Bagasse

Bagasse is a by-product from the sugarcane industry and it consists of the sheath and pith of the cane stalks. It grows abundantly in tropical countries like Brazil, India, Pakistan, Indonesia, Philippines and Jamaica. Bagasse fibre reinforced composites have been used as materials for structural components.

b) Flax

This fibre is extracted from the plant *Linum usitatissimum* *L.* that is grown chiefly in the USSR, Poland, France, Belgium and Ireland. Flax is an annual plant with a slender, grayish green stem growing to a height of 90-120 cm. After deseeding, the straw is retted, i.e. the fibres are liberated through enzymatic action on pectinous binding material in the stem. The fibre is then hackled for alignment and final cleaning.
c) **Hemp**

The hemp fibre is extracted from the plant *Cannabis sativa*. The plant is grown for commercial production of fibre, mainly in China and Eastern Europe. The hemp plant is grown for fibre from the stem, for oil from the seeds or for drugs from the flowers or leaves. The retted and dried stem is further treated by either hand breaking and hackling to remove the woody stem portion by mechanical breaking.

d) **Jute**

The jute fibre is obtained from two species of the annual herbaceous plant *Corchorus capsularis* of Indo-Burma origin and *C. olitorius* from Africa. The major jute production areas are India and Bangladesh. The plants are harvested by hand at an early seed stage using knives and the stems are left on the ground for several days to promote defoliation. The defoliated stems are bundled and taken for wet retting in canals, ditches or ponds for periods of 10-20 days.

e) **Kenaf**

The kenaf fibre is extracted from the plant *Hibiscus cannabinus*. The plant is native to Egypt and USSR. The plant is a herbaceous annual growing in single stem heights of 1-4 m. Kenaf is often stem-retted followed by hand or mechanical stripping and washing.

f) **Ramie**

This fibre also known as China grass is produced from the stems of *Bochmeria nivea*, growing in regions varying from temperate to tropical including China, Brazil, Taiwan and Japan. The plant grows 1-2 m high or higher with stems 8-16 mm in diameter. The ramie fibre is contained in the bark and is usually extracted by hand stripping and scrapping. The plant is cut green and defoliated manually and bast ribbons are stripped from the woody stem.

1.4.2.2. **Leaf fibres**

In general, the leaf fibres are coarser than the bast fibres. e.g. sisal, abaca, banana and henequen. Within the total production of leaf fibres, sisal is the most
important which is obtained from the agave plant. The stiffness is relatively high and it is often applied as binder twines. The abaca fibre that is from the banana plant is durable and resistant to sea water.

a) Banana

Banana fibre is extracted from the plant *Musa sapientum*. Each of the stalks is 2.7-6.7 m tall with a trunk 10-20 cm wide at the base. The sheaths before expanding are 2-4 m long, 13-20 cm wide and about 10 mm thick at the centre. The fibres run lengthwise in the sheaths. The mature stalks are cut off at the roots and at a point just below where they begin to expand. The main countries of origin are India, Indonesia and Philippines.

b) Sisal

Sisal is extracted from the leaves of the plant *Agave sisalana* that is widely cultivated in the Western hemisphere, Africa and Asia. The agaves have rosettes of fleshy leaves, usually long and narrow, which grow out from a central bud. As the leaves mature, they gradually spread out horizontally and are 1-2 m long, 10-15 cm wide and about 6 mm thick at the centre. The fibres are embedded longitudinally in the leaves and are most abundant near the leaf surfaces. The fibre is removed when the leaves are cut because dry fibres adhere to the pulp. The fibre is removed by scraping away the pulpy material, generally by a mechanical decortication process.

c) Pineapple

The fibres are extracted from the leaves of the plant *Ananus comosus* belonging to the Bromeliaceae family. The fibre is extracted by hand scraping after beating the leaves to break up the pulpy tissue or after a retting process that partially ferments and softens the leaves.

1.4.2.3. Seed fibres

Cotton is the most common seed fibre and is used for textile all over the world. Other seed fibres are applied in less demanding applications such as
stuffing of upholstery. Coir is an exception to this and is used to make mats and ropes. Other examples are kapok and oil palm.

a) Coir

The fibre is contained in the husk of coconut tree (*Cocos nucifera*) Sri Lanka and India are important producers of coir. The extraction of the fibre involves retting of husks in water. The retted husks are beaten with sticks to remove extraneous matter and the dried fibre is suitable for spinning.

b) Oil palm

It belongs to the species *Elaeis guineensis* and is commonly found in the tropical forests of West Africa. Its major industrial cultivation is in the Southeast Asian countries such as Malaysia and Indonesia. Oil palm empty fruit bunch (OPEFB) fibre and oil palm mesocarp fibre are two important types of fibrous materials left in the palm-oil mill. OPEFB is obtained after the removal of oil seeds from fruit bunch for oil extraction. The fibres are extracted by retting followed by cleaning and drying.

1.5. Microstructure of natural cellulose fibres

All vegetable fibres predominantly contain cellulose, along with varying amounts of substances like hemicellulose, lignin, pectins and waxes. Cellulose resists alkalis and most of the organic acids, but can be destroyed by strong mineral acids. The single fibre has a diameter of around 10-20 μm. From the living cell, cellulose is produced as micro fibrils of 5 nm diameter; each composed of 30 to 100 cellulose molecules in extended chain conformation and provides mechanical strength to the fibre. A good orientation of micro fibrils along with high cellulose content is essential for obtaining a fibre with good mechanical properties. The microstructure of natural fibres comprises of different hierarchical structures and so it is extremely complicated (Fig.1.6). Each fibre cell is constituted by four concentric layers- i.e. primary wall, outer secondary wall, middle secondary wall and inner secondary wall. Primary wall is porous and these pores act as diffusion paths of
water through the wall. It is initially cellulosic but become lignified on growth. It also consists of pectin and other non-carbohydrates.

**Figure 1.6.** Structural constitution of natural vegetable fibre cell, in which the secondary wall $S_2$ makes up ~ 80% of the total thickness and then act as the main load bearing component


The secondary wall is developed on to the inner surface of the primary wall, which comprises of a number of cylindrical and anisotropic cellulose microfibrils. These are surrounded and joined by a loose and complicated macro molecular network of lignin-hemicellulose matrix. The micro fibrils present in the inner secondary wall are spirally arranged about the fibre axis at an angle called the microfibrillar angle which varies from fibre to fibre.

**Fig. 1.7.** Model for the description of the stiffness of the fibre

(a) layers in a 3D view, (b) layers in a 2D view

The spiral angle of the fibrils and the content of cellulose, determines generally the mechanical properties of the cellulose based natural fibres. The model for the description of the stiffness of the cellulose fibres developed by Hearle et al. [15] is shown in Figure.1.7. The lumen in the centre of the fibre contributes to the water uptake properties of the fibre [16]. Basic properties of some vegetable fibres are given in Table 1.2.

**Table 1.2. Mechanical properties of some natural fibres**


<table>
<thead>
<tr>
<th>Fibre</th>
<th>Density (g/cm³)</th>
<th>Elongation (%)</th>
<th>Tensile strength (MPa)</th>
<th>Young's Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cotton</td>
<td>1.5-1.6</td>
<td>7.0-8.0</td>
<td>287-597</td>
<td>5.5-12.6</td>
</tr>
<tr>
<td>Jute</td>
<td>1.3</td>
<td>1.5-1.8</td>
<td>393-773</td>
<td>26.5</td>
</tr>
<tr>
<td>Flax</td>
<td>1.5</td>
<td>2.7-3.2</td>
<td>345-1035</td>
<td>27.6</td>
</tr>
<tr>
<td>Hemp</td>
<td>-</td>
<td>1.6</td>
<td>690</td>
<td>-</td>
</tr>
<tr>
<td>Ramie</td>
<td>-</td>
<td>3.6-3.8</td>
<td>400-938</td>
<td>61.4-128</td>
</tr>
<tr>
<td>Sisal</td>
<td>1.5</td>
<td>2.0-2.5</td>
<td>511-635</td>
<td>9.4-22.0</td>
</tr>
<tr>
<td>Coir</td>
<td>1.2</td>
<td>30.0</td>
<td>175</td>
<td>4.0-6.0</td>
</tr>
<tr>
<td>Viscose (cord)</td>
<td>-</td>
<td>11.4</td>
<td>593</td>
<td>11.0</td>
</tr>
<tr>
<td>Softwood kraft</td>
<td>1.5</td>
<td>-</td>
<td>1000</td>
<td>40</td>
</tr>
<tr>
<td>Oil Palm</td>
<td>1.4</td>
<td>14</td>
<td>248</td>
<td>2</td>
</tr>
<tr>
<td>OPEFB</td>
<td>-</td>
<td>17</td>
<td>80</td>
<td>0.5</td>
</tr>
<tr>
<td>Mesocarp fibre</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

a-obtained from fruit bunch after removal of oil seeds  
b-obtained from oil seeds after oil extraction
1.6. Chemical structure of Natural fibres

