Chapter 1

Introduction

1.1 Fundamentals of Composite materials

Engineering materials provide the cornerstone of technology, whether it be structural, electrical, mechanical, thermal, environmental, biological, electrochemical, or other in nature. High stiffness, proper surface hardness, improved tribological and mechanical propertiers, better thermal endurance, high strength to weight ratio, improved yield strength under dynamic or static loading, etc., are required properties of these materials. In general, homogeneous materials only meet a subset of the desirable qualities. As a result, there has been a rise in the experimental and computational research involving these heterogeneous materials during the past several decades. Alloys containing several phases, such as grains, precipitates, and pores, are examples of these materials. One of the most widely used heterogenous material is composite material which involes the dispersion of reinforcement or fibers in matrix material [1]. The composite materials were developed by the researchers to partly substitute the existing metals, nonmetals, and alloys in a variety of technical applications. These materials are made up of single or multiple chemically distinct materials that are combined to generate an advance material with increased qualities that are not possible with any of the original materials alone. Within the final product, the constituent components stay distinct and independent. Some of these materials have state of the art properties and are employed in space and aircraft industries. Ancient human civilizations have been employing these composite materials for variety of application around the world. Mud buldings were built with reinforced chopped straw by the Egyptian, while bullock horn and bamboo strips were used as reinforcing materials in pine resin to fabricate archery bows by the Mongol army.

On a macro-scale, composites are materials made up of two or more chemically different elements separated by a discrete interface. The composite material consists of a continuous phase usually referred as matrix where a single or multiple discontinuous phase, referred as reinforcement is embedded into it [2]. The reinforcement materials are generally tougher and sturdier than the matrix material. They provide strength and stiffness to overall structure. The matrix retains the fiber in the proper form and transfers the stress from one fiber to another.

Composite materials are often grouped into two categories. In general, the initial level of categorization is conducted with regard to the matrix phase (Fig. 1.1). Metal matrix composites (MMCs), ceramic matrix composites (CMCs), and polymer matrix composites (PMCs) are the three basic composite classifications based on the matrix material.

Polymeric materials have shown considerable promise in the manufacturing sector as a group of critical manufacturing materials. Polymers found application in our day-to-day life for ages and have become a vital element of human life. Research on polymer materials started on the beginning of nineteenth century with the creation of celluloid, a rigid polymer made from nitro-cellulose. Polymers, in general, are extremely large chain of molecules composed of innumerable tiny molecules known as monomers. Tens of thousands of monomers can be found in a typical polymer. But, the polymer alone fails to meet the criteria required for high end engineering applications. Therefore, fibers are added to the polymers as reinforcement to enhance there engineering properties.

Polymer matrices are often preferred due to their cost effectiveness, ease of producing complicated components with reduced tooling expense, and excellent room temperature features. Polymer matrices are categorized as thermoplastic and thermoset based on their behavior and structure. Fig. 1.2 depicts the type of polymers used in composite fabrication.

Thermoplastics comprise molecules with branched or linear chains with frail inter-molecular interactions and sturdy intra-molecular bonds. Without changing their chemical makeup, they may be repeatedly reheated and shaped into any other shape. Thermosets polymers undergoes a crosslinking process, which promotes chemical interaction between macromolecular chains and results in the formation of a three-dimensional network. These materials cannot be re-melted or moulded once they have solidified due to the cross-linking process. Although fragile, these components have outstanding strength characteristics and will not shed considerable strength when subjected to higher working temperatures [3]. The primary characteristics of thermosets and thermoplastics are presented in Table 1.1.

Acrylic, Teflon, polyphenylene sulfide (PPS), polybenzimidazole, and polysulphone are some of the most prevalent thermoplastic polymers. Because no curing reaction is necessary, they may be processed more quickly than thermoset composites. Thermoplastic composites just need to be heated, shaped, and cooled. They are durable, have a low moisture absorption rate, are chemically resistant, and are non-toxic. The heat-aging performance of thermoplastic components used in a variety of underhood applications was validated with an upper limit in the range of 170°C to 190°C.

