

## **Chapter 1**

# **Introduction**

### **Abstract**

In recent times, increasing attention has been paid to the use of renewable resources, particularly, of plant origin, keeping in view the ecological concerns and renewability. The possibility of mixing reinforcements to prepare hybrid composites is attractive because it allows the designing of composites with mechanical performance to meet the needs of the product. The benefits of replacing synthetic fibres for natural ones, even if only partially, are mainly ecological. Several combinations of different types of natural and synthetic fibres are used to meet design requirements in many different applications. This chapter provides an introduction on the various aspects of natural fibre composites and reinforcement (fibres) in general. A brief literature review on current research in the area of hybrid composites followed by scope and objectives of the present study is also included.

*Part of this chapter has been communicated to Progress in Polymer Science*

### **1.1 Composites**

Polymer based composites are currently a very important and rapidly expanding field of research. The composite materials are inherently heterogenous at a microstructural level consisting of two components having different elastic moduli, different strengths, different thermal expansion coefficients and so on [1]. Composites are increasingly being used as a substitute for many of the conventional materials. A composite can be defined as the material created when two or more distinct components are combined to obtain a system with more useful, structural and functional properties. The different components, the reinforcement and the matrix with the distinct interface in between must have appropriate characteristics and function both individually and collectively to attain the desired superior properties of the composite. Reinforcement provides high strength and modulus. It may be in the form of fibres, particles or whiskers. Particles have no preferred direction. The particle may be metallic, ceramic, manmade or natural materials. Particles have length to diameter ratios of order unity and dimension that range from that of a fibre diameter to several millimetres. Whiskers have length to diameter ratios of order 1000 and diameter of order 0.1-1 micrometer. Whiskers are pure single crystals manufactured through chemical vapour deposition and thus have preferred directions. Whisker reinforced composites are likely to be considered as macroscopically isotropic.

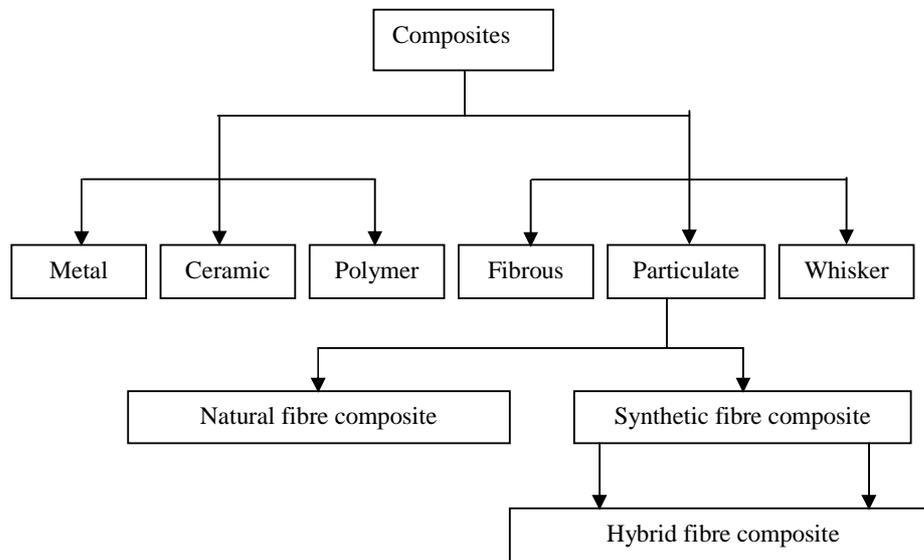
The matrix hold the reinforcement phase in place and it transmits stresses to the reinforcement. The matrix resin fulfills a variety of critical functions in addition to simply maintaining the shape of the composite structure and aligning the reinforcement. The matrix binds together the

composite components and protects the reinforcement from premature wear such as abrasion and environmental corrosion. More importantly, the matrix distributes the applied loads and acts as a stress transfer medium so that when an individual fibre fails, the composite structure does not lose its load carrying capability.

Based on the matrix material which forms the continuous phase, the composites are broadly classified into metal matrix, ceramic matrix and polymer matrix composites. Based on the low processing temperature, the polymer matrix composites are much easier to fabricate than metal matrix and ceramic matrix composites. Among the various polymer matrix composites, fibre reinforced polymer composites have gained much importance in various fields due to high strength to weight ratios. Fibrous composites are composed of reinforced fibres in a matrix. These fibres are having outstanding tensile strength. Fibrous composites are further classified as synthetic fibre, natural fibre and hybrid fibre composites.

The fibre/matrix interface plays a major role in the mechanical and physical properties of composite materials. The 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.

Notable accomplishments for composites have been attained in the automotive, aerospace and sporting goods industries. The aerospace industry has led the way with high performance composites that surpass the specific strength and stiffness of the usual structural materials. Fig. 1.1 gives a schematic representation of the classification of the composites.



**Fig. 1.1** Schematic representation of classification of composites

### 1.1.1 Fibre reinforced composites

Nowadays fibre reinforced composites have emerged as a major class of structural material in many weight critical components in aerospace, marine and other industries. Fibre reinforced composites (FRCs) contain reinforcements having length much larger than their cross-sectional dimensions. Fibres are the load carrying members. The surrounding matrix acts as load transfer medium and protects the fibre from environmental damages due to elevated temperature and humidity. The articles based on FRCs possess high stiffness while having light weight. Fibres are dispersed throughout the polymer matrix to increase its rigidity

and strength and especially to add impact strength which is often lacking in rigid matrices. Based on fibre length, FRCs are grouped as

- 1) long (continuous) fibre reinforced composites
- 2) short (discontinuous) fibre reinforced composites

In continuous long fibre reinforced composites, fibres are oriented to produce enhanced properties in one direction. Discontinuous or short fibre reinforced composite properties vary with fibre length. The reinforcement is uniform in the case of composites containing well dispersed short fibres. The strength of the composite with discontinuous fibre is always lower than that prepared with continuous fibres.

The fibre reinforced composites exhibit anisotropy in properties. They show better dimensional stability over a wide range of temperatures due to their lower coefficient of thermal expansion than those of metals. Fibre reinforced composites exhibit high internal damping. This leads to better vibrational energy absorption within the material and results in reduced transmission of noise and vibrations to neighbouring structures. High damping capacity of composite materials can be beneficial in many automotive applications in which noise, vibration and harshness (NVH) is a critical issue for passenger comfort.

## **1.2 Matrices**

The constituent that is continuous and often (but not always) present in greater quantity is termed as matrix. The main role of the matrix is to transmit and distribute stresses along the reinforcement phase. Durability, interlaminar toughness and shear, compressive and transverse strength are also provided by the matrix resin. Commonly used matrix materials

include polymers, metals, ceramics and carbon. Most of the composites used in the industry today are based on polymer matrices.

### **1.2.1 Thermosetting and thermoplastic polymers**

Based on their structure and behaviour, polymers can be classified as thermoplastics and thermosets. The thermoplastics are incorporated into the composite system by melting and then they are solidified by cooling; the physical action being reversible in nature. It consists of linear or branched chain molecules and can be reshaped by application of heat and pressure without significant changes in their properties and is either semicrystalline or amorphous in structure. Examples include polyethylene, polystyrene, nylon, polycarbonate, polyacetals etc. Only those thermoplastics are usable for natural fibre reinforced composites, whose processing temperature does not exceed 230°C. These are polyolefines like polyethylene and polypropylene. Technical thermoplastics like polyamides and polycarbonates require processing temperatures greater than 250°C and are therefore not usable for such composite processing without fibre degradation.

Thermosetting polymers constitute an important class of materials with a wide variety of applications. They are brittle at room temperature. Thermosetting plastics have crosslinked or network structures with covalent bonds between all molecules. They do not soften but decompose on heating. Once solidified by crosslinking process, they cannot be reshaped. But there are many advantages resulting from the presence of crosslinks. Thermosets can be used at high temperatures and have better creep properties than thermoplastics. Common examples of thermosetting

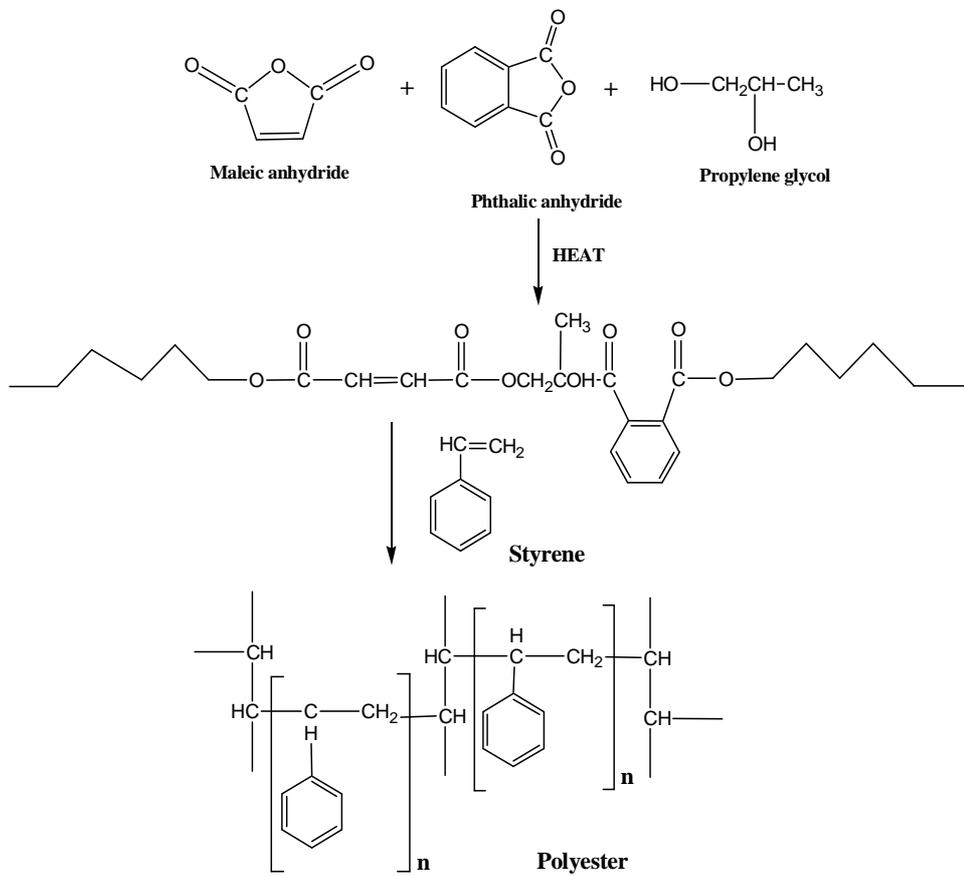
polymers include epoxies, polyester, phenolics, vinyl esters, novolac, polyamide etc. Glass fibre and polyester matrix combination is a good match in terms of both performance and price. Glass/synthetic fibres and a wide variety of natural fibres like sisal, coir, jute, pineapple etc with thermoset matrices have been studied by several authors [2-6]. Fabrication techniques suitable for developing natural fibre reinforced thermoset composites include hand lay-up technique for unidirectional fibres/mats/,sheet moulding (SMC)/ bulk moulding (BMC) for short and chopped fibres, filament winding and pultrusion for continuous fibres. The oldest, simplest and the most commonly used method for the manufacture of both small and large reinforced products is the hand lay-up technique. Prior to lamination, the mould is cleaned carefully and release agent is applied to the mould. Subsequent layers of reinforcement are added to build laminate thickness. The laminating resin is applied by pouring, brushing, spraying, or using paint rollers. Paint rollers, or squeegees are used to consolidate the laminate, thoroughly wetting the reinforcement, and removing entrapped air. The curing of a product takes usually 4–12 hours, depending on the size, thickness and complexity of the product. After curing the product is taken out of the mould.

### **1.2.2 Polyester**

Unsaturated polyesters (UP) are the most commonly used matrices with a world consumption of approximately 1 million tonnes per year [7]. Ups are a major type of practical thermosetting plastic in industry. Unsaturated polyester resin is an economical thermoset material that is widely used, due to its excellent processability and good cross-linking tendency as well as the fairly good oil, moisture and acid resistances and good mechanical

properties when cured [8]. They also possess many advantages compared to other thermosetting resins including room temperature cure capability, and transparency. Unsaturated polyesters [9] are extremely versatile in properties and applications and have been a popular thermoset used as the polymer matrix in composites. They are very popular because of their low cost, low densities, good corrosion resistance and high strength-to-weight ratios. They have excellent flow to impregnate the fibre bundles during the manufacturing process and present better adhesions. One of the major drawbacks for Ups is their brittleness and poor resistance to crack propagation [10] which has confined the application of Ups to situations where the stress is relatively low and preferably static. Unsaturated polyester resin, which is commonly used as the matrix in synthetic glass fibre composites, has been modified to make it more compatible with cellulose fibres [11].

A polyester (PER) resin is unsaturated (reactive) polyester solid dissolved in a polymerisable monomer. Unsaturated polyesters are long chain linear polymers containing a number of carbon double bonds. Their processing involves a radical polymerisation between a prepolymer that contains unsaturated groups and styrene. They are made by a condensation reaction between a glycol and an unsaturated dibasic acid (maleic or fumaric). The general purpose resin is based on maleic anhydride, phthalic anhydride (saturated) and propylene glycol and is prepared by condensing these components. The steps involved in the manufacture of polyester are given in Fig. 1.2.



**Fig. 1.2** Steps involved in the manufacture of polyester

The esterification reaction does not affect double bond or unsaturation in the dibasic acid or the anhydride. A high reactivity polyester resin contains a large proportion of unsaturation. The saturated acid reduces the crosslink density and brittleness of the end product. This is diluted with a low viscosity unsaturated monomer such as styrene due to its high compatibility with the polyester and its low cost. The styrene serves as a solvent for the polymer chain, a viscosity reducer and as a cross-linking agent. It also copolymerises during curing of the resin with the unsaturated group along the polyester chain without the evolution of any by-products.

Cure of unsaturated polyester resin takes place by free radical polymerisation through the unsaturated groups both in the polyester chains and the styrene. This is initiated with compounds often referred to as catalysts although they are in fact consumed during the reaction. The most widely used initiators are the organic peroxides. The decomposition of initiators is induced by heat or by accelerators at temperatures well below their normal thermal decomposition by an oxidation-reduction (redox) mechanism. This phenomenon is utilised in curing the unsaturated polyester at room temperature and also for accelerating their cure at elevated temperatures.

The most commonly encountered peroxide catalysts for room temperature cure are methyl ethyl ketone peroxide (MEKP), cyclohexanone peroxide and acetyl acetone peroxide, each of which is used with a cobalt accelerator [12]. For elevated temperature cure, benzoyl peroxide is most frequently used. Methyl ethyl ketone peroxide is the most widely used organic peroxide because of its low cost. Being a liquid, it is readily

soluble in the resin. Two types of accelerators are used, metal salts (cobalt salts) and amines. Cobalt naphthenate is an excellent accelerator for MEKP. It increases the rate at which the peroxide breaks down into free radicals.

The reinforcement of polyesters with cellulosic fibres has been widely reported. Polyester-jute [13,14], polyester-sisal [15,16], polyester-coir [17,18], polyester-banana-cotton [19], polyester-straw [20], polyester-pineapple leaf [6,21] and polyester-cotton-kapok [22] are some of the promising systems.

In order to improve the mechanical properties of cured UP materials, Martuscelli and co-workers made an attempt chemically to modify commercial liquid rubbers to enhance their reactivity toward the polyester matrix [23]. For many years, unsaturated polyester composites have been used in very varied technologies, like naval constructions, off-shore applications, water pipes, building construction, automotive etc. In addition to their good mechanical resistance; they also show good thermal stability and flame resistance. However, the typical unsaturated polyester resins are not tough enough, and their impact strength is lower than that of other thermoset polymers like epoxy.