The chemical composition and cell structure of natural fibres are quite complex. Each fibre is essentially a composite, in which rigid cellulose microfibrils are immersed in a soft lignin and hemicellulose matrix. The chemical composition of natural fibres varies depending on the type of the fibre. With the exception of cotton, the components of natural fibres are cellulose, hemicellulose, lignin, pectin, waxes and water soluble substances. Cellulose, hemicellulose and lignin are the basic components responsible for the physical properties of the fibres.

a) Cellulose

Cellulose is a linear condensation polymer consisting of D-anhydro glucopyranose units joined together by β-1,4-glycosidic bonds. The structure of cellulose is given in figure 1.8.

![Cellulose Structure](image)

Each unit is rotated through 180° with respect to its neighbours so that structure repeats itself every two units. The pair of units is called cellobiose and since cellulose is made up of cellobiose units, cellulose is technically a polymer of cellobiose rather than α-D glucose. The chemical character of cellulose molecule is determined by the sensitivity of β-glucosidic linkages, between the glucose repeating units to hydrolytic attack and by the presence of three hydroxyl groups, one primary and two secondary in each of the base units. These reactive hydroxyl groups are able to undergo esterification and etherification reactions. The main cause of the relative stiffness and rigidity of the cellulose molecule is the intra molecular hydrogen
bonding, which is reflected in its high viscosity in solution, its high tendency to crystallize and the ability to form fibrillar strands. The β-glycosidic linkages further favour the chain stiffness. The molecular structure of cellulose is responsible for its supramolecular structure and this in turn determines many of the physical and chemical properties of the fibre.

The crystal structure of natural and regenerated cellulose is known as cellulose-I and cellulose-II respectively. In cellulose-I the chains within the unit cell are in parallel configuration [17] while they have anti parallel configuration [18] in cellulose-II.

b) Hemicellulose

Hemicellulose consists of a group of polysaccharides that remain associated with the cellulose after lignin has been removed. The hemicellulose differs 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 polymerization of native cellulose is also hundred times higher than that of hemicellulose. Unlike cellulose, the constituents of hemicellulose differ from plant to plant [19].

c) Lignin

Lignins are complex hydrocarbon with aliphatic and aromatic components. The monomer units present in lignin are various ring substituted phenyl propanes linked together in ways which are still not fully understood and the detailed structure differ from source to source. The mechanical properties are lower than those of cellulose [20].

d) Pectin

Pectin is a collective name for hetero polysaccharides which consists essentially of polygalacturon acid and is soluble in water only after partial neutralization with alkali or ammonium hydroxide [12].
e) Waxes

Waxes make up the part of the fibres, which can be extracted with organic solvents and consists of different types of alcohols which are insoluble in water as well as in acids.

<table>
<thead>
<tr>
<th></th>
<th>Cotton</th>
<th>Jute</th>
<th>Flax</th>
<th>Ramie</th>
<th>Sisal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>82.7</td>
<td>64.4</td>
<td>64.1</td>
<td>68.6</td>
<td>65.8</td>
</tr>
<tr>
<td>Hemi-cellulose</td>
<td>5.7</td>
<td>12.0</td>
<td>16.7</td>
<td>13.1</td>
<td>12.0</td>
</tr>
<tr>
<td>Pectin</td>
<td>5.7</td>
<td>0.2</td>
<td>1.8</td>
<td>1.9</td>
<td>0.8</td>
</tr>
<tr>
<td>Lignin</td>
<td>-</td>
<td>11.8</td>
<td>2.0</td>
<td>0.6</td>
<td>9.9</td>
</tr>
<tr>
<td>Water Soluble</td>
<td>1.0</td>
<td>1.1</td>
<td>3.9</td>
<td>5.5</td>
<td>1.2</td>
</tr>
<tr>
<td>Wax</td>
<td>0.6</td>
<td>0.5</td>
<td>1.5</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Water</td>
<td>10.0</td>
<td>10.0</td>
<td>10.0</td>
<td>10.0</td>
<td>10.0</td>
</tr>
</tbody>
</table>

1.7. Advantages of Natural fibres as reinforcement in composites

Natural fibres, as a substitute for glass components, have gained interest in the last decade, especially in the housing sector. The moderate mechanical properties of natural fibres prevent them from being used in high performance applications where carbon fibre reinforced composites would be utilized, but for many reasons they can compete with glass fibre. The 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. Nowadays natural fibre reinforced polymer composites come prior to synthetic fibre reinforced composites in properties such as biodegradability, combustibility, light weight, non toxicity, decreased environmental pollution, low cost, ease of recyclability etc. These advantages place the natural fibre composites among the high performance composites having economical and environmental advantages. The versatile high performance applications of
natural fibre composites, which can replace glass and carbon fibres, were listed in an article by Hill [21]. The vegetable fibres have density of about half that of glass fibre. During the processing of natural fibre composites, there will be no abrasion of the processing machines. These fibres can withstand processing temperatures up to 250°C. Reinforcement of polymers with vegetable fibres gives good opportunities for the effective utilization of agricultural products. Physical, chemical and mechanical properties of some important natural fibres are given in Table 1.2. They are cent percent combustible without the production of either toxic gases or solid residues. Wright and Mathias succeeded in preparing lightweight materials from balsawood and polymer [22]. Investigations have been carried out by Hedenberg and Gatenholm in recycling the plastic and cellulose waste into composite [23]. Systematic investigations on wood flour reinforced polystyrene composites have been carried out by Maldas and Kokta [24]. The effects of hybridization of saw dust with glass and mica and of the surface treatment of the reinforcing filler on the mechanical properties were studied [25]. The range of products in the automobile industry based on natural fibres is based on polymers like plastics and elastomers and fibres like flax, hemp, sisal etc. The use of natural fibres in automobile industry has grown rapidly over the last five years. Recently value added composite materials were developed from neisan jute fabric and polypropylene having enhanced mechanical properties and reduced hydrophilicity [26]. Yamini et al. [27] investigated the effect of board density on the properties of particle board from oil palm fibre and urea formaldehyde resin.

In recent years, considerable interest has been shown in the potential of bast fibres such as flax and hemp to act as reinforcement in polymer matrix composites (PMCs). Interest in natural fibre reinforced PMCs has been driven by a number of factors including cost, environmental issues and the wish to diversify agricultural practice. This has led to some limited commercialisation of natural fibre reinforced PMCs, most notably in the automotive sector [1].
Nevertheless, uptake in other areas has been minimal, but despite this, there is good potential for bast fibre reinforced composites in many sectors ranging from consumer goods to construction. There are a number of reasons why there has been so little commercial attention paid to these composites, outside the automotive sector, but perhaps the most significant is that the performance of current materials is simply inadequate for most structural applications. Increasing the performance of these materials is therefore essential, if they are to gain widespread acceptance.

Natural fibres enjoy the right potential for utilization in composites due to their adequate tensile strength and good specific modulus, thus ensuring a value added application avenue. Plant based composites have been widely used in construction; the ancient Egyptians used to reinforce clay walls. To eliminate problems resulting from the incorporation of synthetic fibres such as high abrasiveness, health hazards, disposal problems etc. incorporation of natural fibres is proposed. They are abundant, renewable, and cheap and are having low density. Material scientists all over the world focus their attention on natural composites reinforced with fibres like jute, sisal, coir, pineapple, banana etc. primarily to cut down the cost of raw materials.

