CHAPTER II

LITERATURE REVIEW

2.1 Composites at a glance

Common engineering materials that come within the scope of material science may be broadly classified into the following categories:

1. Metals

2. Polymers

3. Ceramics

However, when any two or more than two types of materials are combined on a macroscopic scale to form a useful third material it is called 'composite'. It consists of one or more discontinuous (reinforcements) phases embedded in a continuous (matrices) phase [2]. The reinforcing materials are usually harder and stronger than the matrices which are relatively soft. In composite materials, the matrix holds the reinforcement to form the desired shape whereas; the reinforcement improves the overall mechanical properties of the matrix. The reinforcing materials form the main load carrying component in the composites which provides high strength and stiffness as well as resistance to bending and breaking under the applied load.

The idea of composite materials is not a new one because it was known to rural people who usually mixed mud and straw to make composites for their house building. Another bright example of composite is concrete which is a mixture of aggregate (small stones or gravel), cement and sand. Cement and sand serve as matrix materials whereas, stones / gravels act as reinforcing materials. This comes under particulate composites. Further, in most of the cases rods or wires are being used as reinforcements in order to increase the tensile as well as bending strength of concrete. There are several examples in nature also where the idea of composite materials is used. Wood is a composite material. It is made up of fibrous chains of cellulose molecules which serve as reinforcement. These are bonded together by lignin, a natural matrix material. Cellulose is also found in cotton. Although, both the lignin and cellulose are two weak substances but, when these are bonded together, form a much stronger one which is a natural composite. Other examples of natural composites in God's creation are bone and teeth in human body. These are mainly composed of –

hydroxyapatite and collagen. The hydroxyapatite acts as reinforcement which is hard but brittle inorganic materials of calcium phosphate. Collagen (a protein) is a soft and flexible organic constituent which serves as a matrix material in bone. Hydroxyapatite or collagen alone would not be much use in the skeleton of human body. But when they are combined to form natural composite provides bone, the properties that are needed to support the body.

The origin of the distinct discipline of the composite materials has been started from the beginning of 1960s. Since then, there has been an increasing demand for development of new composite materials. These are more strong and stiff but light which are used in diversified fields such as aerospace, automobile, power and civil constructions. Now, there is a great demand on new materials having better overall performance. But no one material can satisfy all the requirements simultaneously. It led to a resurgence of the ancient concept of combining different materials in an integral-composite material to meet the required purpose. Such composite material systems result in a high performance material whose specific properties are better than the individual constituents. The composite material so formed offer the great advantage of a flexible design, so that one can tailor-make the material as per specifications of an optimum design.

Out of different recently developed advanced materials, composite material is one of the important classes of engineering materials used in diversified field. This is because their specific properties are superior to any other material and their design is flexible. This concept is well illustrated by biological materials such as wood, bone and teeth which are all composites with complex internal structures designed to give mechanical properties well suited to the performance requirements. The role and application of composite materials is becoming overwhelmingly important. The significant benefits of using composites include reduced weight and improved fatigue resistance, however the cost of raw materials and manufacturing are high. Most importantly, composite materials can be recycled without losing their original material properties. Thus, the adaption of manufactured composite structures for different engineering applications requires input from several branches of science.

2.1.1   Classification of composite

Properties of composite materials depend on various factors such as the distribution and properties of constituent materials, the geometry of the reinforcements etc. The strength of composite is strongly influenced by the reinforcing materials. Based on the types of reinforcing material structure, the composites are classified into three types [3] such as:

1. *Particulate composite*: It consists of a matrix reinforced by a dispersed phase in the form of particles. These are again classified as:

➢ Composite with random orientation of particles

➢ Composites with preferred orientation of particles.

In composites with preferred orientation, the dispersed phase of these materials consists of two dimensional flat platelets (flakes) laid parallel to each other.

2. *Fibrous composite*: In fibrous composites the reinforcing materials are in the form of fibers may be natural or synthetic. According to the types of fibers used these are further classified as short fiber reinforced composites and long fiber reinforced composites.

➢ Short fiber reinforced composites: In these composites the reinforcing materials in the form of discontinuous fibers. According to the orientations of fibers, these are further sub-divided into following catagories:

    • Composite with random orientation of fibers.

    • Composites with preferred orientation of fibers.

➢ Long fiber reinforced composites: In long fiber reinforced composite materials the reinforcing materials are in the form of long continuous fibers. As per the orientations of fibers these are again sub-divided into following catagories:

    • Unidirectional orientation of fibers.

    • Bidirectional orientation of fibers (woven).

3. *Laminated composites*: When fiber reinforced composites consist of several layers of fibers held together by matrix, it is called laminated composite. According to the orientations of fibers it is divided into following catagories:

- Unidirectional laminate

- Angle-ply laminate

- Cross-ply laminate

2.1.2 *Components of composite material*

As discussed earlier, in general, most of the composite materials consist of two phases i.e. matrix and reinforcement. Sometimes two or more reinforcing materials are used to enhance the properties of composites as in hybrid composites.