### **1.2.3 Epoxy resin**

Epoxies are most often seen in fields where cost tolerance is the highest, eg. aerospace, defence and sports applications. The most common process for producing epoxies is the reaction of epichlorohydrin with bisphenol A amino or acid compounds and crosslinking is obtained by introducing chemicals that react with the epoxy and hydroxyl groups between the

adjacent chains. Epoxy systems, like polyesters, can be cured at room temperature, but quite often heat is added to accelerate and improve curing.

#### **1.2.4 Phenolic resin**

Phenolic resins have been in commercial use longer than any other synthetic polymer except cellulose nitrate. The prime advantage of phenolics over other composite matrices is their excellent high-temperature and fire tolerance combined with low smoke emission and reasonable price. Phenols react with aldehydes to give condensation products if there are free positions on the benzene ring ortho and para to the hydroxyl group. Formaldehyde is by far the most reactive aldehyde and is used almost exclusively in commercial production. Today, where costs and performance have a high impact on economics, phenolic resins have been accepted in many high performance applications for composites.

#### **1.2.5 Vinyl esters**

Vinyl esters were developed in an attempt to combine fast and simple crosslinking of unsaturated polyesters with mechanical and thermal properties of epoxies. Vinyl esters are more likely to be used in applications where unsaturated polyester does not quite fulfill. Applications and reinforcement areas are the same as for unsaturated polyesters, but where somewhat improved properties are required. Vinylesters have been successful in a corrosive industrial environment.

#### **1.2.6 Other thermosetting polymers**

The important classes of aminoresins are the condensation products of urea and of melamine with formaldehyde. In general, the melamine resins

have somewhat better properties but are higher in price. Amino resins have a distinct advantage over the phenolics that they are clear and colourless, so that objects of light or pastel colour can be produced. Urethane polymers contain the group  $\text{-NHCOO}$  and are formed through the reaction of a diisocyanate and a glycol. Silicone polymers are particularly noted for their stability at temperatures as high as  $150^{\circ}\text{C}$ . Silicone polymers are produced by intermolecular condensation of silanols, which are formed from the halide or alkoxy intermediates by hydrolysis.

### 1.3 Synthetic fibres

Based on their origin and chemical structure, fibres are broadly classified into two types, man-made (synthetic) and natural. Fibres in which the basic chemical units have been formed by chemical synthesis followed by fibre formation are called synthetic fibres [24]. Fibres which come from natural sources like animals, plants and minerals and do not require fibre formation or reformation are classified as natural fibres.

Synthetic fibres are divided into two groups; heterochain and carbochain fibres [25]. The macromolecule of heterochain fibres contains carbon atoms and atoms of other elements such as oxygen and nitrogen in their main chain. They include nylon, polyamide, polyesters, polyurethane, polyurea fibres etc. Carbochain fibres contain only carbon atoms in the main chain. Such polymers are obtained by polymerisation. Examples include poly (acrylo nitrile), poly (vinyl alcohol), polyolefine etc. The most common types of synthetic fibres used in composite applications are glass. Other synthetic fibres include carbon and graphite fibres, aramid fibres and boron fibres.

### 1.3.1 Glass fibre

Glass fibres are the most common of all reinforcing fibres for polymeric (plastic) matrix composites (PMCs). Glass fibres are manufactured from molten glass, from which glass monofilaments are drawn and then gathered to strands. The strands are used for preparation of different glass fibre products (yarns, rovings, woven fabrics, mats). Glass fibre reinforcements all over the world are mostly made out of E-Glass which is calcium alumino boro silicate glass. E-Glass is basically electrically resistant glass, but has been adopted world wide for usage in all sectors, viz electrical, automotive, building etc. because it imparts a balance of properties – mechanical, thermal and electrical at a reasonable cost. Other glass fibres that are available are S-Glass, C-Glass, R-Glass, AR-Glass and D-Glass. S-Glass, stronger than E-Glass fibres is used in military applications and in aerospace. C-glass is used in chemical applications requiring greater corrosion resistance to acids than is provided by E-glass. Although extensively used, glass fibres are still expensive for many applications that require low cost raw materials. Glass fibres have high density and leachable components that can reduce specific mechanical properties (property to weight ratios) and performance of composites. Glass fibre can cause acute irritation to the skin, eyes, and upper respiratory tract.

Fibre glass has been used widely in manufacturing industries, especially marine industries, because of comparatively low cost and high strength. The principal advantages of glass fibre are low cost, high tensile strength, high chemical resistance and excellent insulating properties.

### **1.3.2 Carbon fibre**

Carbon fibres have the highest strength and stiffness of many composite reinforcements. The term carbon fibre describes fibres that have a carbon content of 80-95 %. The term graphite fibre is used to denote fibres that have carbon content in excess of 99 %. Graphite fibres are the predominant high strength, high modulus reinforcement used in the fabrication of high performance resin-matrix composites. The advantages of these fibres also include tolerance to high temperature and corrosive environments, as well as lack of moisture sensitivity. Carbon fibre reinforcement dominates in high performance applications due to its outstanding mechanical properties combined with low weight. The major disadvantage of carbon fibre is their high price, while others include brittleness and conductivity.

Carbon fibres [26] are used for reinforcing certain matrix materials to form composites. Carbon fibres are unidirectional reinforcements and can be arranged in such a way in the composite that it is stronger in the direction, which must bear loads. The physical properties of carbon fibre reinforced composite materials depend considerably on the nature of the matrix, the fibre alignment, the volume fraction of the fibre and matrix, and on the moulding conditions. Several types of matrix materials such as glass and ceramics, metal and plastics have been used as matrices for reinforcement by carbon fibre.

### **1.3.3 Kevlar fibre**

Kevlar belongs to a group of highly crystalline aramid (aromatic amide) fibres that have the lowest specific gravity and the highest tensile strength to weight ratio among the current reinforcing fibres. The aramid fibre

forming polymers, the aromatic polyamides are made by solution polycondensation of diamines and diacid halides at low temperatures. The polymers are spun from strong acid solutions by a dry-jet wet spinning process. Kevlar fibre possesses unique properties. When compared to other organic fibres, tensile modulus is also substantially higher and fibre elongation is significantly lower for Kevlar fibres. They exhibit poor characteristics in compression. They are used as reinforcement in many marine and aerospace applications.

#### **1.3.4 Boron fibre**

The most prominent feature of boron fibres is their extremely high tensile modulus. Boron fibres offer excellent resistance to buckling, which in turn contributes to high compressive strength for boron fibre reinforced composites. Boron filaments are produced by the chemical vapour deposition from the reduction of boron trichloride ( $\text{BCl}_3$ ) with hydrogen on a tungsten or carbon monofilament substrate. The substrate is resistively heated to a temperature of  $1260^\circ\text{C}$  and continuously pulled through a reactor to obtain the desired boron coating thickness.

#### **1.3.5 Other fibres**

Polyethylene fibres (PE) are having tensile properties like aramid fibres dictated by the properties of covalent bonds of molecular backbones. But due to lower density of PE fibres, their specific strength and modulus are higher and comparable to carbon fibres. The main drawback of polyethylene fibres is poor temperature tolerance and poor matrix compatibility. The ceramic fibres combine high strength and elastic modulus with high-temperature capability and, in general, freedom from

environmental attack. Alumina fibres and silicon carbide fibres are among the important ceramic fibres. Silicon carbide fibres are produced by a chemical vapour deposition process as well as by controlled pyrolysis of a polymer precursor. Alumina fibres retain strength to about 1370°C while silicon carbide fibres retain tensile strength well above 650°C. Alumina and silicon carbide fibres are suitable for reinforcing metal matrices in which carbon and boron fibres exhibit adverse reactivities. Polypropylene (PP) and polyester are the two major fibres mainly used in apparels, nonwovens, industrial yarns and fabrics. Polypropylene is a polyolefine made from a polypropylene monomer obtained from naphtha. The most important properties of polypropylene fibres are its low density and low softening temperature range and its hydrophobic nature. Polyester is made from dimethyl terephthalate (DMT) and mono ethylene glycol. Modern processes use pure terephthalic acid in place of DMT.

#### **1.4 Natural fibres**

Natural fibres are subdivided based on their origin, coming from plants, animals or minerals. Mineral fibres are composed of naturally occurring minerals. For example, asbestoes is a mineral fibre with several uses. Chrysotile, the most common type represents more than 95 % of the world's asbestos production. Fibres obtained from living organisms are known as animal fibres. For example, wool is an animal fibre obtained mainly from the vleece of domestic sheep. Silk is also an animal fibre produced by the silk worm in making its cocoon [25]. In contrast to other natural fibres, it does not have a cellular structure. Fibres obtained from the various parts of the plants are known as plant fibres [27,28]. In general, plant-based natural fibres are lignocellulosic in nature and are

composed of cellulose, hemicellulose and lignin, whereas animal-based fibres are of proteins. Depending upon the part from which they are extracted, plant fibres are classified as bast fibres, leaf fibres, and seed/fruit 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, eg. flax, hemp, jute, kenaf and ramie. In general, the leaf fibres are coarser than the bast fibres, eg. pineapple, sisal, abaca, banana and henequen. Cotton is the most common seed fibre and is used for textile all over the world. Coir and oil-palm are other examples of seed fibres.

Different extraction techniques are available for various natural fibres. In general, these fibres are usually extracted by retting or using raspaders. Microbiological retting is also used in the case of sisal fibre. Sisal and pineapple fibres could also be extracted by decortication (mechanical process) [27]. The average length of some common natural fibres like coir, jute, pineapple, sisal are of the range 75-150, 1500, 900-1500 and 900-1200 mm respectively. Plant-based natural fibres like flax, jute, sisal and kenaf have been more frequently utilised and studied so far, due to their natural abundance, cost effectiveness, world annual production and a wide range of properties depending on the plant source. A large body of literature is available on biocomposites based upon these plant-based natural fibres [29-33].

Other sources of lignocellulosics can be agricultural residues such as rice hulls from a processing plant, sun flower seed hulls from an oil processing unit and bagasse from a sugar mill. The properties of natural fibres vary considerably depending on the fibre diameter, structure, degree of

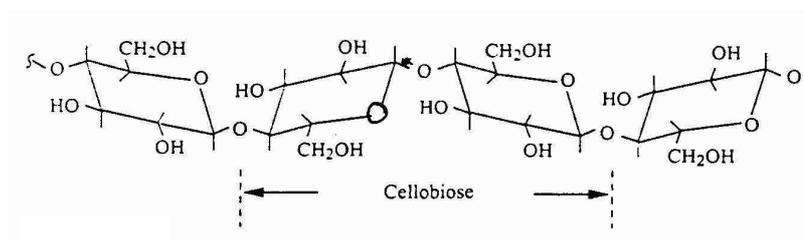
polymerisation, crystal structure and finally whether the fibres are taken from the plant stem, leaf or seed, and on the growing conditions. Natural fibres are emerging as low cost, light weight and apparently environmentally superior alternatives to glass fibres in composites. The fibres obtained from various plant sources are finding improved applications in various fields. The major constituents of lignocellulosic natural fibres are cellulose and lignin. The lignocellulosic fibres are a kind of biopolymer composite, which consists of cellulose fibres embedded in lignin and hemicellulose matrix. These polymers are the basic constituents of cell wall and are responsible for most of the physical and chemical properties such as biodegradability, dimensional instability towards moisture, flammability, thermoplasticity and degradability by ultraviolet light. Vegetable fibres possess many active functional groups susceptible to reaction. These reaction sites or functional groups are primary and secondary hydroxyl, carboxyls, and carbon-carbon and acetyl linkages. Hence, based on the variety of functional groups, etherification, esterification, alkylation, hydroxyl alkylates, graft copolymerisation, crosslinking and oxidation can be done to produce a whole series of products with many applications.

#### **1.4.1 Chemical composition**

Plant fibres as such are composite materials designed by nature [34]. Rigid cellulose microfibrils are embedded in a soft lignin and hemicellulose matrix in these fibres. Most plant fibres, except cotton are composed of cellulose, hemicellulose, lignin, waxes, pectins and some water soluble compounds [28]. Physical properties of natural fibres are basically influenced by the chemical structure such as cellulose content,

degree of polymerisation, orientation and crystallinity which are affected by conditions during growth of plants as well as extraction methods used. The major component of most plant fibres is cellulose ( $\alpha$ -cellulose). Cellulose is a linear macromolecule consisting of D-anhydroglucose repeating units joined by  $\beta$ -1,4 glycosidic linkages. The molecular structure of cellulose, which is responsible for its supramolecular structure determines many of its chemical and physical properties.

Each unit is rotated through  $180^\circ$  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 repeating cellobiose units, cellulose is technically a polymer of cellobiose. The ability of the hydroxyl groups present in each repeating unit to form hydrogen bond plays a major role in directing the crystalline packing and also governs the physical properties of cellulose materials [34]. Fig. 1.3 depicts the structure of cellulose [35].



**Fig. 1.3** Structure of cellulose

[Ref: A. K. Bledzki, J. Gassan. J. Prog. Sci. 24, 221, 1999]

Most of the natural fibres contain hemicellulose in addition to the cellulose component. Hemicellulose consists of a group of polysaccharides that remain associated with the cellulose after lignin has been removed. The hemicelluloses differ from cellulose in that they contain several sugar units

whereas cellulose contains only glucopyranose units. Hemicellulose also exhibits considerable chain branching. The degree of polymerisation of native cellulose is also ten to one hundred times higher than that of hemicelluloses. Unlike cellulose, the constituents of hemicellulose differ from plant to plant [36].

Lignins, complex hydrocarbons with aliphatic and aromatic components, are the other constituents of plant fibres. Lignin is an aromatic biopolymer, an integral cell constituent in all vascular plants including the herbaceous varieties. It is built by oxidative coupling of three major C<sub>6</sub>-C<sub>3</sub> (phenyl propanoid) units namely syringyl alcohol, guaiacyl alcohol and p-coumaryl alcohol which forms a random structure in a tridimensional network inside the cell walls [37]. Lignin is totally amorphous and hydrophobic in nature. It gives rigidity to plants. According to Gram [38], lignin can be broken down or leached out in an alkaline environment. Table 1.1 shows the chemical composition of a few plant fibres [39]. The observed mechanical properties of these fibres seem to depend mainly on the microfibrillar angle and cellulose content.