1.8. Major drawbacks of Natural fibres
1.8.1. Moisture absorption of fibres

    The lignocellulosic natural fibres are hydrophilic and absorb moisture. The swelling behaviour of natural fibres is generally affected by its morphology as well as physical and chemical structures. Bio fibres change their dimensions with varying moisture content because the cell wall polymers contain hydroxyl and other oxygen containing groups, which attract moisture through hydrogen bonding [28]. The hemicelluloses are mainly responsible for moisture absorption. Water penetration through natural fibres can be explained by capillary action [29]. The waxy materials present on the surface help to retain the water molecules on the fibre. The porous nature of the natural fibre accounts for
the large initial uptake at the capillary region. The hydroxyl group (-OH) in the cellulose, hemi cellulose and lignin build a large amount of hydrogen bonds between the macromolecules in the plant fibre cell wall. Subjecting the plant fibres to humidity causes the bonds to break. The hydroxyl group then forms new hydrogen bond with water molecules, which induce swelling [30]. The schematic representation of swelling process in cellulose is given in figure 1.9.

![Schematic representation of water absorption of cellulosic fibres](image)

**Fig. 1.9. Schematic representation of water absorption of cellulosic fibres**


Generally moisture content in natural fibres varies between 5-10%. This can lead to dimensional variations in composites and also affect the mechanical properties of composites. Therefore the removal of moisture from fibres is very essential before the preparation of the composites. The moisture absorption of natural fibres can be reduced by proper surface modifications.

### 1.8.2. 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 fibre is one of their drawbacks. The thermal stability of natural fibres can be studied by Thermo Gravimetric Analysis (TGA).

As mentioned above, natural fibre is composed of mainly cellulose, hemicellulose and lignin. Each of the three major components has its own characteristic properties with respect to thermal degradation which are based in polymer composites. However the microstructure and the three dimensional nature of natural fibre are variables, that also play important roles in terms of their effects on combustion behaviour. Thus the individual chemical components of the fibre behave differently if they are isolated or if they are intimately combined within each single cell of the fibre structure [31].

Lignin, specifically the low molecular weight protolignin, degrades first and at a slower rate than the other constituents. This is shown in Figure 1.10(a). The TGA curve indicates that the beginning of the natural fibre degradation occurs at around 180°C but the rate of degradation is always lower than that of the cellulose, as shown in Figure 1.10(b).

This process has been described by Shurky and Girgis [32] who also presented an analysis of the products of degradation. From Figure 1.10(b) it is observed that the weight loss in the cellulose sample is negligible below 300°C. However above that temperature the cellulose begins to degrade fast and at about 400°C only the residual char is found. Beall [33] has described this process as the loss of hydroxyl groups and depolymerization of the cellulose to anhydroglucose units. The thermal degradation of cellulose based fibres is greatly influenced by their structure and chemical composition. The natural fibre starts degrading at about 240°C. The thermal degradation of lignocellulosic materials has been reviewed by Tinh et al. in detail for modified and unmodified materials [34, 35]. Thermal degradation of natural fibres is a two stage process, one in the temperature range 80-180°C and other in the range 280-380°C.
Gassan and Bledzki [36] studied the thermal degradation pattern of jute and flax and found that at temperatures below 170°C fibre properties were affected only slightly while at temperatures above 170°C significant drop in tenacity and degree of polymerization were observed. Because of chain scissions, a slight increase in the degree of crystallinity was observed. Thermal degradation pattern of other cellulosic fibres like oil palm, sisal, banana, coir, hemp, jute etc. was also reported [37-42]. It was reported that the chemical modification improved the thermal stability of their composites. Chemically modified fibres showed a satisfactory thermal stability at processing temperatures for potential composites. Thermal degradation of natural fibres is a two stage process. The low temperature degradation [80-180°C] process is associated with degradation of lignin, whereas the high temperature degradation [280-380°C] process is due to cellulose. The degradation of natural fibres is a crucial aspect in the development of natural fibre composites and thus has a bearing on the curing temperature in the case of elastomers and thermosets and extrusion temperature in thermoplastic composites [43, 44].
1.8.3. Biodegradation and Photo degradation of Natural fibre

The lignocellulosic natural fibres are degraded biologically by very specific enzymes capable of hydrolyzing the cellulose, especially hemicellulose present in the cell wall into digestible units [45]. Lignocellulosics exposed outdoors undergo photochemical degradation caused by ultraviolet light. Resistance to biodegradation and ultraviolet radiation can be improved by bonding chemicals to cell wall or by adding polymer to the cell matrix. Biodegradation of cellulose causes weakening the strength of the natural fibre. Photo degradation primarily takes place in the lignin component which is responsible for the colour changes [46]. The surface becomes richer in cellulose content as the lignin degrades. In comparison to lignin, cellulose is much less susceptible to ultraviolet degradation.

1.9. Fibre reinforced composites

Fibre reinforced composites consist of fibres of high strength and modulus embedded in a matrix with distinct interfaces between them. Fibre reinforcement improves the stiffness and the strength of the matrix. In the case of polymers that are not tough in the non-reinforced form, the toughness may also increase [47]. The fibre reinforced composites exhibit anisotropy in properties. The maximum improvement in properties is obtained with continuous fibre reinforcement. However, short fibre reinforced composites offer many advantages like ease of fabrication, low production cost and possibility of making complex shaped articles, over continuous fibre reinforcement. The performance of the composite is controlled by the fibres and depends on factors like aspect ratio, orientation of fibres and fibre-matrix adhesion. Discontinuous fibre reinforced composite form an important category of materials used in engineering applications. The use of fibre reinforced plastics (FRP) composites for the production of rebars and prestressing tendons in civil engineering and transportation applications are becoming increasingly important in recent years [48].
Major constituents in a fibre reinforced composite material are the reinforcing fibres and a matrix, which act as a binder for the fibres. Coupling agents and coatings used to improve the wettability of the fibre with the matrix and fillers used to reduce the cost and improve the dimensional stability are the other commonly found constituents in a composite.

1.10. Factors influencing the properties of fibre reinforced composites

1.10.1. Strength, modulus and chemical stability of fibre and matrix

In fibre reinforced composites fibres are the main load carrying members and the matrix keeps them in the desired orientation and location. The final properties of fibre-reinforced composite depend on the strength and modulus of the reinforcing fibre [49-51]. Choice of the matrix depends on the final requirements of the product and other factors like cost, fabrication process, environmental conditions and chemical resistance of the matrix. The function of the matrix will vary depending on how the composite is stressed [52]. For compressive loading, the matrix prevents the fibres from buckling and provides a stress transfer medium, so that when an individual fibre breaks, it does not lose its load carrying capacity. The physical properties of the matrix that influence the behaviour of the composites are shrinkage during cure, modulus of elasticity, ultimate elongation, tensile and flexural strength and compression and fracture toughness.

1.10.2. Fibre length, loading and orientation

Fibre length, loading and orientation play important roles in determining the ultimate properties of the fibre reinforced composites. There are several studies on the effect of fibre length and fibre orientation on the tensile strength of the short fibre composites [53]. In the case of short fibre reinforced composites, there exists a critical aspect ratio at which the properties are maximised. The critical aspect ratio depends on the volume fraction of the fibre and also on the ratio of the modulus of the fibre and matrix [54]. At low volume
fraction, the fibres play no major role and the strength of the composite is matrix dominated. Above a critical volume fraction of the fibre, the strength of the composite increases. The critical volume fraction depends on the fibre aspect ratio and found to decrease with increase in aspect ratio. At low fibre content, the critical aspect ratio remains almost constant and show sharp decrease at higher volume fraction. The critical aspect ratio is given by the equation

\[
\left( \frac{L}{D} \right)_C = \frac{\sigma_f}{2\tau_i}
\]

where,

- \( L \) - length of fibre
- \( D \) - diameter of fibre
- \( (L/D)_c \) - critical aspect ratio
- \( \sigma_f \) - tensile strength of fibre
- \( \tau_i \) - fibre-matrix interfacial shear strength.