Matrix

The reinforcing materials can provide strength and stiffness to the composites unless they are bonded by a suitable matrix. The matrix in a composite material has many functions such as to transfer stresses to the fibers, acts as a bridge to hold the fibres in place, to isolates the fibers from one another in order to prevent abrasion and formation of new surface flaws etc. Hence, a good matrix should possess ability to deform easily under applied load, transfer the load to the fibres and evenly distribute stresses. The matrix material can be any of the three traditional materials e.g. Metal matrix; Ceramics matrix; Polymer matrix.

Metal Matrix

Metals are used as the matrix materials in metal matrix composites because of some specific advantages over polymeric matrix. One of the most important advantages is that it can be used in high temperature environments. In addition to that the metals have high yield strength and modulus in comparison to polymers. These properties of metals enable them to be used in those situations where there is requirement of high transverse strength and modulus as well as compressive strength for the composite. Further, the metals can be strengthened by different thermal and mechanical treatments which increase their properties. However, metals have certain disadvantages which restrict their use in specific situations. These include high densities, high melting points (therefore, high process temperatures), and a tendency toward corrosion at the fiber–matrix interface. Few examples of metal matrices that are generally used in metal-matrix composites are: aluminum and its alloys, titanium alloys, magnesium alloys, copper-based alloys, nickel-based super alloys, stainless steels etc.

Ceramics matrix

Similar to metals ceramics also have some advantages which favor their use as matrix in ceramic-matrix composites. These include high temperature stability, high thermal shock resistance, high modulus, high hardness, high corrosion resistance and low density. However, they have certain disadvantages like low resistance to crack propagation (i.e. low fracture toughness) and brittleness properties which also restrict their applications. Examples of ceramic matrices are: alumina (Al_2O_3) and mullite (Al_2O_3–SiO_2), silicon carbide (SiC), silicon nitride (Si_3N_4), boron carbide (B_4C), and aluminum nitride (AlN) etc.

Polymer Matrix

In reality, the majority of composites that exist in the market are made of polymer matrix composites. The reason is that as per thermodynamic requirement, the surface tension of the matrix (in liquid form) should be less than that of the fibers to ensure proper bonding in composite materials. Since the surface energy of the liquid metals is much larger than that of the solid fibers, it is very difficult for the liquid metals to bond onto the solid fibers. As such, it is difficult to make metal matrix composites, in spite of some desirable properties such as high temperature resistance. Therefore, in most of the composites polymers are used as matrix materials. Major advantages of polymers used as matrix materials are: low densities, good corrosion resistance, low thermal conductivities, low electrical conductivities etc. However, they suffer from certain limitations such as: low transverse strength, low operational temperature limits etc.

There are two types of polymers i.e. thermoplastics and thermosets. In thermoplastic polymers, individual molecules are joined together by weak Van-der Waal and hydrogen bonds. With the application of heat, these secondary bonds temporarily break and the molecules move relative to each other forming a new configuration. On cooling, the molecules can be frozen in their new configuration and the secondary bonds are restored, resulting in a new solid shape. Thus, a thermoplastic polymer can be heat-softened, melted, and reshaped as many times as desired.

In a thermoset polymer, on the other hand, the molecules are chemically joined together by cross-links, forming a rigid, three-dimensional network structure. Once these cross-links are formed during the polymerization reaction (also called the –

curing reaction), the thermoset polymer cannot be melted by the application of heat. However, if the number of cross-links is low, it may still be possible to soften them at elevated temperatures.

Reinforcement

Reinforcement is one of the important components in composite materials. It's primary function is to impart mechanical strength and stiffness to composites. There are different forms of reinforcements such as fibers, particles or powders. Out of these, fibers, particularly natural fibers, play a major role in composite industries. According to the types and arrangements, there are wide varieties of fibres used as reinforcements in composites. These fibers have different properties which affect the properties of the composites in many ways. Depending on the orientation, the fibers may be randomly oriented short fibers or long fibers with unidirectional or multidirectional. In some cases depending on the applications, the fibres are arranged in the form of sheet, known as fabric, which make them possible for easy handling. Desirable properties of composites can be obtained by assembling the fibres into wide varieties of orientations.

Coupling agents

"Wetting" of fibers in matrix is an essential requirement in fiber reinforced composite materials. Well "wetted" fibres increase the interface surfaces area of the composites. Because of this fact, 'interface' comes into picture in fiber reinforcement composite. It is a bounding surface or zone between the matrix and reinforcement where a discontinuity occurs. Generally, failure (i.e. debonding) occurs at the interface which is not desirable for the proper functioning of composites. Hence, the interface must be large and exhibit strong adhesion between fibres and matrix. In order to achieve the above properties, coupling agents are frequently used in fiber reinforced polymer composites which also improve the wettability of fibers.

2.2 Thermoplastic polymer

Thermoplastics polymers have ability to soften when heated. This is due to the fact that there is no covalent bonding between the polymer chains which gives them the ability to rotate and slide. The composition of thermoplastic resins is different from that of thermoset resins.

Whereas thermoset resins depend on the cross linking of many small molecules to provide rigidity to the material, thermoplastic resins depend on the size (length) of the molecules (these molecules are non-reactive) to provide stiffness and strength for the material. Due to this inherent difference in microstructures, thermoplastic resins have advantages and disadvantages as compared to thermoset resins. Some advantages of thermoplastic polymers are:

- There is no shelf life issue. The thermoplastic resin can be placed on the shelf infinitely without concern about the material becoming hard.