**Table 1.1** Chemical composition, moisture content and microfibrillar angle of vegetable fibres [Ref: Natural fibre reinforced polymer composites, Saira Taj, Munawar Ali Munawar and Shafiullah Khan Proc: Pakistan Acad. Sci. 44(2): 129-144, 2007]

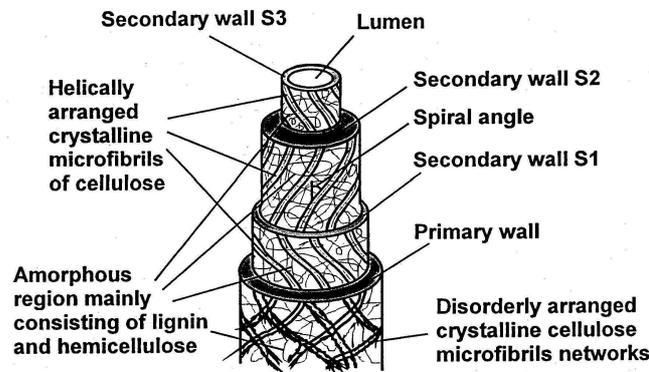
Fibre	Cellulose content (wt%)	Hemicellulose (wt%)	Lignin (wt%)	Pectin (wt%)	Moisture content (wt%)	Waxes	Microfibrillar angle (deg)
Flax	71	18.6-20.6	2.2	2.3	8-12	1.7	5-10
Hemp	70-74	17.9-22.4	3.7-5.7	0.9	6.2-12	0.8	2-6.2
Jute	61 -71.5	13.6-20.4	12-13	0.2	12.5-13.7	0.5	8
Kenaf	45-57	21.5	8-13	3.5	-	-	-
Ramie	68.6-76.2	13.1-16.7	0.6- 0.7	1.9	7.5-17	0.3	7.5
Nettle	86				11-17		
Sisal	66-78	10-14	10-14	10	10-22	2	10-22
Henequen	77.6	4-8	13.1			-	
PALF	70-82	-	5-12.7	-	11.8	-	14
Banana	63-64	10	5		10-12	-	12-14
Abaca	56-63	-	12-13	1	5-10	-	-
Oil-palm EFB	65	-	19	-	-	-	42
Oil-palm Mesocarp	60	-	11	-	-	-	46
Cotton	85-90	5.7	-	0.1	7.85-8.5	0.6	-
Coir	32-43	0.15-0.25	40-45	3-4	8	-	30-49
Cereal Straw	38-45	15-31	12-20	8	-		-

The chemical composition and cell structure of natural fibres are quite complicated. Plant fibres are like microscopic tubes i.e, cell walls surrounding the central lumen. The lumen contributes the water uptake

behaviour of plant fibres [40]. The fibre consists of several cell walls. These cell walls are formed from oriented reinforcing semicrystalline microfibrils embedded in a hemicellulose-lignin matrix of varying composition. Such microfibrils have typically a diameter of about 10-30 nm and are made up of 30-100 cellulose molecules in extended chain confirmation and provide mechanical strength to the fibre. From the structure point of view, natural fibres are multicellular consisting of a number of continuous and mostly cylindrical cells which have different size, shape and arrangement for each type of fibres [41,42]. These cells are cemented together by an intracellular substance which is isotropic, non-cellulosic and ligneous. Each cell is made up of concentric layers, the primary wall and a secondary wall, the layers of which differ in composition and orientation of cellulose microfibrils. The orientation of cellulose macromolecules in the primary wall is low. Primary walls are initially cellulosic but become lignified on growth. This is the intercellular cementing material (non-crystalline) which holds the cells together. It comprises of lignin, pectin and hemicelluloses. Secondary walls develop on the inner surface of the primary cell walls. This is mainly cellulosic (crystalline). The secondary wall has (1) an outer part ( $S_1$ ), (2) central part ( $S_2$ ) and (3) inner layer ( $S_3$ ). The central layer is the thickest and most important one in determining the mechanical properties of the fibre. In the central layers of the secondary wall, the orientation of the cellulose macromolecules is higher; here they form long filamentary fibrils inclined at a small angle to the fibre axis. The angle between the fibre axis and the microfibril is termed the microfibrillar angle. The outer layer of the secondary wall differs from the layers of the central part by a less oriented cellulose structure and a bigger angle of fibrils inclination relative to the

fibre axis. Schematic representation of the fine structure of a lignocellulosic fibre is presented in Fig 1.4 [43]. The properties of single fibres depend on crystalline content, l/d ratio of cells etc. Fibres having high cellulose content and low microfibrillar angle show high tensile strength and initial modulus [27]. Cellulosic fibres have amorphous and crystalline domains with a high degree of organisation. The crystallinity rate depends on the origin of the material. Cotton, flax, ramie, sisal and banana have high degrees of crystallinity (65-70 %), but the crystallinity of regenerated cellulose is only 35-40 %.

Progressive elimination of the less organised parts leads to fibrils with ever increasing crystallinity, until almost 100 % crystallinity leading to whiskers. PALF possesses highest crystallinity among all natural fibres [44]. Crystallinity of cellulose results partially from hydrogen bonding between the cellulose chains, but some hydrogen bonding also occurs in the amorphous phase [45] although its organisation is low. In cellulose there are many hydroxyl groups available for interaction with water by hydrogen bonding. In contrast to glass fibres where water absorption is important only at the surface, cellulose fibres interact with water at the surface as well as in the bulk. The sorption isotherm of cellulosic material depends on the purity of cellulose and the degree of crystallinity. All –OH groups in the amorphous phase are accessible to water whereas only a small amount of water interacts with the surface –OH groups of the crystalline phase.



**Fig. 1.4** Structural constitution of natural vegetable fibre cell

[Ref: M Rong, *Compos. Sci. Technol.* 61, 1437, 2001]

### 1.4.2 Properties

To compare the different kinds of lignocellulosic fibres, knowledge about fibre length and fibre diameter is important. The effective length of the long fibres after processing is based on the type of plant, the processing technology, the pre-cut length of the stalks and the operation data of the decorticator. The length of natural fibres varies in a wide range from 10 to 250 mm. An important parameter is the aspect ratio (length /diameter) that has an influence on the mechanical properties of the composite [46]. A high aspect ratio is very important in agro-based fibre composite as it gives indication of possible high strength properties.

Table 1.2 shows the mechanical properties of some common natural fibres as compared to some common conventional fibres [28]. It can be seen that these fibres possess lower specific stiffness compared to glass fibre even though the specific strength properties are comparable.

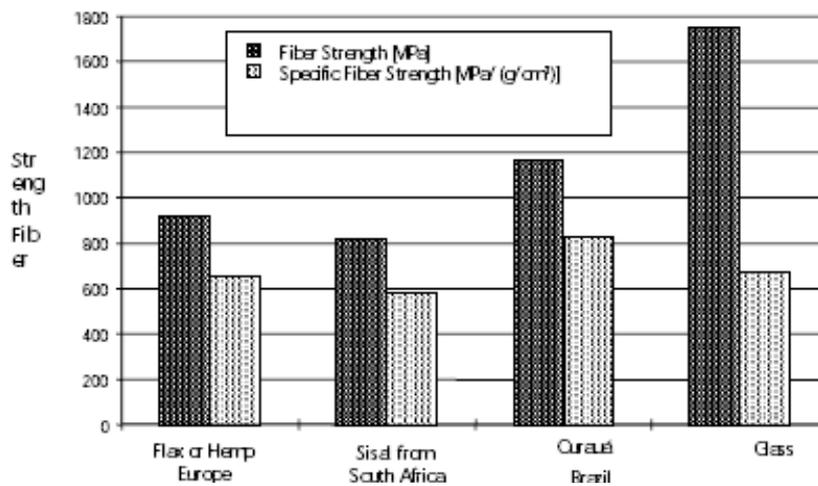
**Table 1.2** Mechanical properties of natural fibres as compared to conventional reinforcing fibres

[Ref: J. G. Cook. Handbook of Textile Fibres-Natural Fibres. 5<sup>th</sup> ed. Merrow Publishing, Durham, England, 1984]

<b>Fibre</b>	<b>Density (10<sup>3</sup> kg/m<sup>3</sup>)</b>	<b>Elongation (%)</b>	<b>Tensile strength (MPa)</b>	<b>Young's modulus (GPa)</b>
Aramid	1.4	3.3-3.7	3000-3450	63 -67
Carbon	1.4	1.4-1.8	4000	230-240
Kevlar 49	1.45	2.0	2800	124
Cotton	1.5	7.0-8.0	287-597	5.5-12.6
Jute	1.3	1.5-1.8	393-773	26.5
Flax	1.5	2.7-2.32	345-1035	27.6
Hemp	-	1.6	690	-
Ramie	-	3.6-3.8	400-938	61.1-128
Sisal	1.5	4-6	511-635	9.4-22
Coir	1.2	30	175	4.0-6.0
Banana	1.3	2-4	750	29-32
Pineapple	1.56	-	172	62
Oil palm	1.55	-	100-400	26.5
Soft wood kraft	1.5	-	1000	40.0
E-glass	2.5	2.5	2000-3500	70.0
S-glass	2.5	2.8	4570	86.0
SiC	3.08	0.8	3440	400
Al <sub>2</sub> O <sub>3</sub>	3.95	0.4	1900	379

### 1.4.3 Advantages

An important step towards higher performance applications was achieved with the door panels of the Mercedes-Benz E-Class. The wood fibre materials previously used for the door panels were replaced by a plant fibre reinforced material consisting of a flax/sisal fibre mat embedded in an epoxy resin matrix.



**Fig. 1.5** Specific strength of plant fibres compared to glass fibre

[Ref : T. G. Schuh, Daimler-Chrysler AG, Stuttgart. Renewable Materials for Automotive Applications. 1999]

A remarkable weight reduction of about 20 % was achieved, and the mechanical properties, important for passenger protection in the event of an accident, were improved. As environmental issues become more stringent, researchers believe that natural fibres are likely to become major components of cars around the world.

Natural fibres have the potential to be used as replacements for glass fibre reinforcements with the added benefits of low cost, low density, acceptable specific strength properties, high toughness, enhanced energy recovery, carbon dioxide balance, recyclability and biodegradability. Fig. 1.5 shows the strength of different plant fibres compared to glass. Considering the specific properties, a weight saving potential of about 15 % compared to glass fibre-reinforced materials is quite possible. At the moment this is one of the most relevant technical driving forces for further developments [47].

In addition to their high strength and stiffness per weight and environmental virtues, the advantages of natural fibre composites are acoustic insulation, easier health and safety management, rapid production by compression or injection moulding and potentially lower cost [48]. A wide variety of fibres have also been used for production of textiles, pulp and paper and fibre boards. The natural fibres can serve as reinforcement by improving the strength and stiffness and also by reducing the weight of the resulting biocomposite materials. The most interesting aspect about natural fibres is their positive environmental impact and they cause no health hazards. They are susceptible to microbial decomposition, including mildew, aerobic bacteria, fungi, moths, carpet beetles, termites and rot. Hence these are biodegradable.

#### **1.4.4 Major issues related to natural fibres**

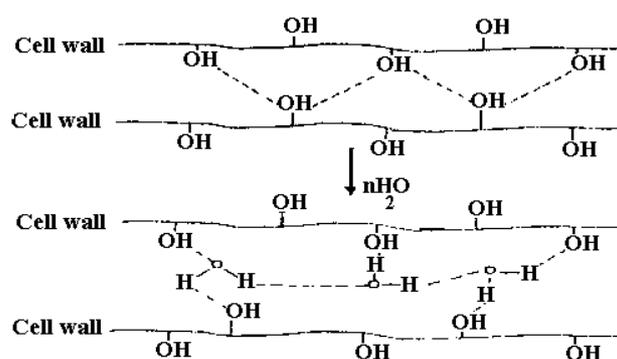
The plant fibres have some disadvantages resulting from their chemical composition and structure. Except for wood, the diameter of natural fibres is about 10 times larger than that of synthetic fibres. This results in increased critical length in short fibre reinforced composites and thus, decreases the load bearing capability. There is an enormous amount of variability in fibre properties depending upon the part of the plant from which the fibres are taken, the quality of the plant and location. Different fibres have different lengths and cross sectional areas and also different defects such as micro compressions, or pits or cracks.

##### **1.4.4.1 Moisture absorption**

It is well established that natural fibres which are hydrophilic in nature are susceptible to moisture absorption [49]. The swelling of natural fibres is generally affected by its morphology as well as physical and chemical structures. Generally the moisture content of natural fibres varies between 5-10 %. This can lead to dimensional variations in composites and also affect the mechanical properties of the composites. Biofibres change their dimensions with varying moisture content because the cell wall of the polymers contain hydroxyl and other oxygen containing groups, which attract moisture through hydrogen bonding [50].

The cross section of the fibres becomes the main access to the penetrating water. The waxy materials present on the fibre surface helps to retain the water molecules on the fibre. The porous nature of natural fibre accounts for the large initial uptake at the capillary region. Moisture absorption of natural fibre plastic composites is one major concern in outdoor

applications. Resistance to moisture absorption of natural fibre can be improved by treating these fibres with suitable chemical agents. Schematic representation of swelling process in cellulose is given in Fig. 1.6 [51].



**Fig. 1.6** Schematic representation of swelling process in cellulose fibre  
 [Ref.: L.Y Mwaikambo, M.P Ansell, J. Appl. Polym. Sci. 84, 2222, 2002]

#### 1.4.4.2 Thermal stability

Thermogravimetry is one of the most widely used techniques to understand the structural dependence on the thermal degradation of natural cellulose fibre. Moreover, it is a useful technique to determine the thermal stability of the materials. Most of the natural fibres lose their strength at about  $160^{\circ}\text{C}$ . The major components of natural fibres, cellulose, hemicellulose and lignin have their own characteristic properties with respect to thermal degradation which are based on polymer composition. However, the microstructure and 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 fibre behave differently if they are isolated or if they are intimately combined within each single cell of the fibre structure [52].

Lignin, specifically the low molecular weight protolignin, degrades first and at slower rate than the other constituent.

#### **1.4.4.3 Biodegradation and photodegradation**

Lignocellulosics exposed to outdoors undergo photochemical degradation caused by ultraviolet light. This degradation primarily takes place in lignin component, which is responsible for the characteristic colour changes [53]. Biodegradation of the high molecular weight cellulose weakens the lignocellulosic cell wall because crystalline cellulose is primarily responsible for the strength of lignocellulosics [54]. Resistance to biodegradation and UV radiation can be improved by bonding chemicals to the cell wall polymers or by adding polymer to the cell matrix.

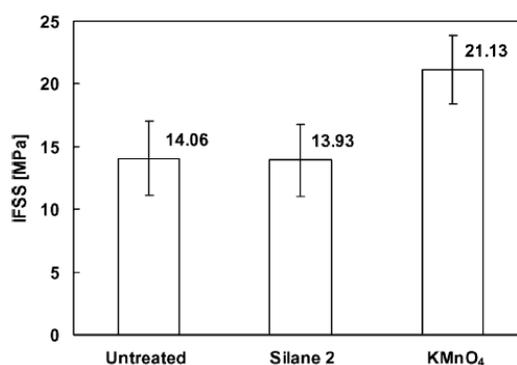
#### **1.5 Fibre/matrix interface**

The quality of the fibre/matrix interface is significant for the application of natural fibres as reinforcement for plastics. The interface is a boundary at which the reinforcement and the matrix meet. It is defined as a two dimensional region between the fibre and the matrix having properties intermediate between those of fibre and matrix.

The physical and mechanical properties of composites are significantly affected by the structure and strength of the interface bond. Since the fibres and matrices are chemically different, strong adhesion at their interfaces is needed for an effective transfer of stress and bond distribution throughout an interface. The interfacial interaction depends on the fibre aspect ratio, strength of interaction, anisotropy, orientation, aggregation etc [55-58].

In composites, the interface plays a key role in transferring the stress from the matrix to the fibre. A strong interface creates a material with high strength and stiffness whereas a weak interface reduces the efficiency of stress transfer from the matrix to the fibre and generally results in low strength and stiffness.

Mechanical properties of fibre reinforced plastics highly depend on the properties of the interface between the fibres and the matrix. Various methods are available for assessing interfacial strength of fibre reinforced polymer composites. Most important are direct methods like single fibre fragmentation, single fibre pull-out, and single fibre microindentation tests [59]. Comparative studies of mechanical and interfacial properties between jute and E-glass fibre-reinforced polypropylene composites were studied by Khan et al. [60]. The interfacial shear strength of the jute and E-glass fibre-based systems was investigated and found to be 2.13 and 4.66 MPa, respectively, measured using the single-fibre fragmentation test. Fig. 1.7 shows IFSS (interfacial shear strength) results of treated and untreated sisal fibres in epoxy resin [61].



**Fig. 1.7** IFSS between treated and untreated sisal fibre and epoxy resin [Y. Li, Y. W. Mai. *J. Adhes.* 82, 527, 2006]

A linear relationship was observed for the maximum pullout load ( $P_{\max}$ ) versus embedded fibre length ( $l$ ) data for all fibre surface treatments. IFSS can be calculated from the equation

$$\text{IFSS} = P_{\max}/2\pi a l \quad (1.1)$$

where  $P_{\max}$  is the maximum pullout load, ' $l$ ' is the embedded fibre length and  $a$  is the fibre radius. The permanganate treatment improves the interfacial shear strength because of the mechanical bonding caused by the enhanced sisal fibre surface roughness and also penetration of epoxy to the fibre. Silane 2(  $\gamma$ - methacryloxy propyl trimethoxy silane) has no effect on interface bonding, and the IFSS is similar to untreated fibre. The functional group of epoxy resin used cannot react with the functional group of silane (i.e, C=C). Thus, no chemical reactions can occur between them, and therefore no improvement of interfacial properties between the silane treated sisal fibre and epoxy resin can be found.