A critical fibre length may be defined as the minimum fibre length at which the maximum allowable fibre stress can be achieved. Fig. 1.11 shows the variation of fibre stress along the fibre length in a fibre-matrix composite.

Fig. 1.11. Variations in fibre stress at a fibre/matrix interface along the fibre length
The increase in fibre length above critical fibre length does not contribute to the increase in composite strength. However, a decrease in fibre length below the critical fibre length results in a decrease in composite strength. When all the fibres are below critical length, the fibre acts only as filler and the strength of the composite decreases. As the critical aspect ratio depends on the efficiency of stress transfer from the matrix to fibre, the critical aspect ratio decreases with improvement in fibre-matrix adhesion.

In the case of fibre-reinforced composites, there is an optimum spacing between the fibres at which the fibre tensile strength is fully exploited [55] and below which the structure starts to disintegrate under loading before the tensile failure. The spacing between the fibres is controlled by the volume fraction of the fibre and fibre dispersion in the composite.

Orientation of the fibre also affects the composite strength and other properties of the composites. The reinforcement provided by each individual fibre depends on the orientation with respect to the loading axis. Longitudinally oriented fibre composites in which the fibres are oriented in the direction of applied forces, the composites are inherently anisotropic, and the maximum stress and reinforcement are achieved in the direction of fibre orientation. In the case of transversely oriented fibre composite, fibre reinforcement is virtually absent and fracture occurs at a very low tensile stress, which is usually lower than the strength of the matrix. In the case of randomly oriented composites, the strength lies between these two extremes.

Although the tensile strength of longitudinally oriented fibre composites are very high, the compressive strength shows lower values due to the buckling of the fibre [4, 56,]. In Table 1.4 the mechanical properties of unidirectionally aligned continuous fibre with polyester matrix are compared with randomly oriented short fibre composites.
Table 1.4. Mechanical properties of unidirectionally aligned continuous fibre with polyester matrix v/s randomly oriented short fibre composites


<table>
<thead>
<tr>
<th>Fibre (wt%)</th>
<th>Tensile Strength MPa</th>
<th>Young’s Modulus GPa</th>
<th>Flexural Strength MPa</th>
<th>Flexural Modulus GPa</th>
<th>Impact Strength KJm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Unidirectional</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sisal (40)</td>
<td>129</td>
<td>8.5</td>
<td>192</td>
<td>7.5</td>
<td>98*</td>
</tr>
<tr>
<td>Banana (30)</td>
<td>121</td>
<td>8.0</td>
<td>-</td>
<td>-</td>
<td>52*</td>
</tr>
<tr>
<td>Coir (30)</td>
<td>45</td>
<td>4</td>
<td>56</td>
<td>4</td>
<td>44*</td>
</tr>
<tr>
<td><strong>Chopped random</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sisal (25)</td>
<td>34.5</td>
<td>1.9</td>
<td>86.4</td>
<td>-</td>
<td>30</td>
</tr>
<tr>
<td>Banana (25)</td>
<td>43.5</td>
<td>2.3</td>
<td>92</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>Coir (25)</td>
<td>14.0</td>
<td>1.4</td>
<td>31.2</td>
<td>-</td>
<td>11</td>
</tr>
<tr>
<td><strong>Fabric</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Banana-cotton</td>
<td>27.9-35.9**</td>
<td>3.3</td>
<td>50.6-64*</td>
<td>-</td>
<td>3.1-7.5**</td>
</tr>
</tbody>
</table>

* Impact Strength (Charpy) for 0.5$V_f$

** Depending on type of fibre in the test direction.

1.10.3. Presence of voids

During the incorporation of fibres into the matrix or manufacture of laminates, air or other volatiles may be trapped in the material. The trapped air or volatiles exist in the cured laminates as micro voids and may significantly affect the mechanical properties of the composites. There are two types of voids in composite materials (a) voids formed along individual fibres and (b) voids formed between lamina and in resin-rich regions. Shrinkages during cure of the resin and the cooling rate play important role in void formation. A high void
content (over 20% by volume) usually leads to lower fatigue resistance, greater susceptibility to water diffusion and increased scattering in mechanical properties. The volatiles produced during the curing cycle in thermosetting resins and during melt processing operation in thermoplastic polymers may also result in the production of voids.

1.10.4. Fibre-matrix interface

The term interface has been defined as the boundary region between two phases in contact. The composition, structure and properties of the interface may be variable across the region and may also differ from composition, structure or properties of either of the two contacting phases [57], fibre and matrix. This interfacial region exhibits a complex interplay of physical and chemical factors that exert a considerable influence in controlling the properties of reinforced composites. The interfacial interaction depends on the fibre aspect ratio, strength of interactions, fibre orientation and aggregation etc.[58-60]. Extensive research has been done to evaluate the interfacial shear strength (ISS) of man made fibres [61-64] and natural fibres [65-68] by using methods such as fibre pull out tests, critical fibre length and micro bond tests.

![Diagram](image)

**Figure 1.12.** Interface/Interphase in a fibre reinforced composite

*(Ref: Newaz G.M., Polym Comp (1986) 7: 421)*

In fibre composites, stresses acting on the matrix are transmitted to the fibre across the interface. For efficient stress transfer, the fibres have to be strongly bonded to the matrix. Composite materials with weak interface have relatively
low strength and stiffness but high resistance to fracture whereas materials with strong interface have high strength and stiffness but are very brittle. The effects are related to the ease of debonding and pull out of fibres from the matrix during crack propagation. The interface/interphase concept in fibre composite is clear from the Figure 1.12 [69]. Interface is defined as a two dimensional region between fibre and matrix having zero thickness. The interphase in a composite is the matrix surrounding a fibre. There is a gradient in properties observed between matrix and interphase. The interface is an area whereas interphase is a volume.

1.11. Mechanisms of fibre-matrix adhesion

The fibre-matrix interface adhesion can be explained by five main mechanisms.

a) **Adsorption and wetting**

This is due to the physical attraction between the surfaces, which is better understood by considering the wetting of solid surfaces by liquids. Between two solids, the surface roughness prevents the wetting except at isolated points. When the fibre surface is contaminated, the effective surface energy decreases. This hinders a strong physical bond between fibre and matrix interface.

b) **Interdiffusion**

Polymer molecules can be diffused into the molecular network of the other surface, say fibre, as shown in Figure 1.13(a). The bond strength will depend on the amount of molecular conformation, constituents involved and the ease of molecular motion.

c) **Electrostatic attraction**

This type of linkage is possible when there is a charge difference at the interface. The electrostatic interaction at the interface is shown in Figure 1.13 (b) & (c). The anionic and cationic species present at the fibre and matrix phases will have an important role in the bonding of the fibre-matrix composites via
electrostatic attraction. Introduction of coupling agents at the interface can enhance bonding through the attraction of cationic functional groups by anionic surface and vice versa.

![Diagram](image)

**Figure 1.13.** Schematic representations of various fibre-matrix adhesions.

*d*) **Chemical bonding**

Chemical bonds can be formed between chemical groups on the fibre surface and a compatible chemical group in the matrix as shown in Figure 1.13 (d). The type of bond determines the strength. Interfacial chemical bonding can increase the adhesive bond strength by preventing molecular slippage at a sharp interface during fracture and by increasing the fracture energy by increasing the interfacial attraction.


1) **Mechanical adhesion**

Mechanical interlocking at the fibre-matrix interface is possible as given in Figure 1.13 (e). The degree of roughness of the fibre surface is very significant in determining the mechanical and chemical bonding at the interface. This is due to the larger surface area available on a rough fibre. Surface roughness can increase the adhesive bond strength by promoting wetting or providing mechanical anchoring sites.