- The processing cycle can be short. Once the preforms have been arranged into a mould, the heating and cooling steps can be done on the order of minutes (rather than hours for thermosets).

- Thermoplastic composites have higher ductility and fracture toughness as compared to thermoset matrix composites.

- Thermoplastic resins can be melted and reused, making them recyclable.

- If there are defects in the thermoplastic composites, the material can be heated up to heal the damage.

In addition to that the main advantage of thermoplastic composites is design flexibility. That means it is easy to mould complex parts. Simple manufacturing processes such as extrusion and injection moulding are generally adopted for fabrication of these composites. The dispersion of fibers in the composite is one of the important parameter to achieve consistency in the product for thermoplastic composites which limits its applicability. However, they possess certain disadvantages such as:

- The preform of thermoplastic composites (tapes made of thermoplastic resin and fibers) is fairly stiff. Placing sheets of these preforms requires efforts in alignment.

- The viscosity of thermoplastic resin is very high as compared to that of thermosets. This high viscosity requires high temperature and pressure for processing. It also creates the problem of occurrence of voids in the composite material.

The vast number of thermoplastic resins used in composite materials can be conveniently separated into two categories:

➢ The traditional industrial thermoplastics that have been used with short fiber reinforcement for many years. Examples for these are polyethylene (PE), poly vinyl chloride (PVC), poly propylene (PP), polystyrene (PS), poly methyl methacrylate (PMMA), poly acrylonitrile butadiene styrene (ABS). The subject of traditional industrial thermoplastics has been covered extensively in the literature and it is not repeated here.

➢ A new set of high performance thermoplastics that have been developed specifically for use in advanced applications.

It has been reported that [4] out of different thermoplastic polymers polyethylene, polypropylene, polystyrene, and polyvinyl chloride are commonly used. Because, in these polymers the processing temperature is below 200°C so that there will be no thermal degradation of the natural fibers when they form composites with them. From application point of view now polyethylene [5] and polypropylene [6] thermoplastic composites are used in interior and exterior building components.

2.3 Natural fibres

Natural fibers are materials which are available in nature. They can be obtained from plants or animals. These are classified into three main categories such as vegetables (plant fibers), animals, and minerals fibers. Further, the plant fibers can be classified into bast fibers (jute, flax, hemp, ramie and kenaf), leaf fibers (banana, sisal, agave and pineapple), seed fibers (coir, cotton and kapok), core fibers (kenaf, hempand jute), grass and reed (wheat, corn and rice), and other types of fibers [7]. The detail classifications have been presented schematically in Fig. 1 [8].

Nowadays, the use of natural fiber polymer composites has attracted the attention of research communities from both economical and ecological point of views [9, 10]. For this reason investigation on polymer-based composite materials is going on for the production of new composites with optimal properties for specific applications [11, 12]. Natural fiber is a good renewable and biodegradable alternative to synthetic reinforcement because of various advantages such as low cost, low density, –

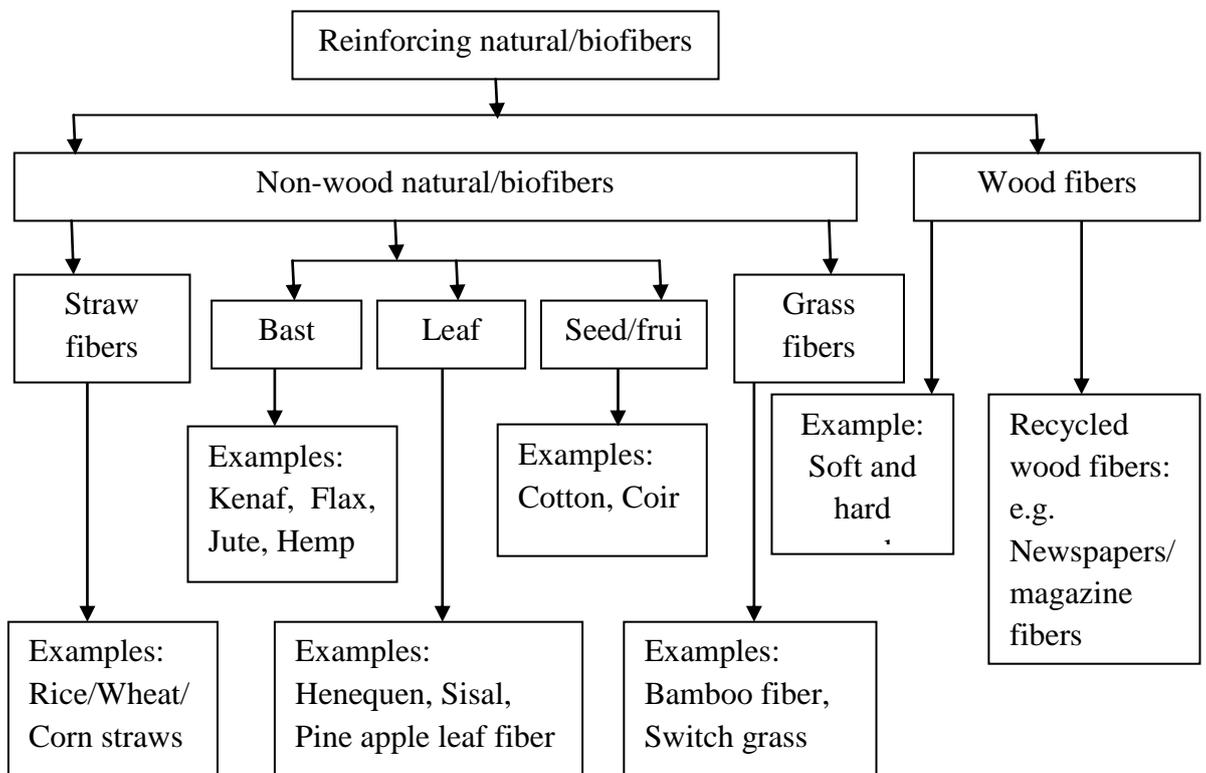nonabrasive, reduced energy consumption, less health risk etc [13-33].