### 1.5.1 Methods to improve interfacial bonding

For better wetting of the polymer on the fibre, surface tension of the polymer must be as low as possible; it should be at least lower than the surface tension of the fibre. This can be achieved by giving physical and chemical surface modifications to the fibre and the polymers, which give rise to enhanced interaction at the interface.

#### 1.5.1.1 Physical modification

Physical methods of fibre surface modification involve surface fibrillation, electric discharge (corona, cold plasma), UV irradiation, electron beam irradiation, laser etc. Physical methods change the structural and surface properties of the fibre and thereby influence the

mechanical bonding to polymers. Physical methods in natural fibre processing are used to separate natural fibre bundles into individual filaments and to modify the surface structure of the fibres so as to improve the use of natural fibres in composites. Steam explosion and thermomechanical processes fall in the first category, while plasma and corona fall in the second. The physical treatments have also been used to modify the thermoplastic polymeric films like polyethylene and polypropylene in a bid to impart reactivity. Among the physical treatments, corona treatment is one of the most interesting techniques for surface oxidation activation. The treatment of rayon fibres with oxygen plasma results in increasing the total and polar part of the free surface energy with increasing treatment time, because of the increased [O]/[C] ratio. Similar results were observed by Belgacem et al. [62] for an increasing corona current level with cellulose fibres. The corona treatment leads to change in the surface energy of cellulose fibres. Corona discharge treatment of cellulose fibres and hydrophobic matrix was found to be effective in improving compatibilisation between hydrophilic fibre and hydrophobic matrix. Also, Sakata et al. [63] found improved wettability of wood with increasing level of corona treatment. In the case of wood, surface activation increases the amount of aldehyde groups according to the report of Wang et al. [64].

Cold-plasma chemistry has received much attention in the last few decades, in the realm of the surface modification of various materials through the use of specific molecules in the gas phase, which undergo decomposition giving reactive species capable of activating and or attacking the substrate. Plasma treatment is an important treatment to

achieve better interfacial bonding of the fibre to matrix. Sinha and Panigrahi [65] studied the influence of plasma treatment on the interfacial adhesion of jute fibre-reinforced unsaturated polyester and plasma treatment resulted in the development of hydrophobicity in fibres. Koichi et al. [66] submitted methanol-extracted cellulose fibre surfaces to vacuum ultraviolet (VUV) irradiation in order to ascertain the efficiency of this technique in terms of oxidation capacity and compared their results with other common oxidation techniques such as ozone, chromic acid, nitric acid and hydrogen peroxide treatments. They monitored the evolution of the surface chemical composition by FTIR spectroscopy through the intensity variations of the band at  $1720\text{ cm}^{-1}$  and showed that VUV irradiation induced surface oxidation as efficiently as chromic and nitric acids.

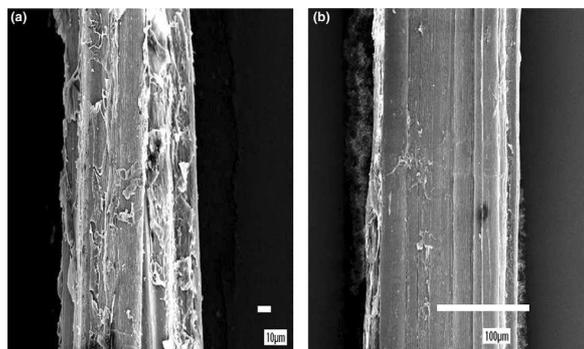
#### **1.5.1.2 Chemical modification**

The surface modification improves fibre/matrix compatibility and bonding characteristics by creating compatible surface energies and formation of physical, mechanical and chemical bond and also creates more trans-active surface molecules that would readily form bonds with matrix. The hydroxyl groups present in the natural fibres may be involved in the hydrogen bonding within the cellulose molecules, thereby reducing the activity towards the matrix. Chemical modifications may activate these groups or can introduce new moieties that can effectively interlock with the matrix. Several methods have been proposed to improve the adhesion between fibre and matrix in order to achieve maximum transfer of load from matrix to fibre in fibre reinforced composites. It is necessary to impart hydrophobicity to the natural fibres by chemical reaction with

suitable coupling agents or by coating with appropriate resins in order to develop composites with better mechanical properties and environmental performance. Such surface modification of fibre decreases moisture adsorption, increases wettability of fibres with resin and improves the interfacial bond strength, which are critical factors for obtaining better mechanical properties of composites.

The importance of the interface and the influence of various types of surface modifications on the physical and mechanical properties of natural-fibre reinforced composites are discussed in detail by Sreekumar et al. [67]. Various surface modifications include treatment with NaOH, peroxide, permanganate, acrylonitrile and coupling agents like silane and titanate.

One of the most common methods of chemical modification is mercerisation or treatment with sodium hydroxide. Joshy et al. [68] discussed the effect of alkali treatment on the mechanical properties of the natural fibre "isora" as reinforcement in unsaturated polyester resin. Tensile and flexural properties of the composite were found to be maximum and impact strength minimum for an alkali treatment time of 4 h. The mechanical properties were found to be optimum for an alkali concentration of 1 %. Mwaikambo and Ansell [51] treated hemp, jute, sisal and kapok fibres with various concentrations of NaOH and found 6 % to be the optimised concentration in terms of cleaning the fibre bundle surfaces, yet retaining a high index of crystallinity. Effects of alkali treatment on the interfacial adhesion of bamboo fibres in polyester composites was evaluated [69]. Results revealed that increase in alkali concentration reduces the strain at failure and ductility of bamboo fibres.



**Fig. 1.6** SEM micrographs of longitudinal views of (a) untreated hemp fibre and (b) 6% NaOH treated hemp fibre

[L. Mwaikambo, and M. Ansell, *J. App. Polym. Sci.* 84, 2222, 2002]

Aziz et al. [70] studied the morphological changes that occurred after alkali treatment of hemp fibres. The SEM micrograph of the longitudinal surface of untreated fibre bundles in Fig. 1.6 (a) shows the presence of wax, oil and surface impurities. The longitudinal view of 6 % NaOH treated hemp fibre in Fig. 1.6 (b) shows a very clean surface. The surface of the treated fibre appears to be quite smooth but in fact is roughened by the chemical treatment. Its surface topography shows the absence of surface impurities, which were present in the untreated fibre.

Coupling agents usually improve the degree of crosslinking in the interfacial region and perfect bonding results. Silanes are commonly used coupling agents. In general, the best silane coupling agents are those where the organo functional group on silicon has maximum reactivity with the particular thermosetting resin during cure. A number of attempts have been carried out to understand the silane-cellulose system [71-73]. Thus, the interaction of silane coupling agents with cellulosic fibres and the effect of some parameters, such as pH, the initial amount of silane

with respect to cellulose and the adsorption contact time, on their anchoring capability onto the fibre surface have been ascertained. Different spectroscopic techniques have been used to show the presence of silane and to quantify its amounts on the substrate and to elucidate the structure of the anchored siloxane network on the fibre surface [73]. Abdelmouleh et al. [73] have shown that the fibre treatment with silane coupling agents enhances significantly the mechanical strength of the final composite using epoxy and unsaturated polyester resins. Recently, Abdelmouleh et al. [74] have studied three silane agents (different by the functionality of the radical moiety appended to silicon atoms) to treat delignified cellulose fibres in order to improve their adhesion with low density polyethylene and nitrile rubber matrix. The effect of these treatments on the mechanical properties of the ensuing composites and on their water uptake ability has been investigated accordingly. Gassan et al. [75] have improved the tensile, flexural strength and stiffness of jute-epoxy composites by treating the fibres with silane. Tripathy et al. [76] found that delignification by bleaching produces better interfacial bond between the jute fibre and the polyester matrix, resulting in better mechanical properties of the composites. Gauthier et al. [77] reported that adhesion may be improved by using coupling agents like maleic anhydride to incorporate hydroxyl groups on the matrix and consequently enhancing the wetting effect of the resin on the fibres.

Graft copolymerisation of acrylonitrile (AN) onto defatted pineapple leaf fibre (PALF) was studied using a combination of  $\text{CuSO}_4$  and  $\text{KIO}_4$  as an initiator in an aqueous medium in the temperature range 30–500°C. Grafting improved the thermal stability of PALF [78].

Pothan et al. [79] determined the polarity parameters of chemically modified cellulose fibres by solvatochromic technique and reported that different silanes, NaOH and long alkyl groups used to modify the cellulose fibre surface have changed the hydrogen bond donating ability of the fibre. The change in the surface composition of the raw and chemically modified banana fibre was also investigated using various techniques such as solvatochromism, electrokinetic measurements, and XPS. Surface characterisation of raw and chemically modified banana fibres with XPS revealed the presence of surface functionalities. Interaction of the fibres with silanes on the surface was also observed. The XPS results were found to perfectly agree with the solvatochromic and electrokinetic measurements [80]. The surface polarity of chemically treated BF has been characterised by solvatochromic and electrokinetic methods [81]. Different chemical treatments like NaOH and silane treatments used to modify the BF surface have decreased the hydrogen-bond donating ability of the fibre.

### **1.6 Natural fibre reinforced polymer composites**

Natural fibres are emerging as low cost, lightweight and apparently environmentally superior alternatives to glass fibres in composites. Due to an occurrence of a wide variety of natural fibres in the country, Indian researchers have directed efforts in developing innovative natural fibre composites for various applications. The developments in composite material after meeting the challenges of aerospace sector have cascaded down for catering to domestic and industrial applications.

In lignocellulosic fibre reinforced composites, different plant fibres and wood fibres serve as reinforcement by giving strength and stiffness to the

structure while the plastic matrix serve as the adhesive to hold the fibres in place so that suitable structural components can be made. The matrix for the lignocellulosic fibres includes thermosets, thermoplastics and rubber. The use of lignocellulosics as fillers and reinforcements in thermoplastics has been gaining acceptance in commodity plastics applications in recent years. The addition of vegetable fillers to thermoset matrices has the additional advantage of reducing the tendency of the resin to crack during cure by reducing the resin shrinkage during the resin impregnation.

Natural fibre composites are likely to be environmentally superior to glass fibre composites in most cases for the following reasons: (1) natural fibre production has lower environmental impacts than glass fibre production; (2) natural fibre composites have higher fibre content for equivalent performance, reducing more polluting base polymer content; (3) the light-weight natural fibre composites improve fuel efficiency and reduce emissions in the use phase of the component, especially in auto applications; and (4) end of life incineration of natural fibres results in recovered energy and carbon credits [82].

Currently, many types of natural fibres [35] have been investigated for use in plastics including flax, hemp, jute, straw, wood, rice husk, wheat, barley, oats, rye, cane (sugar and bamboo), grass, reeds, kenaf, ramie, oil palm empty fruit bunch, sisal, coir, water, hyacinth, pennywort, kapok, paper mulberry, raphia, banana fibre, pineapple leaf fibre and papyrus. Bledzki and Gassan [35] reported that natural fibres were used as early as 1908 in the fabrication of large quantities of sheets, where cotton was used to reinforce sheets made of phenol-or melamine-formaldehyde

resins. Hemp fibres were the world's largest agricultural crop in the early 19<sup>th</sup> century, but the demand for the material declined with advances in the field of synthetic fibres. More recently global environmental issues have led to a renewed interest in bio-based materials with the focus on renewable raw materials that can be made recyclable or biodegradable at a reasonable cost.

Recent advances in the use of natural fibres, eg flax, jute, hemp, straw, coir, bamboo etc in composites have been described by several authors [83-86]. An overview of biodegradable composites based on lignocellulosic fibres, in terms of market, processing methods, matrix–reinforcement systems, morphology, properties and product development is presented by Satyanarayana et al. [87]. The tensile, flexural and dielectric properties of composites made by reinforcing vakka as a new natural fibre into a polyester resin matrix have been investigated recently, by Rao et al. [88]. It has been observed that the tensile properties increase with respect to volume fraction of fibre for vakka fibre composite and are also more than those of sisal and banana composites and comparable to those of bamboo composites. The dielectric strength of vakka fibre composite increases with increase in volume fraction of fibre in the composite unlike the case of sisal, bamboo and banana composites. Rosa et al. [89] have investigated the morphology of Okra technical fibres through optical and electron microscopy and their thermal behaviour through thermogravimetric analysis. Thermogravimetric and weathering study of novolac resin composites reinforced with mercerised bamboo fibre was carried out by Das et al. [90]. The results showed that the composites with treated bamboo strips showed better weathering characteristics compared with untreated

one. Thermogravimetric analysis of all the samples indicated better thermal properties of alkali treated samples.

The effect of fibre surface modification on the mechanical and water absorption characteristics of sisal/polyester composites fabricated by resin transfer moulding was studied by Sreekumar et al. [91]. Sisal fibres were subjected to various chemical and physical modifications such as mercerisation, heating at 100°C, permanganate treatment, benzylation and silanisation to improve the interfacial bonding with matrix. Mercerised fibre reinforced composites showed 36 % of increase in tensile strength and 53 % in Young's modulus while the permanganate treated fibre-reinforced composites performed 25 % increase in flexural strength.

Mukherjee and Satyanarayana [92] reported on the mechanical properties of PALF. Pavithran et al. [93] studied unidirectionally aligned PALF-polyester composites and the toughness of these composites was found to increase with the microfibrillar angle of the fibres. George et al. [94,95] reported on the processing characteristics, viscoelastic properties and mechanical behaviour of PALF-LDPE composites. Longitudinally oriented composites showed maximum value of the storage modulus. From the dynamic viscoelastic properties, it was found that 2 mm is the optimum fibre length for reinforcement. They [96] also analysed the improved interfacial interactions in the chemically reinforced pineapple leaf fibre reinforced polyethylene composites. They used various chemical treatments such as NaOH, PMPPIC (Poly(methylene) poly(phenyl) isocyanate), silane, and peroxide to improve the interfacial bonding and found that the treatment improved the mechanical properties. Among the treatments, PMPPIC treatment of fibre exhibited maximum

interfacial interactions due to the reduced hydrophilicity of the treated fibre. Misra et al. [97] reviewed on pineapple leaf fibres, sisal fibres and their bio-composites. They have shown that the interface quality for PALF/polyester composites could be enhanced through different surface modifications, such as dewaxing, alkali treatment, cyanoethylation, and grafting of acrylonitrile monomer onto dewaxed PALF. Samal and Ray [98] have demonstrated that the treatment of pineapple fibres with alkali (NaOH), 2,4-dinitro chloro benzene, benzoyl peroxide (BPO), BPO/acetylation, significantly increased the resistance to water uptake and the mechanical strength of the fibres. The parent and chemically modified PALFs were characterised by FTIR spectra, pH measurement, and detection of nitrogen. The modified fibres showed significant hydrophobicity, improved mechanical strength, and moderate chemical resistance. The effects of compatibilising agent and surface modification of short pineapple leaf fibre on physical properties of short pineapple leaf fibre reinforced high impact polystyrene (HIPS) composites were investigated by Siregar et al. [99]. The compatibilising agents were used to modify the HIPS which include the polystyrene-block-poly(ethylene-ran-butylene)-block-poly (styrene-graft-maleic anhydride) and poly (styrene-co-maleic anhydride). The results have shown that adding compatibilising agent improved the physical properties of the composites more effectively than by only using alkali treatment to modify the natural fibre surface.

Characterisation of pineapple leaf fibres from selected Malaysian cultivars was done by Mohamed et al. [100]. PALF from three popular cultivars (Josapine, Sarawak and Moris Gajah) were characterised

physically and mechanically in order to identify the best cultivar for producing fibres. The three cultivars had leaves with very similar cross-sections. 'Josapine' fibre bundles were finest and varied least in their diameter followed by those of 'Sarawak' and 'Moris'. 'Josapine' PALF had the highest tensile strength and Young's modulus and the highest elongation at break.