1.12. **Fibre-matrix interface modifications**

Natural fibres are hydrophilic in nature and are incompatible with the hydrophobic polymer matrix and have a tendency to form aggregates. Since they are hydrophilic fibres they are very sensitive to moisture absorption. To eliminate the problems related to high water absorption, treatment of fibres with hydrophobic reagents has been attempted. These reagents contain reactive functional groups that are capable of bonding to the reactive groups in the matrix polymer. The modification of natural fibres is done to make fibres hydrophobic and to improve the interfacial adhesion between the fibre and the polymer matrix [70-80]. In addition to the surface treatments of fibres, use of a compatibilizer or coupling agent for effective stress transfer across the interface can also be explored [81-86]. The compatibilizer can be a polymer with functional groups grafted into the chain of the polymer. The coupling agents are generally tetra functional organometallic compounds based on silicon, called silanes [87]. Pedro et al found that pre impregnation of cellulose fibres in a LDPE/xylene solution and the use of a coupling agent result in small increment in mechanical properties of LDPE, reinforced with green cellulosic fibre composites which are attributed to an improvement in the interface between fibres and matrix. The fibre treatment also improved the shear properties of the composite and fibre dispersion in the matrix [88]. Ishak et al. [89] used silane coupling agents and compatibilizers to improve the mechanical properties of oil palm fibre filled high density polyethylene composites.
In all cases it seems that the mechanical properties of the composites have improved significantly. Usually natural fibres are treated with NaOH to remove lignin, pectin and waxy substances. Alkalization gives rough surface topography to the fibre. It also changes the fine structure of native cellulose I to cellulose II [90]. The increase in the percentage crystallinity index of alkali treated fibre occurs because of the removal of cementing materials which leads to better packing of cellulose chain and increase in molecular orientation. The elastic modulus of the fibre is expected to increase with increasing degree of molecular orientation [91]. Superior mechanical properties of alkali treated jute based biodegradable polyester composites was attributed to the fact that alkali treatment improves the fibre surface characteristics by removing the impurities of the fibre surface thereby producing a rough surface morphology [92]. The effect of alkalization and fibre alignment on the mechanical and thermal properties of kenaf and hemp fibre reinforced polyester composites were studied by Aziz and Ansell [93].

Cao et al. [94] found that the mechanical properties of biodegradable composites reinforced with bagasse fibre were found to be superior after alkali treatment of the fibre.

The study by Van de Weyenberg et al. [95] on improving the properties of UD flax fibre reinforced composites by applying an alkaline treatment proved that it is a simple and effective method to enhance the fibre/matrix bonding with an epoxy resin.

Boynard et al. [96] analyzed the effect of mercerization treatment to improve the strength of fibre/polyester interface. They found that although the surface analysis showed the treatments promote a clear removal of outer surface layer of fibres with exposition of the inner fibrillar structure and the consequent increase of the fibre surface area, only a secondary increase on the mechanical properties was obtained. The slight increase observed was attributed only to mechanical interlock. Samal et al. [97] studied the effect of alkali treatment and cyanoethylation on coir
fibres and found that the modified coir fibre showed significant hydrophobicity, improved tensile strength and moderate resistance to chemical reagents. Hill et al. [98] studied the benefit of fibre treatment by chemical modification (acetylation) of the fibres and by the use of silane coupling agent on the mechanical properties of oil palm and coir fibre reinforced polyester composites. They found that acetylation of coir and oil palm fibres resulted in the increase in the interfacial shear strength (ISS) between the fibre and the matrix and increase in the mechanical properties of the composites. The ISS between acetylated fibres and various polymer matrices-polyesters, epoxy and polystyrene showed that improvements in the ISS were observed upon acetylation of the fibres. Whilst those with thermoset systems show the highest magnitude in ISS, the greater improvement upon acetylation was shown by polystyrene [67]. Increased hydrophobicity of fibres has also increased the ISS values. The introduction of the acetyl group on the fibre surface has increased the ISS of the composites with polystyrene (as compared to the unmodified) significantly than those of epoxies and polyesters. This resulted in improved wetting of polystyrene on to the unmodified fibre surface thereby increasing the work of adhesion. The work of adhesion is increased by an increase in the surface tensions.

Bessadok et al. [99] studied the effect of chemical treatments of Alfa (Stipa tenacissima) fibres on water sorption properties. The chemical treatments were acetylation, treatments with styrene, acrylic acid and maleic anhydride. It was found that chemical treatments, especially styrene treatment, reduced water uptake of Alfa fibre.

A study of the effect of acetylation and propionylyation surface treatments on flax, hemp and wood fibres was done by Tserki et al. [100]. The highest extent of esterification was achieved for the wood fibres due to their high lignin/hemicellulose content. It was also shown that the fibre crystallinity decreased slightly as a result of esterification.
The work carried out by Bairdo et al. [101] showed that acetylation of the fibre surface remarkably increased the strength of a Bionelle/flax fibre composite, by improving the interfacial strength of natural fibres. George et al. [102] analyzed the improved interfacial interaction in chemically modified pine apple leaf fibre reinforced polyethylene composites. They used various reagents like NaOH, silanes and peroxides to improve the interfacial bonding. The influence of fibre surface modification on the mechanical performance of oil palm fibre reinforced phenol formaldehyde composites were studied by Sreekala et al. [103].

Cyanoethylation of jute fibres using acrylonitrile monomer was done by Saha et al. [104] using acrylonitrile monomer, which reacts with hydroxyl group of fibre constituents. The degree of cyanoethylation to different extents was varied by the reaction time. The moisture regain, water absorption and thickness swelling of jute fibre based composites were significantly reduced by cyanoethylation of fibre. The dimensional stability of composite was also improved by the cyanoethylation of jute fibre. A significant improvement on the tensile and the flexural properties of jute-PP composite was also observed which is associated with improved bonding at the interface between jute fibre and polyester. The improved mechanical properties of cyanoethylated jute polyester amide composites may be due to bonding of \(\beta\)-cyanoethyl group of fibre with the polyester matrix thereby improving the fibre-matrix interaction [105]. Reddy and Bhaduri modified cellulose fibre by cyanoethylation [106]. The moisture regain, water absorption and thickness swelling of jute fibre based polyester composites were significantly reduced when cyanoethylated fibre was used [107].

Surface modification of coir fibre was done by Rout et al. [108] by dewaxing, using an alkali treatment, vinyl grafting with methyl methacrylate and cyanoethylation. The morphology studies showed the removal of tyloses from the surface of coir as a result of alkali treatment, resulting in a rough fibre surface with regularly spaced parts. At a lower percentage of grafting (PMMA)
the surface became more or less uniform, while the surface of the coir fibres with a higher percentage of grafting were increasingly covered with grafted material, resulting in canal-like cavities between the overgrowths of grafted material on the unit cells. Cyanoethylated coir fibre surfaces showed an insufficient deposit of cyanoethyl groups. The morphological features correlated with the mechanical properties of modified fibres.

The effects of various chemical modifications of jute fibres as a means of improving its suitability as reinforcement in biopol based composites were done by Mohanty et al. [109]. Sisal fibres were chemically treated with a two step treatment with sodium sulphate solution followed by acetic anhydride to promote adhesion to a polyester resin matrix [110]. It was found that the chemical treatment improved the fibre-matrix interaction as revealed by the brittle behaviour of the composites reinforced with treated fibres. Though the treatment improved the fibre behaviour in relation to moisture, the water absorption capacity of the composites was increased by the treatment. This should be due to the failure to remove all the unreacted hydrophilic species left by treatment or to the formation of acetyl cellulose micro tubes in the treated fibre. Rozman et al. [111] employed lignin as compatibilizer in coconut fibre polypropylene composites. Since lignin contains both polar hydroxyl groups and non polar hydrocarbon and benzene ring, it can play a role in enhancing the compatibility between both components. The composite with lignin as a compatibilizer possessed higher flexural properties compared to the control composites. Lignin also reduced water absorption and thickness swelling of the composites.

Development, optimization and characterization of two treatments; acetylation and stearation of flax fibres were done by Zafeiropoulos et al. [112]. The two treatments were applied on two grades of flax fibres (green and dew retted flax). Three characterization techniques were applied on the treated and untreated fibres; X-ray diffraction, Scanning electron microscopy and inverse gas chromatography. It was found that both treatments resulted in removal of non-crystalline constituents of
the fibres and alter the characteristics of the surface topography. It was also found that both treatments changed the fibre surface free energy, with acetylation increasing it and stearation decreasing it. Butyrated kraft lignin was added to an unsaturated thermosetting resin, consisting of a mixture of acrylated epoxidized soybean oil (AESO) and styrene. Composites were made by the vacuum assisted transfer moulding process with varying amounts of butyrated kraft lignin dissolved in the unsaturated resin system. These results suggest that addition of lignin-BA to the AESO/styrene resin results in the natural fibre-AESO/styrene interface, by compatibilizing the resin and the natural fibre [113].