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                    ┌─────────────────────────────┐
                    │ Reinforcing natural/biofibers│
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Reinforcing natural/biofibers

Non-wood natural/biofibers

Wood fibers

Straw fibers

Bast

Leaf

Seed/frui

Grass fibers

Examples: Kenaf, Flax, Jute, Hemp

Examples: Cotton, Coir

Example: Soft and hard

Recycled wood fibers: e.g. Newspapers/ magazine fibers

Examples: Rice/Wheat/ Corn straws

Examples: Henequen, Sisal, Pine apple leaf fiber

Examples: Bamboo fiber, Switch grass

Fig. 2.1 - classification of natural fibers [8]

Till date, extensive studies [34-73] have been carried out on preparation and properties of polymer matrix composite (PMC) replacing the synthetic fibers with natural fibers like jute, sisal, pineapple, bamboo, kenaf, flax and bagasse. Recently, Dhal and Mishra [74] have developed a novel low cost polymer using brown grass flower broom as reinforcement. Yu and his co-workers [75], Saheb and Jog [76], Avella [77], Holbery and Houston [78] and Begum and Islam [79] have reviewed natural fibre composites with their classifications, properties and potential applications. Now a day, natural fiber composites are used in wide variety of applications such as aerospace, leisure, construction, sport, packaging and especially in automotive industries [80-88]. However, the use of natural fiber polymer composites could not compete with that of synthetic fiber reinforced polymer composites because of several issues such as thermal degradation, high moisture content, incompatibility -

with hydrophobic polymer matrix etc. In spite of certain disadvantages, more and more research works are going on for the last decades to develop new natural fiber polymer composites which offer the potential to replace the synthetic fibers in numerous applications.

2.3.1   Structure of natural fibers

Natural fibers are considered as composites derived from nature. In natural fibers cellulose serves as reinforcing materials which are held together by lignin and hemicelluloses matrix [89]. As depicted in Fig. 2.2 [90] each fiber has a complex, layered structure. It consists of a thin primary wall (first layer) encircling a secondary wall. The secondary wall is again made up of three layers out of which the thick middle layer determines the mechanical properties of the fiber.
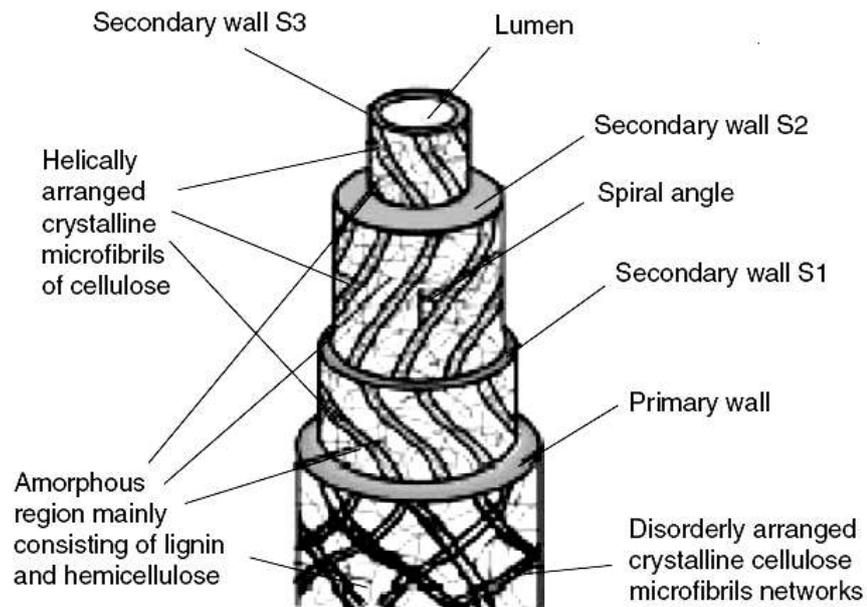

Fig. 2.2 – Structure of natural fiber [90]

This layer consists of a series of helically wound cellular micro-fibrils formed from long chain cellulose molecules. The angle between the fiber axis and the micro-fibrils is called the micro-fibrillar angle whose characteristic value varies from one fiber to another [91]. Hemicellulose, lignin, and in some cases pectin, serve as amorphous matrix phase. The hemicelluloses molecules act as cementing matrix between the cellulose micro-fibrils, forming the cellulose–hemicellulose network.