Mohanty et al. [101] prepared green composites from soy based plastic and pineapple leaf fibre and evaluated their thermal and mechanical properties. Kinetics of crystallisation in pineapple leaf fibre reinforced phenol formaldehyde (PF) composites has been studied employing differential scanning calorimetry (DSC). Kinetic parameters such as activation energy in crystallisation as well as in glass transition region have been investigated at different loadings of fibre [102].

### **1.6.1 Applications of natural fibre reinforced composites**

Natural fibres are replacing synthetic fibres as reinforcement in various matrices. The composites so prepared can effectively be used as substitute for wood and also in various other technical fields, e.g. automotive parts. Natural fibre composite materials are being used for making many components in the automotive sector. These materials are based largely on polypropylene or polyester matrices, incorporating fibres such as flax, hemp, and jute.

In Germany, natural fibres are now being used to reinforce exterior components of the vehicle, whereas in the past the application was confined to interior components [34]. Bio-fibre composites in the automotive industry both reduce material waste and increase fuel

efficiency. The good damping properties which reduce unwanted noise and prevent vibration fatigue failure, have found numerous applications in the aircraft, automobile and machinery industries [34]. In Germany, car manufacturers aim to make every component recyclable and biodegradable. If glass fibre composites are replaced by natural fibre composites; there will be a reduction in the weight of 10-20 kg. This can bring about a significant reduction in fuel consumption leading to a positive effect on the environment [103]. Use of natural fibres as reinforcement in cement matrix has also been practiced for making low cost building materials such as claddings, roofing panels, sheets and tiles, slabs and beams [104,105].

The high-tech revolution in the use of natural fibres could end in replacement of synthetic materials. The diverse range of products now being produced, utilising natural fibres and bio-based resins derived from soya beans, is giving life to a new generation of bio-based composites for a number of applications. Bio-based polyurethane composites are finding application in automotive market as they are light weight, durable and cost effective [106].

### **1.7 Green composites**

The development of commercially viable “green products” based on natural resources for both matrices and reinforcements for a wide range of applications is on the rise. "Green" and "truly green" composites are being developed worldwide. It is generally accepted that "green" composites consist of natural fibres and biopolymers, with the latter usually produced from petrochemical or renewable sources [107,108]. "Truly green" composites incorporate renewable sourced biopolymers produced from

cellulose and soya-based plastics, starch, lactic acid, bacterial cellulose, among others [108] usually reinforced with plant fibres, specifically lignocellulosic fibres.

The major attractions of green composites are that they are environmental friendly, fully degradable and sustainable. Composites made of biodegradable, primarily plant-derived materials are light and can be as strong as conventional plastics. Yet at the same time they provide superior insulation against noise and heat. This makes the green composites particularly desirable for interior door and ceiling panels and panels separating the engine and passenger compartments in vehicles [109]. Life cycle assessment is of paramount importance at every stage of a product's life, from initial synthesis through to final disposal and a sustainable society needs environmentally safe materials and processing methods. The design and life cycle assessment of green composites have been exclusively dealt with by Baillie [110]. Aliphatic polyesters are among the most promising materials for the production of high-performance, environment-friendly biodegradable plastics [111-114]. One of the aliphatic polyesters is poly(lactic acid) (PLA) which is produced via the ring-opening polymerisation of lactide (a cyclic dimer of lactic acid). Wang et al. developed novel reinforced biodegradable composites by incorporating water bamboo husk powder screened to a very small size (~0.05 mm) into PLA. The thermal and mechanical properties were increased. The storage moduli of powder-containing samples were found larger than that of pristine PLA [115]. Furthermore, the production of such green composites will reduce the amount of agricultural wastes, and

increase the economic value of the water bamboo, and lead to the low cost of PLA products.

Effect of chemical modifications of the pineapple leaf fibre surfaces on the interfacial and mechanical properties of laminated biocomposites prepared from biodegradable poly(lactic acid) (PLA) and untreated or surface-treated pineapple leaf fibres (PALF) by compression moulding. The mechanical properties of the PLA laminated composites were improved significantly after chemical treatment with silane and alkali. It was found that pineapple leaf fibres are good candidates for reinforcement of high performance laminated biodegradable biocomposites [116].

The large number of biodegradable polymers (biopolymers) which are commercially available show a range of properties and can compete with non-biodegradable polymers in different industrial fields (eg, packaging). Green composites reinforced with hemp nanocrystals (HCN) in plasticised starch were studied by Cao et al. [117]. The films exhibited significant increases in the tensile strength and Young's modulus, from 3.9 to 11.5 MPa and from 31.9 to 823.9 MPa, respectively, with increasing HCN content from 0 to 30 wt %. In addition to the improvement in mechanical properties, the incorporation of HCN into the PS matrix also led to a decrease in the water sensitivity of the final composite materials. It is also observed that the mechanical properties of coir-based green composites increase as a result of chemical composition modification and surface modification [118].

Fibres such as graphite, aramid, glass etc. are commonly used to fabricate high strength composites. These so called 'advanced composites' have revolutionised the materials world by providing very strong but light

weight materials in place of metals for many years. Significant amount of research is being conducted to develop environment friendly and fully sustainable 'Green' polymers, resins and composites that are based on sustainable sources such as plants.

The most recent development in the fabrication of advanced green composites using high strength liquid crystalline cellulose fibres and plant-based resins is expected to change the green composite landscape completely [119-121]. The highest strength of these experimental, hand-laid unidirectional composites was in excess of 600 MPa. This compares to about 350-400 MPa for soft steel. What is interesting is that these composites had a density of about 1.4 g/cc (1400 kg/m<sup>3</sup>) compared to above 7.8 g/cc (7900 kg/m<sup>3</sup>) for steel. While the experimental composites were reinforced using only 42 % fibres by volume, with automation the fibre content of 60 %, as in most advanced composites, could be easily achieved. In that case the strength could be in the range of 950 MPa making the advanced green composites more than 5.5 times stronger than some of the strongest varieties of steel on 'per weight' basis. These composites may be used in primary structural applications such as I-beams for construction. The mechanical and thermal properties of the composites may be further improved by adding nano- and micro-fibrillar-cellulose (NFC and MFC) and nano-clay to the resin. NFC and MFC are produced by mechanical and/or hydrostatic shearing plant fibres under high pressure. Addition of NFC and MFC has been shown to increase both the strength and toughness of the soya based resins significantly and thus should improve the composite properties as well. At present, cellulose/soya resin base advanced green composites can be used in

interior applications. They may be easily protected from water by varnish, paint or other methods that are commonly used for wood for exterior applications.

There is also significant research effort in developing spider-silk like fibres using genetic engineering to obtain high strength protein fibres. These fibres, when fully developed, would also provide excellent reinforcement for composites. At the end of their life, the fully sustainable 'advanced green composites' can be easily disposed of without harming the environment, infact, helping it.

### **1.8 Cellulose nano composites**

The use of nano-scale fillers as reinforcement in bio-based composites is another technology that has been extensively investigated [122,123]. With their nanometric size effect and extremely high specific-surface area, nano-fillers have the potential for significant reinforcement in composite materials at very small filler loadings and provide some unique outstanding properties as compared to their conventional microcomposite counterparts, eg. natural fibre reinforced composites.

One of the problems in making cellulose nanocomposites is the difficulty in dispersing the nanofibres into the polymer matrix. To solve poor dispersion, researchers have attempted mechanical and chemical treatments such as the use of surfactants. Instead of first making the nanofibres and then trying to disperse it in a polymer matrix, the cellulose nanofibers are directly synthesised in the matrix. Bacteria are used to synthesise the cellulose chains into a polymer rich medium. The resulting cellulose/polymer compound is therefore a good mix/dispersion of the

two components. In addition to improving the dispersion of the cellulose into the matrix, this insitu bioproduction of nanocomposites allows a control of the size and crystallinity and morphology of the cellulose fibres. Bacterial cellulose is an excellent reinforcement material for nanocomposites due to its high purity, high crystallinity, biodegradability, water holding capacity, and excellent biological affinity.

Gindl and Keckes [124] produced cellulose-based nanocomposite films with different ratios of cellulose I and II by means of partial dissolution of microcrystalline cellulose powder in lithium chloride/*N,N*-dimethylacetamide and subsequent film casting. The mechanical and structural properties of the films were characterised using tensile tests and X-ray diffraction. The results show that, by varying the cellulose I and II ratio, the mechanical performance of the nanocomposites can be tuned. Depending on the composition, a tensile strength upto 240 MPa, an elastic modulus of 13.1 GPa, and a failure strain of 8.6 % were observed. Their greatest advantage is that they are fully biobased and biodegradable.

The efficiency of poly( $\epsilon$ -caprolactone) (PCL) as a matrix polymer for cellulose nanocomposites has been investigated at the macromolecular contact level using atomic force microscopy in a colloidal probe configuration. Model cellulose microspheres grafted with PCL were prepared via ring-opening polymerisation. Force measurements between the functionalised particles revealed the adhesion to be highly dependent on the contact time because of a diffusion-controlled mechanism [125].

### 1.9 Synthetic fibre reinforced composites

Mechanical strength of the composite is dependent upon the amount, type and arrangement of the fibre within the composite. On the application basis, glass is used as a continuous strand mat, milled fibres and as glass flakes. Karger-Krocsis and co-workers [126,127] have worked on the failure behaviour of short and long glass fibres and glass mats-reinforced-polypropylene composites. Glass fibre represents excellent performance reinforcement for fibre reinforced-plastic composites. High strength, light weight, dimensional stability, resistance to corrosion and electricity etc are major advantages of the glass reinforced composites. Glass has demonstrated its major contributions in the marine transportation, communication, housing, chemical processing, construction industries etc. Glass fibre effectively reinforces thermoplastics as well as thermosets. Glass fibre reinforced plastics have been used in many structural applications for the last 40 years.

Polyalkenyl-poly-maleic-anhydride-ester/amide type new experimental additives have been developed and used to achieve the better properties of glass fibre reinforced polyester composites [128]. The surfaces of reinforcements, chopped glass fibre and a glass woven [0/90°] fabric materials have been treated with the dissolved form of polyalkenyl-poly-maleic-anhydride-ester, polyalkenyl-poly-maleic-anhydride-amide and polyalkenyl-poly-maleic-anhydride-ester-amide type experimental coupling additives and then they have been used in fibre reinforced thermoset. The most favourable effects have been found in the case when the glass fibre surface was modified by polyalkenyl-poly-maleic-anhydride-ester-amide type additives. Moreover, results have referred to more favourable effects

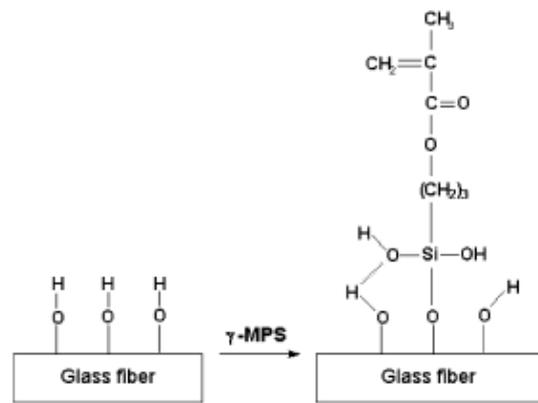
in case of chopped glass fibre mat than in glass woven fabric composites. Tensile properties could be improved by 39 % with that additive and flexure properties with 22 % in those laminates. Tensile and flexure properties of glass woven [0/90°] fabric reinforced composites could be improved by 18 %, and 40 % comparing to the untreated glass fibres containing polyester composites with the same reinforcement.

Carbon fibre composites, particularly those with polymer matrices, have become the dominant advanced composite materials for aerospace, automobile, sporting goods and other applications due to their high strength, high modulus, low density, and reasonable cost for application requiring high temperature resistance as in the case of spacecrafts.

Carbon-carbon composites use carbon fibres in a carbon matrix. These composites are used in very high temperature environments of upto 6000<sup>o</sup>F, and are twenty times stronger and thirty times lighter than graphite fibres. D'Almeida et al. [129] investigated ballistic impact damage of glass fibre reinforced epoxy composites, while Hasur et al. [130] reported on the response of carbon/epoxy composites under high velocity impact.

Synthetic fibre reinforced composites impart good long term behaviour to various aggressive environments and an enhancement in strength and stiffness. Castaing and Lemoine [131] studied the effect of water sorption and osmotic degradation on long-term behaviour of glass fibre reinforced polyester. They found that plasticisation of the matrix with water remains the main consequence of absorption.

The effects of surface modification of the glass fibre with a silane coupling agent,  $\gamma$ -methacryloxypropyl trimethoxy silane ( $\gamma$ -MPS) on the flow characteristics of unsaturated polyester resin in the RTM process were investigated by Lee et al. [132]. Fig. 1.7 shows a scheme of the  $\gamma$ -MPS modified glass fibre surface. ( $\gamma$ -MPS) treatment onto the glass fibre surface made the surface energy of glass plate lower due to the hydrophobic character of hydrocarbon.



**Fig. 1.7** Surface treatment of glass fibre with hydrolysed  $\gamma$ -MPS

[Ref : G. W. Lee, N. J. Lee, J. Jang, K. J. Lee and J. D. Nam. *Compos. Sci. Technol.* 62, 9, 2002]

Several reports are there in literature on the hybridisation of different synthetic fibres for preparing composite with improved strength and decreased cost. Giancaspro et al. [133] investigated the flexural response of hybrid composites with E-Glass and carbon fibres.

Researchers at the centre of lightweight structures have compared properties of natural fibre sheet molding compound (SMC) with widely used glass-based SMCs (Table 1.3). Results are encouraging when long fibres are used. The research has been carried out under the Dutch

Biolicht R&D programme, which has also resulted in experimental fabrication of semistructural parts such as ventilator housing made from SMC containing 21 % by volume of flax [134].

**Table 1.3** Comparison of properties of sheet moulding compounds produced from glass (two different volume fractions) and natural fibre (two different diameters).

[Ref : Centre of Lightweight Structures, [www.clc.tno.nl](http://www.clc.tno.nl)]

SMC	Glass SMC 20 % wt.cont. ( $V_f = 15\%$ )	Glass SMC 40 % wt.cont. ( $V_f = 31\%$ )	Flax SMC 21 % wt. cont. ( $V_f = 22\%$ ) fibres 6.25 mm	Flax SMC 21 % wt.cont. ( $V_f = 22\%$ ) fibres 25 mm
E-modulus (GPa)	8.5	10.5	7	11
Tensile strength (MPa)	9.5	130	40	80
Flexural modulus (GPa)	10	13.5	7	13
Flexural strength (MPa)	12.5	240	83	144
Impact strength (kJ/m <sup>2</sup> )	50	85	11	22

### 1.10 Hybrid fibre composites

The incorporation of several different types of fibres into a single matrix leads to the development of hybrid fibre composites. In practice, a combination of two types of fibres would be most useful [135]. Hybrid composites offer a range of properties that cannot be obtained with a single kind of reinforcement. By using a hybrid composite that contains two types of fibres, the advantage of one type of fibre can complement

what is lacking in the other. Hybrid reinforcement with good fibre selection will produce excellent properties, reduce the material cost and fulfil a current demand for polymer matrix composites. Glass fibres impart excellent performance when used as reinforcement in polymeric matrices. High strength, light weight, dimensional stability and resistance to corrosion are the major advantages of glass fibre reinforced composites. Hybridisation is commonly used for improving the properties and lowering the cost of conventional composites. Hybridisation offers a method of fabricating products with reduced cost, high strength, and corrosion resistance and in many cases excellent thermal stability.