Conventional compatibilization techniques involve wet chemical methods for the modification of lignocellulosic components and involve mainly the primary and secondary hydroxyl groups of the polysaccharide chain [114-116]. Cold plasma chemistry opens up a new way for the surface modification of materials for composites and other applications [117-1119]. The energies of neutral and charged plasma species, including electrons, ions of either polarity, free radicals, excited species, atoms, molecules and photons are comparable to bond energies involved in all organic compounds and as a consequence, both the gas phase and surface molecular fragmentation and recombination processes can be controlled by selecting the proper plasma parameters [116,120].

Cold plasma enhanced functionalisation reactions will only be adequate for the modification of components for melt processing compounding if the surface area of the substrate is very large relative to its volume, which is crucial for the development of interaction between the fibre and matrix [121,122]. Interfacial properties and micro failure degradation mechanisms of the oxygen plasma treated biodegradable poly (p-dioxanone) (PPDO) fibre/poly (l-lactide) (PLLA) composites were investigated for the orthopaedic applications as implant materials using micromechanical technique and nondestructive acoustic emission (AE). PLLA oriented in melt state was brittle and their mechanical strength was not high, whereas PPDO fibre appeared to have high mechanical strength and flexibility [123].
Thomas and coworkers [124-129] have carried out systematic studies on the chemical modification of various natural fibres like sisal, coir, oil palm, banana and pineapple and its reinforcing effect on various thermosets, thermoplastics and rubbers. In all cases it was observed that the composite properties have greatly improved by using treated fibres due to better fibre-matrix interaction.

The studies so far reported proved that the utilization of natural fibres in polymeric matrices offer economical, environmental and qualitative advantages. Owing to the uncertainties prevailing in the supply and price of petroleum based products, it is highly important to use the naturally occurring alternatives. Proper utilization of indigenously available raw materials will open up new markets for these natural resources. Hence studies on composites containing natural fibres are important.

1.13. Fabrication of composites

The fabrication and shaping of composites into finished products are often combined with 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.

1.13.1. Hand lay-up

The hand lay-up technique (Fig.1.14) is the oldest, simplest and most commonly used method for the manufacture of both small and large fibre reinforced plastic 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 quality of the product depends on the skill of the personnel in
removing air bubbles and voids. The hand lay-up method is labour intensive and is suitable for low rate of production.

1.13.2. Spray-up technique

Spray-up technique is the principal fabrication process used by the FRP industry. The catalysed resin and chopped fibre are laid down simultaneously on the mould surface with specialised spray equipment. The chopped fibre, 3.8-5.0 cm long is produced by feeding continuous fibre roving into a rotating chopper at the head of the spray gun. The technique requires skilled operators to get uniform products and to prevent excessive scrap by overspraying.

1.13.3. Bag moulding process

Bag moulding is one of the oldest and most versatile of the processes used in manufacturing composite parts. The lamina is 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 an 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.

1.13.4. 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 prescribed 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.

1.13.6. Pultrusion

Pultrusion is an automated process for manufacturing composite materials into continuous, constant-cross-section profiles. In pultrusion 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.

1.13.7. Compression moulding

Compression moulding offers a method for large volume production of components with excellent dimensional accuracy and good finish on both
surfaces. Compression moulding is done by pressing and shaping the moulding charge in a matched die and curing the products by fast curing methods. The products take the shape of the cavity.

1.13.8. Resin transfer moulding (RTM)

RTM [130,131] is unique in that it permits the manufacture of high performance composite parts of essentially unrestricted geometry with fast cycle times. A dry reinforcement preform is placed in the mould and the mould is closed. The preform is impregnated with a thermoset liquid resin which is injected into the mould. The injection is done by an applied pressure difference created by an external source of elevated pressure. 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.

1.13.9. Modern developments using thermosets

A series of processes have 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 warmed to accommodate to the mould. It is simply dropped into place at the moulding stage.

1.14. 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 thermosets 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 thermosets, 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 mixture 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 [132]. Cox models the composite as a pair of concentric cylinders. The representative element used in the Cox analysis is shown in Figure 1.15.

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 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 1.16.

![Figure 1.15. The representative element used in the Cox analysis.](Ref: F. R. Jones, Hand Book of Polymer-Fibre Composites, Longman Scientific, (1994))
One shortcoming of the Cox model 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 [133] 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 ($\tau_i$). This concept is often used for the experimental estimation of interface shear strength by the fragmentation or pull out 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 fibre 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 1.16. (a) The tensile stress profiles in the fibre and interface according to the Cox model](image-url)
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.

1.15. Hybrid composites

The development of composite materials based on reinforcement of two or more fibres in a single matrix, which leads to the development of hybrid composites with a great diversity of material properties. Research revealed that the behaviour of hybrid composites appears to be the weighed sum of the individual components in which there is a more favourable balance between the advantages and disadvantages inherent in any composite material [134]. It is generally accepted that properties of hybrid composites are controlled by factors such as nature of matrix; nature, length and relative composition of the reinforcements; fibre-matrix interface and hybrid design [135,136]; Sisal and glass fibres are good examples of hybrid composites possessing very good combined properties [137]. Due to the superior properties of glass fibres, the mechanical properties of the hybrid composites increase with increase in the volume fraction of glass fibres. Thomas et al. [136] have studied the properties of sisal/sawdust hybrid fibre composites with phenol formaldehyde resin as a function of sisal fibre loading. It has been found that mechanical properties like
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tensile and flexural strength increases with sisal fibre content. This is due to the fact that the sisal fibre possesses moderately higher strength and modulus than saw dust. Mishra [138] studied the mechanical properties of sisal and pineapple/glass fibre reinforced polyester composites. They found that the addition of small amount of glass fibres to the pineapple leaf fibre and sisal fibre reinforced polyester matrix enhanced the mechanical properties of the resulting hybrid composites. Rozman et al. [139] studied the tensile and flexural properties of polypropylene/oil palm/glass fibre hybrid composites and found that incorporation of both fibres into the polypropylene matrix improved the tensile and flexural strength by the increasing level of overall fibre loading. Junior et al. [140] used plain weaved hybrid ramie-cotton fibres as reinforcement for polyester matrix. The tensile behaviour was dominated by the volume fraction of the ramie fibres aligned with the test direction. Cotton fibre had a minor reinforcement effect. This was due to the weak cotton polyester interface as well as poor cotton alignment. Hybrid composites containing glass fibre mat and coir fibre mat in polyester matrix was prepared by Rout et al.[141]. Hybrid composites containing surface modified coir fibres showed significant improvement in flexural strength and reduced water absorption. Sreekala et al. [142] prepared high performance phenol formaldehyde composite reinforced with oil palm and glass fibres. It has been found that there exists a positive hybrid effect for the flexural modulus and unnotched impact strength. Natural rubber composite reinforced with sisal/oil palm, sisal/coir hybrid fibres were prepared by Maya et al.[143] and Haseena et al. [144] found that the hybridization has a significant effect in improving the mechanical properties of the natural rubber composite when compared with the composite containing individual fibres. Burgueno et al. [145] studied on Cellular biocomposite cores made from industrial hemp or flax fibres with unsaturated polyester were hybridized with woven jute, chopped glass and unidirectional carbon fabrics and found that the composite possessed improved stiffness, strength, moisture absorption ability and enhanced structural behaviour. Clark et al. [146] have reported on the jute and glass fibre
hybrid laminates and optimum ply conditions are identified which offer respectable mechanical properties at an attractively low cost. Pavithran et al. [147] established that hybridization of sisal fibre with glass in polyester composites, in view of improving the impact performance of the former, can be better utilized in glass core-sisal shell laminates than in sisal core-glass shell laminates.