The lignin, which is hydrophobic in nature, acts as a coupling agent and increases the stiffness of the cellulose/hemicellulose composite.

2.3.2   Composition of natural fibers

The cell wall of a matured natural fiber contains cellulose, hemicellulose, lignin and pectin as major constituents which are distributed throughout the fiber wall [92]. However, the percentage composition of the above constituents varies according to the origin, area of production, variety and maturation of plant. The chemical composition of some natural fibers has been presented in Table 1 [93].

Table 2.1 – Composition of few natural fibers [19]

Fiber	Cellulose (%)	Lignin (%)	Hemicellulose (%)	Pectin (%)	Ash (%)
Abaca	56.0 – 63.0	7.0 – 9.0	15.0 -17.0	-	3.0
Sisal	47.0 -78.0	7.0 -11.0	10.0 – 24.0	10.0	0.6 – 1.0
Henequen	77.6	13.1	4.0 – 8.0	-	-
Kenaf (core)	37.0 – 49.0	15.0 – 21.0	18.0 – 24.0	-	2.0 – 4.0
Jute (core)	41.0 – 48.0	21.0 – 24.0	18.0 – 22.0	-	0.8
Fiber flax	71.0	22.0	18.6 - 20.6	2.3	-
Seed flax	43.0 – 47.0	21.0 – 23.0	24.0 – 26.0	-	5.0
Kenaf (bast)	31.0 – 57.0	15.0 – 19.0	21.5 – 23.0	-	2.0 – 5.0
Jute (bast)	45.0 - 71.5	12.0 – 26.0	13.6 – 21.0	0.2	0.5 – 2.0
Hemp	57.0 – 77.0	3.7 – 13.0	14.0 - 22.4	0.9	0.8
Ramie	68.6 – 91.0	0.6 - 0.7	5.0 - 16.7	1.9	-

Cellulose

Cellulose is one of the important constituents of natural fiber which serves as reinforcing material imparting mechanical strength and stiffness to the God made composite. It is long thin crystalline micro-fibril present in secondary cell wall. It consists of a linear polymer of D-anhydroglucose unit where two adjacent glucose units are linked together by β-1, 4-glycosidic linkages with elimination of one water molecule between their -OH groups at carbon atoms 1 and 4. Cellulose is defined as a highly crystalline segment. Hydrogen bonds are formed between the glucose monomers within its own chain (intermolecular) which forms fibrils. Whereas, the glucose monomers in cellulose forms hydrogen bonds with neighbouring chains (intermolecular) giving rise to micro-fibrils. These hydrogen bonds lead to formation of a linear crystalline structure with high rigidity and strength. The amorphous cellulose regions have a lower frequency of intermolecular hydrogen bonding, thereby exposing reactive intermolecular -OH groups to be bonded with water molecules. For that reason, amorphous cellulose is considered as hydrophilic in nature due to their tendency to bond with water. In case of crystalline cellulose, very few accessible intermolecular –OH groups are available. This crystalline cellulose is less hydrophilic than amorphous cellulose. The crystalline micro-fibrils are tightly packed cellulose chains within the fibrils whose surface are filled with –OH groups.

Hemicelluloses

It has been observed that the structure of hemicelluloses is different from that of cellulose. Cellulose contains one sugar unit as given above, whereas hemicellulose contains several different sugar units. Hemicelluloses contain branched chain are having considerable degree of chain branching, while cellulose is a linear polymer. Further, the degree of polymerization of native cellulose is ten to hundred times higher than that of hemicelluloses. The constituents of hemicelluloses contain mainly acetyl (-$COCH_3$) groups and glucoronic acid which differ from plant to plant. It can form covalent bonds with lignin when attached with ferulic acid and p-coumaric residues. Due to this linking ability, the degradation of hemicelluloses leads to disintegration of the fibers into cellulose micro-fibrils thereby giving lower fiber bundle strength [94]. The hemicellulose is highly hydrophilic (fiber water uptake property) due to the acid residues attached to it which increases the risk of microbiological fiber degradation.–

It has been reported [95] that hemicellulose thermally degrades more at lower temperatures (150-180°C) than cellulose (200 -230°C).

Lignin

Lignin is another important polymeric organic constituent whose main function is to act as a matrix material in natural fiber. It also transfer stresses to cellulose (the reinforcing material) on both micro-fibril scale and also single fiber scale. Further, it provides compression strength by gluing the fibers together to form a stiff structure. This is the main reason why the trees of 100 meters long remain upright. Generally, lignin is a disordered, poly-aromatic, and cross-linked polymer arising from the free radical polymerizations of two or three monomers structurally related to phenyl-propane [96]. Free radical coupling of the lignin monomers gives rise to a very condensed, reticulated, and cross-linked structure similar to a thermoset polymer. The dissolution of lignin using chemicals treatments aids fiber separation. Photochemical degradation takes place when lignin is exposed to ultraviolet light.