There are several types of hybrid composites characterised as: (1) interply or tow by- tow, in which tows of the two or more constituent types of fibre are mixed in a regular or random manner; (2) sandwich hybrids, also known as core-shell, in which one material is sandwiched between two layers of another; (3) interply or laminated, where alternate layers of the two (or more) materials are stacked in a regular manner; (4) intimately mixed hybrids, where the constituent fibres are made to mix randomly and uniformly as far as possible. (5) other kinds, such as those reinforced with ribs, pultruded wires, thin veils of fibre or combinations of the above.

The properties of a hybrid composite mainly depend upon the fibre content, length of individual fibres, orientation, extent of intermingling of fibres, fibre to matrix bonding and arrangement of both the fibres. Maximum hybrid results are obtained when the fibres are highly strain compatible [136]. The properties of the hybrid system consisting of two components can be predicted by the rule of mixtures

$$P_H = P_1 V_1 + P_2 V_2 \quad (1.2)$$

where  $P_H$  is the property to be investigated,  $P_1$  the corresponding property of the first system and  $P_2$  the corresponding property of the second system.  $V_1$  and  $V_2$  are the relative hybrid volume fractions of the first and second system and

$$V_1 + V_2 = 1 \quad (1.3)$$

A positive or negative hybrid effect is defined as a positive or negative deviation of a certain mechanical property from the rule of hybrid mixture. The term hybrid effect has been used to describe the phenomenon of an apparent synergistic improvement in the properties of a composite containing two or more types of fibre [137]. The properties of the composite may be higher than would be predicted from a simple application of the rule of mixtures. This is a positive hybrid effect. Positive and negative hybrid effects have been reported in various hybrid combinations [136,138,139].

Hybrid biocomposites can be designed by the combination of a synthetic fibre and natural fibre (biofibre) in a matrix and a combination of two natural fibre/biofibre in a matrix. Thomas and coworkers [140,141] have incorporated two natural fibres in a matrix system. The mechanical performance of short randomly oriented banana and sisal hybrid fibre reinforced polyester composites [140] was investigated with reference to the relative volume fraction of the two fibres at a constant total fibre loading of 0.40 volume fraction ( $V_f$ ), keeping banana as the skin material and sisal as the core material. A positive hybrid effect was observed in the flexural strength and flexural modulus of the hybrid composites. The tensile strength of the composites showed a positive hybrid effect when the relative volume fraction of the two fibres was varied, and maximum tensile

strength was found to be in the hybrid composite having a ratio of banana and sisal 4:1. The mechanical performance of different layering patterns of the banana/sisal hybrid composites was also reported [142]. Trilayer composite showed higher tensile properties while flexural and impact properties were higher for bilayer composite. In an innovative study, a unique combination of sisal and oil palm fibres in natural rubber was utilised to design hybrid biocomposites [141]. It was seen that the incorporation of fibres resulted in increased modulus. Chemical modification of both sisal and oil palm fibres was imperative for increased interfacial adhesion and resulted in enhanced properties [143]. Recently, the mechanical behaviour of two natural fibre hybrid unsaturated polyester composites prepared by hand lay-up were also reported [144,145].

The thermal diffusivity, thermal conductivity and specific heat of jute/cotton, sisal/cotton and ramie/cotton hybrid fabric-reinforced unsaturated polyester composites were investigated by Alsina et al. [146]. These properties were measured both parallel and perpendicular to the plane of the fabrics. The results obtained show that higher values were obtained parallel to the plane of the fibres. In an interesting study [147], hybrid biocomposites from natural fibres were fabricated by a novel high volume processing technique named 'biocomposite sheet moulding compound panel'(BCSMCP) manufacturing process. The natural fibres used were jute and hemp and were found to have promising impact and thermal properties.

Additional possibilities are the use of woven fabrics with one fibre type in the warp and another in the weft, and further variations using interspersed tows in woven configurations. Piles containing different fibres or mixtures

of fibres may be stacked with the fibres aligned in different direction to form still another combination. The development of textile technologies such as weaving, knitting and braiding has resulted in the formation of hybrid textile bio-composites that have superior mechanical properties, as continuous orientation of fibres is not restricted at any point. Novolac type phenolic composites reinforced with jute/cotton hybrid woven fabrics were fabricated and their properties were investigated as a function of fibre orientation and roving/fabric characteristics [148]. Results showed that the composite properties were strongly influenced by test direction and rovings/fabric characteristics. The effect of hybridisation on mechanical properties of untreated woven jute and glass fabric-reinforced isophthalic polyester composites fabricated using hand lay-up technique has been evaluated experimentally. Addition of 16.5 wt% glass fibre, in a total fibre weight fraction of 42 % enhances the tensile, flexural, and interlaminar shear strength (ILSS) by 37, 31.23, and 17.6 %, respectively [149].

Hybridising natural fibre with stronger synthetic fibres like glass can improve the stiffness, strength and moisture resistant behaviour of the composite. Glass fibres are most widely used compared to aramid and carbon due to their low cost and fairly good mechanical properties. Hybridisation with glass fibre provides a method to improve the mechanical properties of natural fibre composites and its effect in different modes of stress depends on the design and construction of the composites [150].

The tensile and impact properties of thermoplastic natural rubber reinforced short glass fibre and empty fruit bunch (EFB) hybrid composites was reported by Anuar et al. [151]. The study also focused on

the effect of fibre (glass and EFB) treatment using silane and maleic anhydride grafted polypropylene (MAPP) as a coupling agent. In general, composite containing 10 % EFB/10 % glass fibre gave an optimum tensile and impact strength for treated and untreated hybrid composites. Tensile properties were found to increase with addition of coupling agent.

Polypropylene-bamboo/glass fibre reinforced hybrid composites (BGRP) were developed by Nayak et al. [152]. Maleic anhydride grafted polypropylene has been used as a coupling agent to improve the interfacial interaction between the fibres and matrix. Thermogravimetric analysis (TGA) indicates an increase in thermal stability of the matrix polymer with incorporation of bamboo and glass fibres, confirming the effect of hybridisation and efficient fibre matrix interfacial adhesion. The dynamic mechanical analysis (DMA) showed an increase in storage modulus ( $E'$ ) indicating higher stiffness in case of hybrid composites as compared with untreated composites and virgin matrix.

Samal et al. [153] studied the mechanical, morphological, thermal, and dynamic mechanical behaviour of hybrid composites of polypropylene reinforced with bamboo and glass fibres. About 69, 86, and 83 % increase in tensile, flexural and impact strength, respectively, was observed as compared with virgin PP. The crystallisation, melting behaviour and thermal stability of the hybrid composites were investigated employing differential scanning electron microscopy (DSC) and thermogravimetric analysis (TGA). Hybrid composites of thermoplastic natural rubber (TPNR) reinforced with Hibiscus cannabinus, L fibre (kenaf fibre: KF) and short glass fibre (GF) were prepared via melt blending method by

Anuar et al. [154]. The tensile strength results showed that the increase in kenaf fibre content substantially reduced the tensile strength and modulus. The effect of hybridisation of glass fibre in thermoset biocomposites was discussed in detail [155]. Short and Sommerscales [156] reviewed properties of hybrid composites. The tensile and impact behaviour of oil palm fibre-glass fibre-reinforced epoxy resin was investigated by Bakar et al. [157]. The hybridisation of oil palm fibres with glass fibres increased the tensile strength, Young's modulus, and elongation at break of the hybrid composites. A negative hybrid effect was observed for the tensile strength and Young's modulus while a positive hybrid effect was observed for the elongation at break of the hybrid composites. The impact strength of the hybrid composites increased with the addition of glass fibres. The hybrid effect of glass fibre and oil palm empty fruit bunch (OPEFB) fibre on the tensile, flexural and impact response of the phenol formaldehyde (PF) composites was investigated by Sreekala et al. [136]. With the addition of a small amount of glass fibre, the impact performance of the OPEFB/PF composite was increased by more than 100 %. The maximum impact strength was observed for hybrid composites having 0.74 volume fraction of the OPEFB fibre. The value is higher than glass/PF composites. The degree of mechanical reinforcement that can be obtained by the introduction of glass fibres in biofibre (silk fabric) reinforced epoxy composites was assessed experimentally. The addition of a relatively small amount of glass fabric to the silk fabric reinforced epoxy matrix enhances the mechanical properties of the resulting hybrid composites [158]. Silva et al. [159,160] developed hybrid composite by combining natural fibres (curaua fibres) and glass fibres (glass-E) in orthophthalic polyester resin.

The mechanical properties of hybrid composites and fibreglass composites were comparatively close, while the composites of curaua fibres alone showed inferior performance. The hybridisation was efficient in terms of lowering water absorption by composites. The mechanical properties were also evaluated after water ageing.

Li et al. [161] developed and characterised a super-hybrid (natural composite/fibre reinforced composite/metal hybridisation) eco-material, reformed bamboo/glass fabric/aluminum (RB/GF/Al). The addition of a sparse glass fabric/epoxy resin layer between reformed bamboo and aluminum proved to be effective in increasing the compressive tensile strength of the composite material. In particular, the interfacial shear strength between the reformed bamboo and aluminum was improved.

Cellular biocomposite cores fabricated from industrial hemp or flax fibres with unsaturated polyester were hybridised with woven jute, chopped glass, and unidirectional carbon fabrics [162]. Material characterisation showed improved stiffness, strength, and moisture-absorption stability, while flexural tests on laboratory-scale plates demonstrated enhanced structural behaviour. These hybrid cellular biofibre-based composites were found to provide an economic and environmentally friendlier alternative to entry-level synthetic composites. Mehta et al. [163] examined the properties of hybrid hemp/glass fibre reinforced polyester composites. They observed a balance of properties for the hybrid systems when compared to single systems. Hybridisation with a synthetic fibre also has a profound effect on the water absorption property of composites. Mishra et al. [164] studied the moisture uptake characteristics of hybrid composites. The systems chosen were sisal/glass and pineapple/glass fibre

reinforced polyester composites. Optimum glass fibre loadings for PALF/glass hybrid polyester composite is 8.6 wt% at a total loading of 25 wt%. A comparative study of the water absorption of coir/glass hybrid polyester composite, glass fibre (7 wt%) and coir fibre (13 wt%) with that of non-hybrid composites is given in Table 1.4. A lowering in water absorption was observed [165].

**Table 1.4** Comparative study of the water absorption of the glass fibre/natural fibre with that of non-hybrid composite

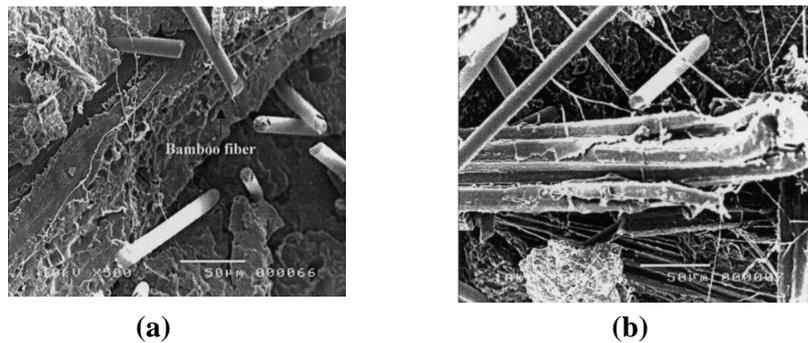
[ Ref: J Rout., M Mishra., S.S Tripathy., S.K Nayak., A.K Mohanty. Compos. Sci. Technol. 61, 1303, 2001]

Sample	Water absorption %	
	Nonhybrid [Coir-polyester composite]	Hybrid [Coir/glass - polyester composite]
Untreated	8.53	5.186
Alkali- treated (5 %)	4.994	3.147
PMMA grafted (5 %)	3.98	2.663
PAN grafted (10 %)	4.119	2.997
Cyanoethylated	3.6	3.138
Bleached	5.8	3.718

Effect of moisture absorption on the mechanical properties of randomly oriented natural fibres/polyester hybrid composite was studied by Athijayamani et al. [166]. When the samples were subjected to moisture environment, decrease in tensile and flexural strength was observed. The maximum percentage of strength reductions in tensile and flexural

strength were observed for the composites having the fibre length of 150 mm and 30 wt% fibre content. For impact strength, it was with the composites of 20 wt% and 150 mm at wet conditions compared to dry conditions. The percentage of strength reductions increased with fibre content and length in wet conditions. A scatter in the impact strength values was identified on both the conditions.

Ageing studies of hybrid biofibre reinforced natural rubber biocomposites was studied by Jacob et al. [167]. Biodegradation tests were carried out under soil burial conditions and it was seen that the durability of the composites was greatly dependent on chemical treatment and fibre content.



**Fig. 1.8** SEM image of bamboo fibre surface morphology (a) after ageing of BGRP for 520 h (b) in water after ageing of BGRP in water for 1200 h

[Ref : M. M. Thwe, K. Liao, Compos. Part A 33, 43, 2002]

SEM micrographs of the fracture surfaces of BGRP (Bamboo-glass fibre reinforced polypropylene composites) tested after ageing are shown in Fig. 1.8 (a) and (b) [168]. Degradation in bamboo fibre resulting from ageing is indicated by morphology changes of the fracture surfaces. The bamboo fibre surface has become rougher and porous after ageing. Some

split in to thinner fibrils which is evident in Fig. 1.8 (b). Degradation of bamboo fibres as a result of moisture attack is also observed. No significant change of surface morphology is found on glass fibre. However, obvious interfacial gaps between the fibre and matrix are seen as a result of dimensional instability due to moisture absorption.

Effect of glass fibre hybridisation on various properties such as mechanical, dynamic mechanical, thermal and ageing of natural fibre composites was studied by several authors [169-173]. The hybridisation of glass fibres with natural fibres for applications in the piping industry was investigated by Cicala et al. [174]. The hybrid design for the pipe which makes use of glass woven fabrics and natural fibre mats allowed for a cost reduction and a weight saving.

### **1.11 Motivation for the study**

Natural fibre incorporated composites have good potential to become one of the engineering materials for non critical societal applications. A large number of studies have been reported in literature concerning natural fibre /glass hybrid composites. A natural fibre namely pineapple leaf fibre (PALF) is used in this study. Among various natural fibres, PALFs exhibit excellent mechanical properties. It is well understood that the strength of a fibre increases with increasing cellulose content and decreasing microfibrillar angle. These fibres have high cellulose content and low microfibrillar angle. PALF also possess highest crystallinity among all natural fibres [43].

In the present work PALF is hybridised with small quantities of glass fibre to prepare PALF/GF hybrid composites in order to achieve cost effectiveness. The processing of the composites is carried out by a

simplest fabrication technique for making reinforced composite structures namely hand lay-up technique. Composites with different GF/PALF ratios and different fibre arrangements were prepared and properties studied. The study is aimed at analysing the mechanical, dynamic mechanical, ageing, thermal and water sorption studies of different configurations of PALF/GF hybrid polyester composites. Although composites based on polyester matrix resin are well known, there have been only limited studies of the properties of PALF reinforced polyester composites. The effects of compatibilising agent and surface modification of short pineapple leaf fibre on physical properties of short pineapple leaf fibre reinforced high impact polystyrene (HIPS) composites were investigated by Siregar et al. [99]. The potential of PALF as a reinforcement in PALF/polyester composites is reported by several authors [6,93,97]. The usage of PALF based composites is restricted because of poor weatherability characteristics. The ageing studies of PALF/polyester composites have also been studied by us earlier [21]. The influence of several chemical treatments of the fibres on the mechanical, water absorption, thermal and ageing properties of PALF/PER composites are evaluated in the present study. The treatments were done to improve the adhesion between resin and fibre and to retain the properties after environmental exposure or ageing. The degree of mechanical reinforcement that could be obtained by the introduction of glass fibres in bio fibre (pineapple leaf fibre/sisal fibre) has been assessed experimentally by Mishra et al. [164]. However, no studies have been reported in literature about intimately mixed PALF/GF hybrid composites and other layered PALF/GF hybrid composites at the experimental conditions till date. Moreover the dynamic mechanical, thermal, water

sorption and ageing characteristics of PALF/GF hybrid composites of different configurations were not studied so far. Dynamic mechanical, thermal, water absorption, ageing, thermophysical studies etc have been employed to study the effect of GF loading and layering pattern of PALF/GF hybrid composites. The thermophysical measurement of the above composites is a new venture in the literature. PALF was also characterised by a novel technique, solvatochromism.