1.16. Applications of composites:

Reinforced plastics have gained popularity over conventional materials because of the following advantages:

1. High strength to weight ratio and rigidity.
2. Unlimited moulding size used.
3. Wide range of manufacturing techniques.
4. Ease of fabrication.
5. Versatility in design.
6. Low capital outlay (low cost) as has been visualised for hand-lay-up technique.
7. Resistance to water, weathering and corrosion.
8. Resistance to various chemical reagents.
9. Can be made fibre retardant, electrically and thermally resistant.
10. If needed, good degree of transparency can be achieved.

Due to these overwhelming advantages of composites, there is wide range of applications of fibre reinforced plastics. Some important applications are given below:

1. **Transportation:** Manufacture of vehicle bodies, cooling system components and farm equipments.

2. **Marine:** Fuel and water tanks in ships, submarine and ship hulls for recreation.
3. **Material handling:** Pharmaceutical trays and boxes, storage tanks etc.

4. **Sporting goods:** Fishing rods, Tennis racquets, Hockey sticks etc.

5. **Construction:** Structured shapes, panelling, sliding etc.

6. **Electrical applications:** In transformers, motors, generators, switch gears and electronics equipments.

7. **Corrosion applications:** Fuel and chemical tanks, fertiliser storage hoppers etc.

8. **Aerospace and Military:** Rocket motor cases, nozzles, nose cones, blades, pressure bottles, assault boat and rifle stocks, bullet proof helmet, bridge sections, ladders etc.

9. **Railways:** Window frames, window guides, axle box cover, battery box, flooring for toilets, Laboratory Chula, roof ventilator, sliding doors, rotary switch panels, emergency lead terminals, fan blade assembly etc.

1.17. **Isora fibre**

Various natural fibres like sisal, coir, jute, oil palm, bamboo etc. have been proved to be a better reinforcement in thermoset matrix. Incorporation of natural fibres resulted in better long term mechanical performance of thermosets. However studies on isora fibre as reinforcement have not yet been reported. Isora is a bast fibre presented in the bark of *Helicteres isora* plant. Two varieties of the plant are distinguished, *tomentosa* and *glabrescens* in which in the former, the bottom side of the leaves is glabrous and in the latter, both sides of the leaves are glabrous. The plant occurs as undergrowth especially as a secondary growth in forests. Seed sown during the rainy season easily propagates it. Roots, stem and fruits of the plant are used for medicinal applications. The stem bark is exploited for the fibre. The best type of fibre is obtained when the plants are 1-1.5 years old; plants older than 2 years, yield coarse and brittle fibre. Stalks can be harvested annually for fibre extraction from regenerated shoots. It occurs as undergrowth, especially as a
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secondary growth in forests. It coppices well, shooting up rapidly when cut or burnt back. In some places the plant forms dense, almost impenetrable thickets covering large areas practically to the exclusion of other growths. The fibre which is present in the inner bark of the plant is polygonal in cross section with a circular or oval lumen. The cell wall of the fibre element is thick and lignified. The fibre is extracted from the stem by retting the stem in running water for 18-24 days. The retted stalks were taken out of the water, beated gently with wooden mallets and fibres are peeled off, washed with water and dried. Fibre of good quality and colour is obtained when retting is effected in running water.

Properties of natural fibres depend mainly on the nature and age of the plant, and the extraction method used. The data of production of isora fibre are not available. According to the estimate made in 1951 the yield of fibre is 50-60 md per acre [148]. The fibre is used mostly for rough sacking or canvas and as cordage for sewing gunny bags and cattle harness. It is especially valued for container bags and used as pans in lever weighing systems. The quality of fibre is amenable to considerable improvement. By selecting stalks of equal age and maturity, and retting them under proper conditions and switching the dried fibre on suitable mechanical appliances, it is possible to obtain fibre which can be spun into good yarn and woven into canvas and other durable fabrics of excellent quality. Woven materials can be dyed and printed in attractive designs for making shopping bags. Ropes and cordages made of the fibre are better and smoother than coir products. Stalks and twigs of the plant with and without bark are also suitable for the manufacture of writing or printing paper in combination with long fibre pulp of bamboo species. Fruits disperse during April to June, and about 620 dried seeds weigh 1 kg. The seeds sown during rainy season will germinate and grow without much care or other inputs. The total turn over of the dried fruits of the plant was about 1200 kg. in one year as recorded by Kerala state SC & ST Federation 1998. The cost of the seed was around Rs. 1.50 per kg. Certain quantity of seed collected from forest areas might have also gone to the general market, on which there is no quantified data available.
1.17.1. Characterisation of Isora fibres

(Ref: Ph. D. Thesis, Dr. Lovely Mathew, Cochin University of Science and Technology, Kochi.)

The photograph of isora fibre is shown in Figure 1.17 and that of stem, leaves, fruits and the dried seeds are given in Figures 1.18 (a-d).

![Photograph of isora fibre](image1)

Figure 1.17. Photograph of isora fibre

![Helicteres isora plant](image2)

Figure 1.18. Helicteres isora plant

(a) stem (b) dried seed (c) leaves (d) fruit
**a) Chemical analysis:** The chemical components present in the isora fibre and the solubility of the fibre in different solvents are given in Table 1.5.

**Table 1.5. Chemical constituents of Isora fibre**

<table>
<thead>
<tr>
<th>Chemical constituents</th>
<th>(%)</th>
<th>Solubility in various solvents</th>
<th>(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>74.8</td>
<td>Alcohol-benzene</td>
<td>6.3</td>
</tr>
<tr>
<td>Lignin</td>
<td>23.0</td>
<td>Ether</td>
<td>5.7</td>
</tr>
<tr>
<td>Ash</td>
<td>0.92</td>
<td>1% caustic soda</td>
<td>14</td>
</tr>
<tr>
<td>Fat</td>
<td>1.09</td>
<td>Cold water</td>
<td>10</td>
</tr>
<tr>
<td>Moisture content</td>
<td>5-6</td>
<td>Hot water</td>
<td>12</td>
</tr>
<tr>
<td>Ca(ppm)</td>
<td>713.45</td>
<td>Acetone</td>
<td>5.6</td>
</tr>
<tr>
<td>Mg(ppm)</td>
<td>37.93</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(ppm)</td>
<td>16.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K(ppm)</td>
<td>10.54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na(ppm)</td>
<td>10.42</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It is clear from Table 1.5 that isora is a cellulose rich fibre with comparatively low lignin content, which contributes to better performance of the fibre as reinforcement in polymers. The fibre is hygroscopic and its moisture content is found to be 5-6%. From the Table it is clear that the fibre contains about 12% water soluble materials.

The physical and mechanical properties of the fibre are given in the Table 1.6. After chemical treatment there is a slight positive change in the density which normally signifies cell wall densification.
Table 1.6. Physical and Mechanical properties of isora fibre

<table>
<thead>
<tr>
<th>Properties</th>
<th>U</th>
<th>A</th>
<th>Si</th>
<th>γ irradiated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength (MPa)</td>
<td>565</td>
<td>500</td>
<td>475</td>
<td>350</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>6</td>
<td>7.0</td>
<td>7.0</td>
<td>8.0</td>
</tr>
<tr>
<td>Young's modulus (GPa)</td>
<td>18-20</td>
<td>15</td>
<td>16</td>
<td>12</td>
</tr>
<tr>
<td>Density (gm cm(^{-3}))</td>
<td>1.39</td>
<td>1.42</td>
<td>1.51</td>
<td>1.40</td>
</tr>
<tr>
<td>Crystallinity Index (%)</td>
<td>70.9</td>
<td>80.6</td>
<td>77.8</td>
<td>71.3</td>
</tr>
<tr>
<td>Micro fibrillar angle (degrees)</td>
<td>20-26</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Intrinsic strength (g denier(^{-1}))</td>
<td>0.987</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Length to diameter ratio</td>
<td>99</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Diameter (μm)</td>
<td>10</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>10</td>
</tr>
</tbody>
</table>

U-Untreated, A-Alkali treated, Si-Silane treated

The tensile stress strain curves of the raw and modified isora fibres are given in Figure 1.19. Fibre modifications lead to major changes on the fibrillar structure of the fibre. Brittleness of the fibre is substantially reduced upon treatments.