Pectin

The last constituent of natural fiber is pectin which is a complex branched structure of acidic polysaccharides. Pectin is the most hydrophilic compound found in fruits and bast fibers. The hydrophilic nature of pectin is due to the presence of carboxylic acid groups which can be easily removed by defibration with fungi. Pectin along with lignin and hemicelluloses present in natural fibers can be hydrolyzed at elevated temperatures.

2.3.3   Surface modification of natural fibres

Starting from academic institutions to industries all are interested to use natural fibers to develop polymer based composites materials due to their advantages such as: high-specific strength and stiffness, lightweight, nonabrasive, combustible, nontoxic, low cost and biodegradable properties. However, natural fibers are hydrophilic nature and are not compatible with hydrophobic polymer matrices giving rise to poor –

interfacial adhesion which restricts their application [97–99]. The structure, microfibrillar angle, cell dimensions, defects, and the chemical composition of fibers are the most important variables that determine the overall properties of the fibers [100]. The mechanical properties of natural fiber based polymer composites are strongly influenced because of their affinity towards moisture [101, 102]. Over and above this low melting point of natural fiber reinforced composites also restricts their application in some situations. To overcome this issue, surface modifications of the fiber are done which can clean the fiber surface, chemically modify the surface, stop moisture absorption process, increase surface roughness and also improve mechanical properties of composites [103, 104]. The main reason is due to the presence of hydroxyl groups which causes the fiber to swell. Because of this they are incompatible when mixed with hydrophobic polymers giving rise to poor wetting of the fiber and adversely affects the fiber-matrix interfacial bonding. In order to improve fiber-matrix interfacial bonding the fiber surface is modified by various chemical treatments [105–117] such as; bleaching, alkali, silane, acetylene, benzoylation and acrylation. Sometimes coupling agents are added in matrix in order to improve fibre-matrix interfacial bonding. Out of these methods, alkali treatment method is the most common chemical treatment method given to the natural fibers. This treatment removes plenty of impurities and waxy substances from the surface of fibers thereby increasing surface roughness. Because of this the mechanical properties of the composites increases by proper interlocking of the fibres with the resin.

2.3.4 *Mechanical properties of natural fiber polymer composites*

It has been verified that [118-123] the mechanical performances of fibre-reinforced polymer composites is governed by several factors including fibre–matrix interfacial adhesion and the ability to transfer stress from the matrix to fibre.

In order to achieve good mechanical properties of the composite, the properties of matrix and fibers as well as processing conditions play important role. The strength parameter of the composite is influenced by matrix properties, whereas the modulus is sensitive to fiber properties. The mechanical strength of the composite is dependent on fiber-matrix interfacial adhesion, stress concentration and fiber orientation. In contrast, the fiber concentration, fiber wetting in the matrix and fiber aspect ratio control the stiffness property. The parameters responsible for obtaining good impact property of –

the composites are: optimum bonding level, long and stronger fibers etc. In addition to that the degree of adhesion, fiber length and mechanism to absorb energy are the other parameters which have tremendous influence on the impact strength of a composite. Further, it is seen that processing of short natural fiber composites (e.g. injection molding) is simple and, therefore, and economically attractive. But, the mechanical performance of injection molded composites is rather low and suitable only for non-loaded applications. Whereas, composites reinforced with long natural fibers are better suitable for medium and heavily loaded applications.

It has been proved [120, 124, 125] that the interfacial adhesion between the fibres and the polymer matrix is one of the most important parameters which controls the mechanical properties of natural fiber reinforced polymer composites. The reason is quite clear. Cellulose, hemicelluloses, pectins and lignin present in all most all natural fibers contain hydroxyl groups. They have strong affinity towards water because of polar nature of hydroxyl groups. Therefore, in natural fiber reinforced polymer composites the natural fibers are hydrophilic in nature whereas, the polymer matrices are hydrophobic. Due to this fact, there are significant problems of compatibility between the fiber and the matrix. This weakens the interface area between the natural fibres and matrices which in turn decreases the mechanical properties of composites. However, this problem can be easily overcome by giving various surface treatments to fibers such as bleaching, acetylation and alkali treatment may improve the matrix–fibre interfacial adhesion [120, 121, 125-127].

Obviously, there is a strong relationship between the fiber volume fraction (V_f) on modulus and strength of the composite. The more is the fibers in the composite; the better is the mechanical property. As per some theoretical model it has been observed that there is a proportional relation [116, 123,128] between the two. However, from experimental point of view, the increase of V_f over specific value always deteriorates the mechanical properties. Several methods have been adopted to determine the optimum value of the fiber volume fraction in natural fiber composites to obtain the optimum mechanical properties. It is obvious that there is no universal value of fiber volume fraction of natural fibers at which optimum tensile strength of the composite can be achieved, i.e. for each type of fiber there is an optimum volume fraction exhibiting good tensile strength. This can be related to the nature of natural fibers and their characteristics in term of strength, interfacial adhesion,

physical property, etc. At high volume fraction (i.e. >> 50% of fiber loading) the fibers tend to aggregate in the composite which weakens the interfacial area and debonding between the fibers and matrix [125].