### **1.12 Scope and objectives**

Natural fibre reinforced polymer composites became more attractive due to their light weight, high specific strength, low cost, high performance in terms of mechanical properties, renewability and environmental concern. Unsaturated polyester resin, which is commonly used as the matrix in synthetic glass fibre composites, is used as the matrix material. Unsaturated polyester (PER) resin is an economical thermoset material that is widely used, due to its excellent processability and good cross-linking tendency as well as the fairly good oil, moisture and acid resistances and mechanical properties when cured. This has excellent flow to impregnate the fibre bundles during the manufacturing process and therefore present better adhesions.

PALF has been gaining much attention as reinforcement in polymer composites and in the present work PALF and GF together have been used as the reinforcement. PALF is biodegradable, and has low density (compared to glass fibre) and exhibits good mechanical properties. A large quantity of this renewable fibre resource is being underutilised. The major chemical constituents of the fibre are cellulose 70-82 % and lignin 12.7 %. These properties can be utilised in reinforcing PALF with

polyester which can increase the stiffness and favour good mechanical properties.

Although glass and other synthetic fibre reinforced plastics possess high specific strength, their fields of application are limited because of their inherent higher cost of production. This study looked at the possibility of substituting glass fibre with natural fibre in composite materials. In this connection, an investigation has been carried out to make use of a natural fibre namely PALF which is abundantly available. For the successful design of a composite material from PALF, several parameters such as fibre length, fibre loading, fibre surface modifications, hybridisation with other fibres and fibre/matrix adhesion have to be optimised. Glass fibre, being inorganic in nature and having very high mechanical strength properties, can improve the weatherability characteristics as well as the strength properties of the hybrid composites. Since the basic properties of reinforcements viz, PALF and GF differ widely in their properties, the incorporation of these two fibres in the same matrix is of considerable significance. Such an investigation is highly fruitful in the industrial as well as engineering areas. Modification of the PALF also improves the optimum fibre/matrix properties. The study is mainly aimed at developing new cost effective structural composite materials having better performance properties using PALF and small quantities of GF. The major objectives of the present study include

### **1. Chemical modification of PALF and characterisation of the fibre surface using solvatochromism, SEM, optical microscopy and FTIR.**

Changes in the modified fibre surfaces can be studied using techniques like solvatochromism. An insight into chemical interaction that has occurred on the fibre surface can be obtained using FTIR.

### **2. Fabricaton of PALF/PER, GF/PER and chemically modified PALF/PER composites**

GF/PER composites and short randomly oriented PALF/PER composites of different fibre loading were prepared. The effect of fibre loading on the mechanical and dynamic mechanical properties of both PALF/PER and GF/PER composites has been analysed.

Chemically modified PALF/PER composites of optimum fibre loading is fabricated and characterisation done.

### **3. Fabrication of PALF/GF hybrid polyester composites**

PALF/GF hybrid fibre composites of different hybrid configuration (intimately mixed and different layering patterns of varying PALF/GF ratio) were prepared by compression moulding technique and optimum loading determined.

### **4. Mechanical properties**

The strength of the interface and fibre/matrix interactions can be clearly understood based on the mechanical properties of the composite. The fracture mechanism and the strength characteristics point to the fibre/matrix interactions. Tensile, flexural and impact properties of the composites were studied. Experimental results were compared with theoretical predictions.

## **5. Dynamic mechanical properties**

The nature of fibre/matrix interactions can be evaluated on the basis of dynamic mechanical analysis. The nature of modulus curves and damping peaks are indications of fibre/matrix interactions and nature of interface. Dynamic mechanical properties were evaluated as a function of fibre length, fibre loading, chemical treatment, fibre ratio, layering pattern and frequency with temperature. The experimental and theoretical storage moduli of the composites were compared.

## **6. Thermal studies**

The examination of thermal degradation behaviour of treated and untreated fibres was done by thermogravimetric analysis. The effect of chemical treatment on the thermal stability of the fibre was determined from TG curves. The thermal degradation behaviour of PALF/PER composites of different fibre loading and the chemically treated PALF/PER composites was analysed. The thermal stability of PALF/GF hybrid composites has also been analysed.

Thermal conductivity is a bulk property analogous to mechanical modulus. Moreover it is well accepted that a mathematical analogy exists between thermal conduction and elasticity of fibre composites. The thermophysical properties were characterised as a function of fibre loading and chemical modification.

## **7. Water absorption behaviour**

Water absorption affects the physical properties of the composites and can affect the matrix structure and fibre/matrix interface resulting in changes of bulk properties such as dimensional stability, mechanical and electrical

properties. Since most of the applications of the composites are affected by temperature variations, the influence of temperature on moisture diffusion of the composites has great importance. In order to fully utilise the potential of composite materials, their behaviour during and after exposure to high humidity environments at various temperatures must be investigated.

The water absorption studies of PALF/PER, GF/PER and hybrid fibre reinforced composites of optimum fibre concentration were carried out at different temperatures. It has been generally seen that chemical modification of fibres reduces the water uptake of the composites. Experimental results were compared with theoretical predictions.

#### **8. Ageing studies**

The effects of chemical treatments and hybridisation using glass fibres on the ageing and weathering resistance of the composites have been evaluated. The percentage weight change and change in tensile and impact properties before and after ageing have been analysed.

## References

1. K. K. Chawla. *Composite Materials*, Springer-Verlag, New York, **1987**.
2. E. Ruiz and F. Trochu. *J. Compos. Mater.* 39, 881, **2005**.
3. T. H. D. Sydenstricker, S. Mochnaz and S. C. Amico. *Polym. Test.* 22, 375, **2002**.
4. S. Harish, D. P. Michael, A. Bensely, D. M. Lal and A. Rajadurai. *Mater. Character.* 60, 44, **2009**.
5. D. Ray, B. K. Sarkar and N. R. Bose. *Compos. Part A* 33, 233, **2002**.
6. L. U. Devi, S. S. Bhagawan and S. Thomas. *J. Appl. Polym. Sci.* 64, 1739, **1997**.
7. A. A. Abdel-Azim, B. H. E. Mahmood and M. S. Farha. *Polym. Adv. Technol.* 5, 269, **1993**.
8. Composite Design Guide, Centre for Composite Materials, University of Delaware, **1983**.
9. J. K. Kim, S. Lu, and Y. W. Mai. *J. Mater. Sci.* 29, 554, **1994**.
10. C. K. Riew, E. H. Rowe, and A. R. Siebert. Rubber toughened thermosets. In: R. D. Deanin and A. M. Crugnola (Eds) Toughness and brittleness of Plastics, Adv.Chem.Ser. No.154.Washington DC: ACS. 326-343, **1976**.
11. S. H. Aziz, M. P. Ansell, S. J. Clarke and S. R. Panteny. *Compos. Sci. Technol.* 65, 525, **2005**.

12. R. G. Weatherhood. F. R. P. Applied Science Publishers Ltd. London. **1980**.
13. P. Roe and M. Ansell. *J. Mater. Sci.* 20, 4015, **1985**.
14. A. De Albuquerque, K. Joseph, L. Hecker de Carvalho, and J. Morais d'Almedia. *Compos. Sci. Technol.* 60, 833, **1999**.
15. S. Pal, D. Mukhophadhyay, S. Sanyal and R. Mukherjee. *J. Appl. Polym. Sci.* 35, 973, **1988**.
16. V. M. Fonseca, V. J. Fernandes Jr, L. H. de Carvalho and J. R. M. d'Almeida. *J. Appl. Polym. Sci.* 94, 1209, **2004**.
17. O. Owolabi, T. Czvikovszky and I. Kovacs. *J. Appl. Polym. Sci.* 30, 1827, **1985**.
18. S. V. Prasad, C. Pavithran and P. K. Rohatgi. *J. Mater. Sci.* 18, 1443, **1983**.
19. K. G. Satyanarayana, A. G. Kulkarni, K. Sukumaran, S. Pillai, P. Cherian and P. K. Rohatgi. Performance of banana fabric-polyester resin composites. In: *Composite structures. Proc. of the International Conference, London, Applied Science*. Ed. I.H Marshall. 535-48. **1983**.
20. N. M. White and M. P. Ansell. *J. Mater. Sci.* 18, 1549, **1983**.
21. L. U. Devi, K. Joseph, K. C. M. Nair and S. Thomas. *J. Appl. Polym. Sci.* 94, 503, **2004**.
22. L. Mwaikambo and E. Bisanda. *Polym. Test.* 18, 181, **1999**.

23. E. Martuscelli, P. Musto, G. Ragosta, G. Scarinzi and E. Bertotti. *J. Polym. Sci. Polym. Phys. Ed.* 31, 619, **1993**.
24. J. V. Milewski and H. S. Katz. *Hand book of Reinforcements for plastics*, Van Nostrand Reinhold Company, New York, **1987**.
25. F. Sadov, M. Korchagin and A. Matetsky. *Chemical Technology of Fibrous Materials*, Mir Publishers, Moscow, **1978**.
26. P. K. Mallick. *Fibre reinforced composites*. Marcel Dekker, New York, **1993**.
27. K. G. Satyanarayana, B. C. Pai, K. Sukumaran and S. G. K. Pillai. *Hand book of Ceramics and Composites*. N. P. Cheremisinoff (Ed.) Marcel Dekker, New York, 1, 339, **1990**.
28. J. G. Cook. *Handbook of Textile Fibres-Natural fibres*, 5<sup>th</sup> edn, Merrow Publishing, Durham, England, **1984**.
29. S. A. Paul, K. Joseph, G. Mathew, L. A. Pothan and S. Thomas. *Compos. Part A* 41, 1380, **2010**.
30. S. Alix, E. Philippe, A. Bessadok, L. Lebrun, C. Morvan and S. Marais. *Bioresource. Technol.* 100, 4742, **2009**.
31. N. Sgriccia, M. C. Hawley and M. Misra. *Compos. Part A* 39, 1632, **2008**.
32. A. N. Towo and M. P. Ansell. *Compos. Sci. Technol.* 68, 925, **2008**.
33. D. N. Saheb and J. P. Jog. *Adv. Polym. Technol.* 18, 351, **1999**.

34. C. Brett, Suddell and W. J. Evans. *Natural Fibres, Biopolymers and Biocomposites*. (Eds) A. K. Mohanty, M. Misra and L. T. Drazal. CRC Press, Boca Raton, London, 231, **2005**.
35. A. K. Bledzki and J. Gassan. *J. Prog. Polym. Sci.* 24, 221, **1999**.
36. N. J. Parrat and K. D. Potter. *Advances in Composite Materials*. (Eds) A. R. Bunsell, C. Bathias, A. Martrenchar, D. Menkes, G. Verchery. Pergamon Press, 313-26, **1980**.
37. E. Ammalahti, G. Brunow, M. Brunow, M. Bardet, D. Robert and I. Kirpelainen. *J. Agric. Food. Chem.* 46, 5113, **1998**.
38. H. E. Gram. *Durability of natural fibres in concrete*. Swedish Cement and Concrete Research Institute, Stockholm, Research Fo. 1, 83, 225, **1983**.
39. S. Taj, M. Ali Munawar and S. Khan. *Natural fibre reinforced polymer composites. Proc. Pakistan Acad. Sci.* 44(2), 129-144, **2007**.
40. G. T. Toumis. *Science and Technology of wood: Structure, properties utilization*, Van Nostrand Reinhold, New York, **1991**.
41. E. C. McLaughlin and R. A. Tait. *J. Mater. Sci.* 15, 89, **1980**.
42. K. G. Satyanarayana, A.G. Kulkarni and P. K. Rohatgi. *Proc. Ind. Acad. Sci.* 4, 419, **1981**.
43. M. Rong. *Compos. Sci. Technol.* 61, 1437, **2001**.
44. P. S. Mukherjee and K. G. Sathyanarayana. *J. Mater. Sci.* 21, 51, **1986**.

45. J. S. Han, and J. S. Rowell. in *Paper and Composites from Agro-Based Resources* (Eds) R. M. Rowell and J. Rowell. CRC Press, 83-130, **1996**.
46. B. Singh, and M. Gupta. *Proceedings of the International Symposium on Biocomposites and Blends Based on Jute and Allied Fibres*, India, Vol 111, **1994**
47. T. G. Schuh. *Renewable Materials for Automotive Applications*. Daimler-Chrysler AG, Stuttgart, **1999**.
48. G. Marsh. *Materials Today*, 37, April **2003**.
49. A. W. Mechenzie and J. P. Yuritha. *Appita* 32 (b), 460, **1979**.
50. R. M. Rowel and W. B. Banks. Gen. Tech. Rep. FPL-GTR-50; USDA Forest service, Forest Products Laboratory, Madison, WI. 24, **1985**.
51. L. Y. Mwaikambo and M. P. Ansell. *J. Appl. Polym. Sci.* 84, 2222, **2002**.
52. A. P. Schniewind. Wood and fire, in: M. B. Bever (Ed) *Encyclopedia of Materials Science and Engineering*, Vol. 7, 1<sup>st</sup> edn, Pergamon Press, Oxford. **1986**.
53. R. M. Rowell. (Ed) *The Chemistry of Solid Wood*, Adv. Chem. Ser 207, American Chemical Society, Washington. DC, **1985**.
54. R. M. Rowell, G. R. Esenther, J. A. Youngquist, V. D. Nicholas, P. Nilsson, Ymamura, W. K. Gang, L. Trong and G. Deon. *Proc. IUFRO wood protection subject group*. Honey Harbour, Ontario, Canada, Canadian Forestry service 238, **1988**.

55. M. Brahmakumar, C. Pavithran and R. M. Pillai. *Compos. Sci. Technol.* 65, 563, **2005**.
56. P. Ivarez, C. Blanco, R. Santamarý and M. Granda. *Compos. Part A* 36, 649, **2005**.
57. B. Kchaou, C. Turki, M. Salvia, Z. Fakhfakh and D. Treheux. *Compos. Sci. Technol.* 64, 1467, **2004**.
58. V. N. Hristov, R. Lach and W. Grellmann. *Polym. Test.* 23, 581, **2004**.
59. A. Kelly and C. Zweben. *Comprehensive Composite Materials*, Vol. 2, Pergamon, **2000**.
60. R. A. Khan, M. A. Khan, H. U. Zaman and S. Pervin. *J. Reinf. Plast. Compos.* 29, 1078, **2010**.
61. Y. Li and Y. W. Mai. *J. Adhes.* 82, 527, **2006**.
62. M. N. Belgacem, P. Bataille and S. Sapieha. *J. Appl. Polym. Sci.* 53, 379, **1994**.
63. I. Sakata, M. Morita, N. Tsuruta, and K. Morita. *J. Appl. Polym. Sci.* 49, 1251, **1993**.
64. Q. Wang, S. Kaliaguine, and Ait-Kadi-A. *J. Appl. Polym. Sci.* 48, 121, **1993**.
65. E. Sinha and S. Panigrahi. *J. Compos. Mater.* 43, 1791, **2009**.
66. K. Koichi, V. N. Victor, F. N. Mikhail, M. Masashi, I. Yoshito and N. Katsuhiko. *J. Polym. Sci. Part A Polym. Chem.* 37, 357, **1999**.
67. P. A. Sreekumar and S. Thomas. (Eds) Pickering and L. Kim. *Properties and Performance of Natural Fibre Composites*, 67, **2008**.