![Figure 1.19. Stress-strain curves of raw and modified fibres.](image)
Important tensile properties like tensile strength, Young's modulus and elongation at break of the raw and modified fibres are given in Table 1.16. Chemical modifications of the fibre surface decreased the tensile strength. Tensile strength of the treated fibre is less than that of the untreated fibre (Figure 1.19). Elongation at break shows a slight increase after chemical treatment. The reinforcing ability of the plant fibres does not depend upon the mechanical strength of the fibres but on many other factors like polarity of the fibre, surface characteristics, the moisture content, presence of reactive centres and cellulose content. These factors control the interfacial interaction.

b) Morphological analysis of fibre

i. Scanning Electron Microscopic studies

The SEM photograph of a single fibril of isora fibre is given in Figure 1.20. The diameter of the fibre was found to be 10\mu m.

![SEM photograph of a single fibril of isora fibre](image)

Figure 1.20. SEM photograph of a single fibril of isora fibre

Isora fibres are composed of aligned fibrils with materials cementing the fibres together. Based on the results of FTIR and the structure of the natural fibre, the cementing material would be expected to be hemi cellulose and lignin. It is well known that hemi cellulose is a branched amorphous polymer with a low degree of polymerization, which is always associated with cellulose by hydrogen bonding. Isora fibre is a composite material with fibrous reinforcement and a mixture of hemi cellulose and lignin as matrix.
ii. Thermal studies

When cellulosic fibres are heated, a series of interrelated physical and chemical changes occur. The physical properties affected include enthalpy, weight, crystallinity etc. The chemical reactions involved are the decomposition of the glycosyl units of cellulose at about 300°C. At temperatures above 400°C depolymerization of the molecule take place by the cleavage of glycosyl units. This reaction is always accompanied by the decomposition of some anhydro sugar products. At still higher temperature, direct fission of the substrate and the intermediate products takes place forming low molecular weight gaseous products and metallic oxides.

The thermal degradation [DTG] of the raw and treated fibres in Nitrogen atmosphere is given in Figure 1.21. In thermo-gravimetric tests, a common behaviour observed in all the samples was the dehydration process below 100°C, in which 5-8% of adsorbed water was removed. The majority of the weight loss of the raw and treated fibres took place above 300°C. The fibre treatments slightly improved the thermal stability of the fibres, showing a higher temperature of decomposition compared to the raw fibre.

![Figure 1.21. Derivative thermograms (DTG) of untreated and chemically modified fibres in Nitrogen atmosphere](image-url)
From the DTG curves shown in Figure 1.21, it was observed that the thermal stability of the fibres increased in the following order: Untreated < Gamma irradiated < Silane treated < Alkali treated.

![DSC curves of untreated and chemically modified fibres in Nitrogen atmosphere](image)

**Figure 1.22.** DSC curves of untreated and chemically modified fibres in Nitrogen atmosphere

The DSC studies in nitrogen also show a similar trend (Figure 1.22). A broad endotherm in the temperature range of 75-120°C was observed which may be due to the dehydration of fibres. The first exothermic DSC peak corresponds to the decomposition of cellulose. The exothermic peak of alkali treated fibre is shifted to a higher temperature. The second and strong endothermic peak corresponds to the reduction in crystallinity found at around 350°C which also shifted to a higher temperature in the case of alkali treated fibres. This is evident from the DSC curves (Figure 1.22) which is an indication of the increase in the crystalline cellulose, which is known to have good thermal resistance.

**iii. WAXRD studies**

From Table 1.6 and Figure 1.23 it is clear that the treated fibres show an overall initial increase in the crystallinity index, with maximum for alkali treated fibres, which is an indication of the improvement in the order of crystallites as the
cell wall thickens upon chemical treatment. The use of WAXRD counts offers a simple and quick method of determining the crystallinity index and the minimum between 101 and 002 peaks (Figure 1.23) is an indication of the reflection intensity of the amorphous material. Alkali and silane treatments increase the crystallite packing order. Crystallinity index is a measure of the order of the crystallites rather than the crystallinity of the crystallites. Alkali treatment is reported to reduce the proportion of crystalline material present in plant fibres.

![WAXRD Spectra of untreated, alkali treated, silane treated and gamma irradiated fibres](image)

**Figure 1.23.** WAXRD Spectra of untreated, alkali treated, silane treated and gamma irradiated fibres

1.18. Scope and objectives of the present work

The aim of the present work is to investigate the prospect of using isora fibre as reinforcement in polyester and epoxy matrix. Helicteres isora plant from which the fibre is separated is abundantly available in India, especially in Kerala. Currently the fibre is being utilized for the preparation of ropes, cordages, gunny bags etc. These fibres, if put to better use, as reinforcement in polymers, will definitely contribute to the development of the economy of the country and will open up new avenues for our natural resources. The
factors which affect the properties of natural fibres are the cellulose content and micro fibrillar angle. Isora fibre has relatively high cellulose content and a low micro fibrillar angle. Earlier reports have shown that the natural fibres are susceptible to moisture absorption, thermal degradation and biodegradation. Therefore strategies need to be worked out to overcome these limitations. For the successful design of a composite material from isora fibre and polyester / epoxy matrix, several parameters like fibre length, fibre loading, fibre surface modification, fibre-matrix adhesion etc. have to be optimized. Careful analysis of the literature indicates that no systematic studies have been reported about the use of isora fibre as reinforcement in polymers.

In the present study it is proposed to focus on the following aspects:

1.18.1. Characterization of the properties of randomly oriented isora fibre-polyester composites

The properties of randomly oriented isora fibre-polyester composites are proposed to be studied as a function of fibre length and fibre loading. A comparison is also proposed to be made between theoretical and experimental tensile properties.

1.18.2. Alkalization of isora fibre surface

The polar natural fibre and non polar polymer matrix are likely to end up in relatively weak bonding. The bonding can be improved to a great extent by varying the polarity of the fibre surface. In view of this, it is proposed to modify short isora fibre with alkali and to investigate the effect of alkalization on the surface morphology by Infra red (IR) Spectroscopy and Scanning electron microscopy (SEM) studies. The effect of concentration of alkali and duration of alkali treatment of fibre on the properties of the composite will also be evaluated.
1.18.3. Chemical modification of isora fibre surface

As a further step to change the surface polarity and thereby improve the fibre-matrix interaction short isora fibre is also proposed to be subjected to various chemical treatments like acetylation, benzoylation, silane and triton. SEM and IR spectroscopy will be used to characterize the untreated and treated fibre surface. The effect of fibre modification on the properties of the composites also will be evaluated.

1.18.4. Characterization of the properties of oriented long isora fibre-polyester composites

The properties of untreated long oriented isora fibre-polyester composites are proposed to be studied as a function of fibre loading. The fibre/matrix interface is proposed to be modified by various fibre treatments and the role of improved fibre/matrix interactions on the properties of the composites will be evaluated. The untreated and treated fibre surface will be characterized by SEM. The effect of fibre modification on the properties of the composites will also be evaluated. A comparison is proposed to be made between theoretical and experimental tensile properties.

1.18.5. Characterization of the properties of isora fibre-epoxy composites

The properties of untreated and alkali treated randomly oriented isora fibre-epoxy composites are proposed to be studied. The properties of untreated oriented long isora fibre-epoxy composites will be studied as a function of fibre loading. The fibre/matrix interface is proposed to be modified by various fibre treatments and the role of improved fibre/matrix interactions on the properties of the composites will be evaluated. SEM will be used to characterize the untreated and treated fibre surface. The effect of fibre modification on the properties of the composites will be evaluated. A comparison is proposed to be made between theoretical and experimental tensile properties.
1.18.6. Dynamic mechanical properties of the composites.

The dynamic mechanical properties of the untreated and chemically modified randomly oriented isora-polyester, isora-epoxy; oriented long isora-polyester and isora-epoxy composites are proposed to be analyzed. The dependence of storage modulus, loss modulus and damping factor of the composites on the temperature will also be studied.

1.18.7. Water absorption and thermal aging studies of isora fibre reinforced polyester and epoxy composites

The water absorption behaviour of and the effect of thermal aging on the tensile and flexural properties of the composites will be investigated as a function of fibre loading and fibre modification.

References


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