Herrera-Franco and Valadez-Gonzalez [129] have studied the effect of saline treatment of henequen fibers on mechanical properties of continuous henequen fiber reinforced high density polyethylene (HDPE) composites. They have observed that due to surface treatments the fibers aligned in perpendicular direction have better mechanical properties in comparison to untreated fiber composites. Rozman et al. [130] have found that flexural, tensile and impact strengths of coconut-glass fiber reinforced PP hybrid composite have been reduced in comparison to unreinforced PP by introducing both coconut fiber and glass fiber into the PP matrix. Further, it has been observed by Uma Devi et al. [131] that the tensile strength, modulus and impact strength of pine apple leaf (PALF) reinforced polyester composites increase linearly with fiber content. However, in the case of flexural strength there is a leveling off beyond 30 wt % fiber content. When the pine apple leaf fibers are treated there is a significant improvement in the mechanical properties of the composite.

2.3.5   *Tribological properties of natural fiber polymer composites*

Machine components are frequently exposed to tribological environment where wear and tear occurs. Therefore, tribological performance of materials becomes an essential element to be considered in design of mechanical parts. While developing a composite material based on natural fiber for tribological application, its tribological behavior has to be considered along with mechanical properties [132]. It has been observed that the tribological behavior of natural fiber/polymer composites is not intrinsic property. It strongly depends on many parameters such as operating parameters, characteristics of polymer martial, physical and interfacial adhesion properties of fiber, additives and contact condition. Some works have been done to investigate the tribological behavior of polymeric composites based on natural fibers such as Kenaf [133], Oil palm [134], Sisal [135], Cotton [136], Jute [137], Betelnut [132], Bamboo [138]. From those reported works, it has been found that there are certain issues that have to be considered while analyzing the tribological behavior natural fiber composites. These are:

➢ *Operating parameters*: The wear and frictional behavior of most of natural fiber polymer composites are strongly affected by operating parameters.

➢ *Reinforcement*: The orientation and types of reinforcement of natural fibers also controls the wear performance of the composite.

➢ *Surface modification*: The interfacial adhesion between the fibers and the matrix are improved by surface modification of natural fibers which consequently increases the wear performance of composites.

➢ *Addition of solid lubricants*: Addition of solid lubricants controls the shear resistance in the interface zone which consequently enhances wear performance of composites.

The fiber matrix interfacial adhesion is one of the important parameters which controls the tribological behavior of polymeric composite based on the natural fibers[133, 134, 139].As discussed earlier, natural fibers are hydrophilic in nature which is not compatible when reinforced with hydrophobic polymers. Hence, there is a lack of good interfacial adhesion property of natural fibers with polymers. Different surface modification methods improve the interfacial adhesion property thereby increasing both mechanical as well as tribological properties. It has been reported that surface modification of some natural fibers such as kenaf, oil palm, betelnut and sisal [133-135, 140] enhances their tribological behavior.

In addition to that various operating parameters like applied loads, sliding velocities, sliding distances etc. also affects the tribological properties of natural fiber composites. It has been observed [141] that there is a strong influence of applied load on wear resistance of sugarcane fibre/polyester composite which increases with increasing load. Almost same thing has been observed by Chand and Dwivedi [135] while investigating the effect of applied load on the abrasive wear behavior of sisal fiber reinforced polyester composite. The linear relationship of applied load with wear resistance is mainly caused by the greater frictional heat which softens the matrix on the composite surface. Further, Chin and Yousif [133] while investigating the specific wear rates (W_s) of kenaf fibre reinforced epoxy composite have observed that applied loads and sliding velocities have less effect on the specific wear rates. Yousif [142] has studied the effect of operating parameters such as applied load (10–30 N) and sliding distance (0–4.2 km) on the tribological behavior of coir fibre-reinforced polyester –

(CFRP)composites.

Friction is another parameter, which controls the tribological behavior of natural fiber reinforced polymer composites under dry sliding conditions. The friction coefficient of composite material is determined based on three friction mechanisms i.e. asperity deformation, adhesion and ploughing. Each mechanism depends on the contact surface topology, operating conditions and the type of materials used. Some investigators have focused on the friction behaviour of polymeric composites based on the natural fibres under dry sliding conditions [133-136,142]. As observed from the work of Chin and Yousif [133], kenaf fibres reduces the frictional coefficient of neat epoxy from 0.75 to 0.56. It has been reported that [132, 134,142] a reduction of friction coefficient can be achieved when polyester was reinforced with coir, betelnut and oil palm fibres by about 30%, 46% and 60%, respectively.

2.3.6 *Advantages and limitations of natural fibres*

In this section some of the advantages and limitations of natural fibers over synthetic fibers have been highlighted.

Advantages

1. Natural fibers have low specific weight, which results in a higher specific strength and stiffness than synthetic fibres. This is a benefit especially in parts designed for bending stiffness.
2. It is a renewable resource and the production requires little energy. During fabrication, CO_2 is used while oxygen is given back to the environment which is an added advantage.
3. Producible with low investment at low cost, which makes the material an interesting product for low wage countries.
4. Friendly processing, no wear of tooling, no irritation of skin.
5. Thermal recycling is possible, where glass causes problems in combustion furnaces.
6. Good acoustic and thermal insulation properties.

Limitations

1. Lower strength, especially of impact strength.
2. Variable quality due to the unpredictable influence of weather.
3. Moisture absorption causing swelling of the fibre.
4. Restricted upper range of processing temperature.
5. Lower durability.
6. Poor fire resistance.