68. M. K. Joshy, L. Mathew and R. Joseph. *Prog. Rubber. Plast. Technol.* 24, 255, **2008**.
69. K. J. Wong, B. F. Yousif and K. O. Low. *Proc. I. Mech. E. Vol 224. Part L, J. Mater. Design. Applications*, **2010**.
70. S. H. Aziz and M. P. Ansell. *Compos. Sci. Technol.* 64, 1219, **2004**.
71. M. Abdelmouleh, S. Boufi, A. Ben Salah, M. N. Belgacem and A. Gandini. *Langmuir* 18, 3203, **2002**.
72. M. Abdelmouleh, S. Boufi, M. N. Belgacem, A. P. Duarte, A. Ben Salah, and A. Gandini. *Int. J. Adh. Adhes.* 24, 43, **2004**.
73. M. Abdelmouleh, S. Boufi, M. N. Belgacem, A. Dufresne and A. Gandini. *J. Appl. Polym. Sci.* 98, 974, **2005**.
74. M. Abdelmouleh, S. Boufi, M. N. Belgacem, A. Dufresne and A. Gandini. *Comp. Sci. Technol.* 67, 1627, **2007**.
75. J. Gassan and A. Bledzki. *Polym. Compos.* 20, 604, **1999**.
76. S. Tripathy, S. Mishra and S. Nayak. *Polym. Compos.* 20, 62, **1999**.
77. R. Gauthier, C. Joly, A. Campas, H. Gaultier and M. Escoubes. *Polym. Compos.* 19, 287, **1998**.
78. A. K. Mohanty, P. C. Tripathy, M. Misra, S. Parija and S. Sahoo. *J. Appl. Polym. Sci.* 77, 3035, **2000**.
79. L. A. Pothan, Y. Zimmermann, S. Thomas and S. Spange. *J. Polym. Sci. B* 38, 2546, **2000**.
80. L. A. Pothan, F. Simon, S. Spange and S. Thomas. *Biomacromolecules* 7, 892, **2006**.

81. Shirly Anne Paul. Ph.D Thesis, Mahatma Gandhi University, Kottayam, **2008**.
82. S. V. Joshi, L. T. Drzal, A. K Mohanty and S. Arora. *Compos. Part A* **35**, 371, **2004**.
83. Y. F. Shih. *Mater. Sci. Eng. A* 445, 289, **2007**.
84. P. A. de Arcaya, A. Retegi, A. Arbelaz, J. M. Kenny and I. Mondragon. *Polym. Compos.* 30, 257, **2009**.
85. H. Cheung, M. Ho, K. Lau , F. Cardona and D. Hui. *Compos. Part B Eng.* 40, 655, **2009**.
86. H. M. Akil, L. W. Cheng, Z. A. M. Ishak, A. A. Bakar and M. A. A. Rahman. *Compos. Sci. Technol.* 69, 1942, **2009**.
87. K. G. Satyanarayana, G. G. C. Arizaga and F. Wypych. *Prog. Polym. Sci.* 34, 982, **2009**.
88. K. M. M. Rao, K. M. Rao and A. V. R. Prasad. *Mater. Design* 31, 508, **2010**.
89. I. M. De Rosa, J. M. Kenny, D. Puglia, C. Santulli and F. Sarasini. *Compos. Sci. Technol.* 70, 116, **2010**.
90. M. Das , V. S. Prasad and D. Chakrabarty. *Polym. Compos.* 30, 1408, **2009**.
91. P. A. Sreekumar, S. P. Thomas, J. M. Saiter, K. Joseph, G. Unnikrishnan and S. Thomas. *Compos. Part A* 40, 1777, **2009**.
92. P. S. Mukherjee and K. G. Satyanarayana. *J. Mater. Sci.* 21, 51, **1986**.

93. C. Pavithran, P. S. Mukherjee, M. Brahmakumar and A. D. Damodaran. *J. Mater. Sci. Lett.* 6, 882, **1987**.
94. J. George, K. Joseph, S. S. Bhagawan and S. Thomas. *Mater. Lett.* 18, 163, **1993**.
95. J. George, S. S. Bhagawan and S. Thomas. *J. Appl. Polym. Sci.* 57, 843, **1995**.
96. J. George, S. S. Bhagawan and S. Thomas. *Compos. Interf.* 5, 201, **1998**.
97. S. Misra, M. Misra, S. S. Tripathy, S. K. Nayak and A. K. Mohanty. *J. Reinf. Plast. Compos.* 20, 321, **2001**.
98. R. K. Samal and M. C. Ray. *J. Appl. Polym. Sci.* 64, 2119, **1997**.
99. J. P. Siregar, S. M. Sapuan, M. Z. A. Rahman and H. M. D. K. Zaman. *Polym. Polym. Compos.* 17, 379, **2009**.
100. A. R. Mohamed, S. M. Sapuan, M. Shahjahan and A. Khalina. *J. Food. Agri. Envir.* 7, 235, **2009**.
101. W. Liu, M. Misra, P. Askeland, L.T. Drzal and A.K. Mohanty. *Polymer* 46, 2710, **2005**.
102. R. Mangal, N. S. Saxena, G. P. Joshi, G. P. Singh, M. S. Sreekala and S. Thomas. *Ind. J. Pure. Appl. Phys.* 41, 420, **2003**.
103. L. A. Pothan, A. S. Luyt and S. Thomas. *Polyolefin Composites*. (Eds) D. Nwabunma and T. Kyu, John Wiley and Sons, **2007**.
104. B. Singh and M Gupta. *Natural Fibres, Biopolymers and Bio composites*. (Eds) A. K. Mohanty, M. Misra and L. T Drzal. CRC Press, Boca Raton, London, 1, **2005**.

105. Z. Li, X. Wan and L. Wang. *Compos. Part A* 37, 497, **2006**.
106. J-P.L. Dwan' Isa, A. K. Mohanty, M. Misra and L. T. Drzal. *Natural Fibres, Biopolymers and Biocomposites*. (Eds) A. K. Mohanty, M. Misra and L. T. Drzal. CRC Press, Boca Raton, 775, **2005**.
107. B. van Voorn, H. H. G. Smit, R. J. Sinke and B. de Klerk. *Compos. Part A* 32, 1271, **2001**.
108. L. Xue, G. T. Lope and P. Satyanarayan. *J. Polym. Environ.* 15, 25, **2007**.
109. A. N. Netravali and S. Chabba. *Materials Today* 6, 22, **2003**.
110. C. Baillie. *Green composites; Polymer Composites and the Environment*, CRC Press, **2005**.
111. H. Tsuji and Y. Ikada. *J. Appl. Polym. Sci.* 67, 405, **1998**.
112. H. Urayama, T. Kanamori and Y. Kimura. *Macromol. Mater. Eng.* 287, 116, **2002**.
113. R. A. Jain. *Biomaterials* 21, 2475, **2000**.
114. U. Edlund and A. C. Albertsson. *Adv. Polym. Sci.* 157, 67, **2002**.
115. K. H. Wang, T. M. Wu, Y. F. Shih and C. M. Huang. *Polym. Eng. Sci.* 48, 1833, **2008**.
116. M. S. Huda, L. T. Drzal, A. K. Mohanty and M. Misra. *Compos. Interf.* 15, 169, **2008**.
117. X. Cao, Y. Chen, P. R. Chang, M. Stumborg and M. A. Huneault. *J. Appl. Polym. Sci.* 109, 3804, **2008**.
118. C. Asasutjarit, S. Charoenvai, J. Hirunlabh and J. Khedari. *Compos. Part B Eng.* 40, 633, **2009**.

119. A. N. Netravali. *Towards Advanced Green Composites, 3rd International Workshop on Green Composites (IWGC-3) Kyoto, JAPAN, Proc.* 11-15, March 16-17, **2005**.
120. A. N. Netravali and X. H Huang. *Advanced Green Composites, 4<sup>th</sup> International Workshop on Green Composites (IWGC-4), Tokyo, JAPAN. Proc.* 23-27, September 14-15, **2006**.
121. A. N. Netravali, X. Huang and K. Mizuta. *Adv. Compos. Mater.* 16, 269, **2007**.
122. *Cellulose Nanocomposites. Processing, Characterisation, and Properties* (Eds) K. Oksman and M. Sain. Vol. 938, July **2006**.
123. X. Cao, Y. Chen, P. R. Chang, A. D. Muir and G. Falk. *Express. Polym. Lett.* 2, 502, **2008**.
124. W. Gindl and J. Keckes. *Polymer* 46, 10221, **2005**.
125. N. Nordgren, Hanna Lonnberg, A. Hult, E. Malmström and M. W. Rutland. *ACS Appl. Mater. Interf.* 1, 2098, **2009**.
126. J. Karger-Kocsis, T. Harmia and T. Czigany. *Compos. Sci. Technol.* 54, 287, **1995**.
127. J. Karger-Kocsis. *Compos. Sci. Technol.* 48, 273, **1993**.
128. Cs. Varga, N. Miskolczi, L. Bartha and G. Lipoczi. *Mater. Design* 31, 185, **2010**.
129. J. R. M. D'Almeida, L. M. Nunes and S. Paciornik. *Compos. Sci. Technol.* 64, 945, **2004**.

130. B. L. Lee, T. F. Walsh, S. T. Won and H. M. Patts. *J. Compos. Mater.* 35, 1605, **2001**.
131. Ph. Castaing and L. Lemoine. *Polym. Compos.* 16, 349, 1995.
132. G. W. Lee, N. J. Lee, J. Jang, K. J. Lee and J. D. Nam. *Compos. Sci. Technol.* 62, 9, **2002**.
133. J. W. Giancaspro, C. G. Papakonstantinou and P. N. Balaguru. *J. Eng. Mater. Technol.* 132, 021005, **2010**.
134. G. T. Pott, R. J. Pilot and J. M. Van Hazendonk. *Upgraded Flax Fibres as Reinforcement in Polymer Composites*, in *Proc. 5th European Conference on Advanced Materials and Processes and Applications (Euromat 97)*, Vol. 2. *Polymers and Ceramics*, 107, April 21-23, Maastricht, **1997**.
135. A. R. Bunsell and Harris. *Composites* 5, 157, **1974**.
136. M. S. Sreekala, J. George, M. G. Kumaran and S. Thomas. *Compos. Sci. Technol.* 62, 339, **2002**.
137. F. R. Jones. *Handbook of Polymer Composites*, Longman Scientific and Technical, **1994**.
138. G. Marom, S. Fischer, F. R. Tuler and H. D. Wagner. *J. Mater. Sci.* 13, 1419, **1978**.
139. G. Kalaprasad, S. Thomas, C. Pavithran, N.R. Neelakandan and S. Balakrishnan. *J. Reinf. Plast. Comp.* 15, 48, **1996**.
140. M. Idicula, N. R. Neelakantan, Z. Oommen, K. Joseph and S. Thomas. *J. Appl. Polym. Sci.* 96, 1699, **2005**.

141. M. Jacob, K. T. Varughese and S. Thomas. *J. Appl. Polym. Sci.* 93, 2305, **2004**.
142. M. Idicula, K. Joseph and S. Thomas. *Reinf. Plast. Compos.* 29, 12, **2010**.
143. M. Jacob, K. T. Varughese and S. Thomas. *Compos. Sci. Technol.* 64, 955, **2004**.
144. M. Thiruchitrambalam, A. Alavudeen, A. Athijayamani, N. Venkateshwaran and A. Elaya Perumal. *Mater. Phys. Mechanics* 8, 165, **2009**.
145. Y. P. Noorunnisa Khanam, G. Ramachandra Reddy, K. Raghu and S. Venkata Naidu. *J. Reinf. Plast. Compos.* 20, 2124, **2010**.
146. O. L. S. Alsina, L. H. D. Carvalho, F. G. R. Filho and J. R. M. D. Almeida. *Polym. Test.* 24, 81, **2005**.
147. G. Mehta, A. K. Mohanty, K. Thayer, M. Misra and L. T. Drzal. *J. Polym. Env.* 13, 169, **2005**.
148. E. S. De Medeiros, J. A. M. Agnelli, L. H. De Carvalho and L. H. C. Mattoso. *Polym. Compos.* 26, 1, **2004**.
149. K. S. Ahmed, S. Vijayarangan and C. Rajput. *J. Reinf. Plast. Compos.* 25, 1549, **2006**.
150. B. Singh, M. Gupta and A. Verma. *Const. Build. Mater.* 9, 39, **1995**.
151. H. Anuar, S. H. Ahmad, R. Rasid and N. S. Nik Daud. *Polym. Plast. Technol. Eng.* 45, 1059, **2006**.

- 
152. S. K. Nayak, S. Mohanty and S. K. Samal. *Mater. Sci. Eng. A* 523, 32, **2009**.
  153. S. K. Samal, S. Mohanty and S. K. Nayak. *J. Reinf. Plast. Compos.* 28, 2729, **2009**.
  154. H. Anuar, W. N. Wan Busu, S. H. Ahmad and R. Rasid. *J. Compos. Mater.* 42, 1075, **2008**.
  155. D. Ray and J. Rout. *Natural Fibres, Biopolymers and Biocomposites*. (Eds) A. K. Mohanty, M. Misra and L. T. Drzal. CRC Press 347, **2005**.
  156. D. Short and J. Summerscales. *Composites* 10, 215, **1979**.
  157. A. Bakar, A. Hariharan and H.P.S A. Khalil. *J. Compos. Mater.* 39, 663, **2005**.
  158. S. P. Priya and S. K. Rai. *J. Indus. Textiles* 35, 217, **2006**.
  159. R. V. Da Silva, E. M. F. Aquino, L. P. S. Rodrigues and A. R. F. Barros. *Revista Materia* 13, 154, **2008**.
  160. R. V. Da Silva, E. M. F. Aquino, L. P. S. Rodrigues and A. R. F. Barros. *J. Reinf. Plast. Compos.* 28, 1857, **2009**.
  161. S. H. Li, J. R. De Wijn, K. De Groot, Q. Y. Zeng. and B. L. Zhou. *J. Mater. Sci.* 33, 2147, **1998**.
  162. R. Burgueno, M. J. Quagliata, A. K. Mohanty, G. Mehta, L. T. Drzal and M. Misra. *Compos. Part A* 3, 581, **2005**.
  163. G. Mehta, L. Drzal, A. K. Mohanty and M. Misra. *J. Appl. Polym. Sci.* 99, 1055, **2006**.

164. S. Mishra, A. K. Mohanty, L.T. Drzal, M. Misra, S. Parija, S. K. Nayak and S. S. Tripathy. *Compos. Sci. Technol.* 63, 1377, **2003**.
165. J. Rout, M. Mishra, S. S. Tripathy, S. K. Nayak and A. K. Mohanty. *Compos. Sci. Technol.* 61, 1303, **2001**.
166. A. Athijayamani, M. Thiruchitrambalam, U. Natarajan and B. Pazhanivel. *Mater. Sci. Eng.* 517, 344, **2009**.
167. M. Jacob, S. Thomas and K. T. Varughese. *J. Biobased Mater. Bioenergy* 1, 118, **2007**.
168. M. M. Thwe and K. Liao. *Compos. Part A* 33, 43, **2002**.
169. S. C. Amico, C. C. Angrizani and M. L. Drummond. *J. Reinf. Plast. Compos.* 29, 179, **2010**.
170. V. A. Patel and P. H. Parsania. *J. Reinf. Plast. Compos.* 29, 52, **2010**.
171. N. M. Kumar, G. V. Reddy, S. V. Naidu, T. S. Rani and M. C. S. Subha. *J. Reinf. Plast. Compos.* 28, 2605, **2009**.
172. S. K. Samal, S. Mohanty and S. K. Nayak. *Polym. Plast. Technol. Eng.* 48, 397, **2009**.
173. K. Jarukumjorn and N. Suppakarn. *Compos. Part B* 40, 623, **2009**.
174. G. Cicala, G. Cristaldi, G. Recca, G. Ziegmann, A. El-Sabbagh, and M. Dickert. *Mater. Design* 30, 2538, **2009**.