2.4 Date palm leaf (DPL) fibre

The date palm tree, a member of the palm tree family (*Phoenix dactylifera*), is normally found in the Middle East, Northern Africa, the Canary Islands, Pakistan, India, and in the United States (California). Some important species of date palm tree found in India are shown in Fig. 2.3.

Fig. 2.3 - Date Palm Trees

The genus Phoenix belongs to the Arecaceae family. As a group, there are about 13 different species of *Phoenix*. As per the reported work [143] there are approximately 62 million of date palm trees found in the Middle East and North Africa and 100 million worldwide. Traditionally, the leaves of date palm tree are used in making ropes, baskets and mats in many parts of the world. However, these applications account for a small percentage of the total world production. The bulk of the material is discarded as waste. In Saudi Arabia alone, 15000 tons of date palm leaves are produced as waste. Therefore, efficient utilization of this natural resource in making natural fiber composite would have a positive impact on environment and may improve the economic standard of rural people.

2.5 Date palm leaf fiber polymer composites

Earlier, few works have been undertaken by various researchers to develop polymer composite materials using the fibers obtained from different parts of date palm tree. Sbiai et. al. [144] have investigated various properties of short date palm leaf fiber reinforced in a poly-epoxy thermoset resin. Mahdavi et. al. [145] have studied the morphological and mechanical properties of wood plastic composite fabricated by reinforcing the fibers obtained from trunk, rachis and petiole of date palm tree in high density polyethelyne (HDPE) matrix. They have observed that there is significant difference between trunk and petiole on fiber length but rachis has no significant difference relative to the other parts. The tensile strength of fibers obtained from leaves and stems of date palm tree have been investigated and compared with other natural fibers by Rao and Rao [146]. They observed that the tensile strength of date palm fiber is comparable to that of other fibers such as banana, bamboo, coconut and sisal. The effect of various surface modifications on date palm fiber obtained from stems has been investigated by Alawaret et. al. [119]. From the above study it has been found that date palm fiber when treated with 1% NaOH gives maximum mechanical properties while the same fiber when treated with HCL reduces the mechanical properties. Al-Sulaiman [143] have fabricated date palm leave reinforced laminated composites by autoclaving technique and tested various properties. He has used two types of resins i.e. Phenol formaldehyde and Bisphenol for the production of composite panels and found that the thermal conductivities of the composites vary with the type of resin used, fiber to resin ratio and curing pressure. However, the size-

and orientation of fibers have no remarkable effect on the thermal conductivity of the composites. Recently, Shalwan and Yousif [109] have studied the effect of NaOH concentration and fiber diameter on the interfacial adhesion behaviour of the date palm fiber reinforced epoxy composite. They have taken 0 to 9 weight percentages of NaOH and 0.3 to 0.7 mm fiber diameter and observed that 6% NaOH and 0.3 mm fiber diameter is the optimum values to obtain better properties of composite. In another work AlMaadeed et al. [147] have studied LDPE blended date palm wood powder composite and observed that 70 wt% of the filler gives optimum mechanical properties. In addition to that some material scientists [148-152] have investigated various properties of polymer composites obtained from date palm leaf fibers.

2.6 Summary

In the present investigation a short precise survey has been conducted on natural fiber reinforced polymer composite with a special emphasis on date palm fibers. From the survey it has been observed that various fibers obtained from different parts of plant have been reinforced in either thermoset or thermoplastic polymers to obtain polymer composite materials. The natural fibers which have been commonly used in polymer composite fabrication for its use in wide variety of fields include Kenaf, Oil palm, Sisal, Cotton, Jute, Coconut, Betelnut, Bamboo, Pineapple, Flax and many more. As far as date palm fiber is concerned few works have been done in this direction. However, most of the works focus on manufacturing polymer composite materials utilizing fibers obtained from trunk, rachis, petiole and stems of date palm trees. Some investigator has also used date palm wood powder to fabricate polymer composites.

It is observed that the leaves of date palm tree are generally used in making ropes, baskets and mats in many parts of the world. But the consumption of date palm leaves towards this application is only a fraction of the total world production. The major portion of the material is wasted. Therefore, this natural resource can be efficiently utilized in making natural fiber composite. This will not only create a positive impact on environment but also improve the economic standard of rural people. In this regard the most of the research works undertaken till date to utilise date palm leaves as reinforcement in polymer composite have been done in thermosetting –

polymers as matrix material. With some specific advantages of thermoplastic polymers over thermosetting, other natural plant fibers have been utilised for development of new composites. The different thermoplastic polymers commonly used are polyethylene, polypropylene, polystyrene, and polyvinyl chloride. However, two polymers chosen in this investigation i.e. poly vinyl alcohol (PVA), polyvinyl pyrrolidone (PVP) are quite new to act as matrix materials to manufacture natural fiber composite by reinforcing date palm leaf fibers. After fabrication with different weight percentage of fiber loadings the optimum weight percentage has been determined for maximum tensile properties. Taking the optimum fiber loading, different properties such as mechanical, thermal, tribological, rheological and biodegradable properties have been investigated.