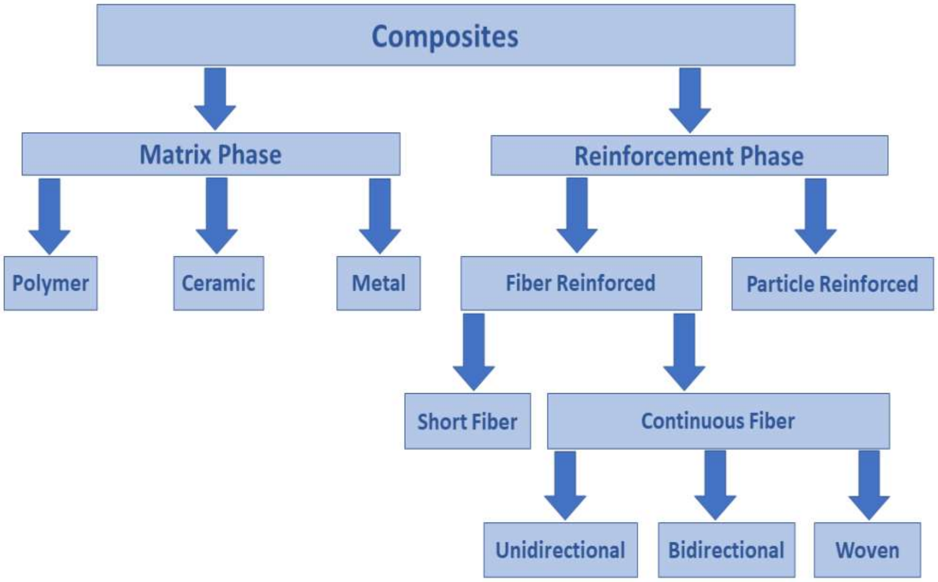


Figure 1.1 Classification of Composites [7]

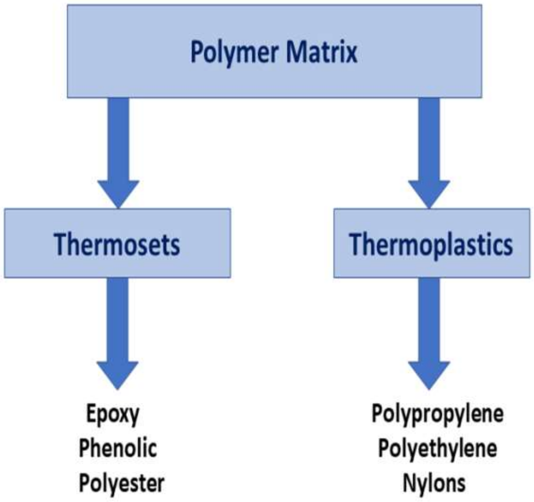
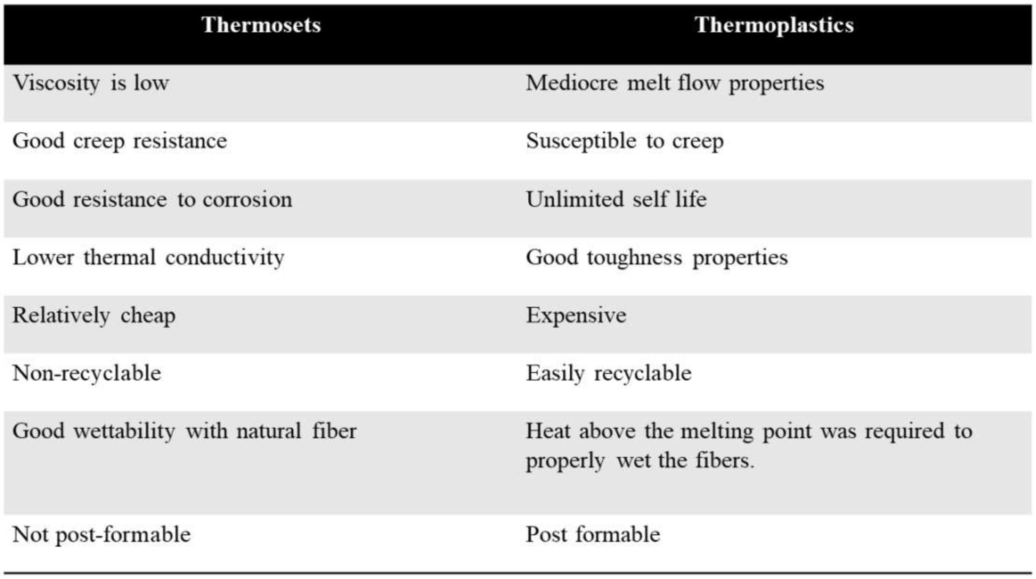


Figure 1.2 Classification of polymer matrix [8]

Table 1.1 Characteristics of Thermosets and Thermoplastics [17]



Thermosets	Thermoplastics
Viscosity is low	Mediocre melt flow properties
Good creep resistance	Susceptible to creep
Good resistance to corrosion	Unlimited self life
Lower thermal conductivity	Good toughness properties
Relatively cheap	Expensive
Non-recyclable	Easily recyclable
Good wettability with natural fiber	Heat above the melting point was required to properly wet the fibers.
Not post-formable	Post formable

Polyesters, epoxies, and polyamides are among the thermoset resins. Polyesters have a cheap cost, strong mechanical strength, low viscosity, and adaptability, as well as superior electrical and heat resistance. With a curing temperature of 120°C, they may be utilized in both cold and hot moulding. For the most sophisticated composites, epoxy resins are commonly employed. They offer minimal shrinkage while curing, excellent strength and flexibility, a wide curing range, higher fiber-matrix adhesion, improved electrical characteristics, and chemical and solvent resistance. Polyamides are characterized by appreciable mechanical properties and they do-not undergo any change in the properties upto 260-315°C. They are also characterized by efficient electrical properties and offer better resistant to fire. The composites prepared with polyamides can be cured at a temperature range of 175ºC to 315ºC.

The polymers are often chosen as matrices depending on their fatigue resistance, adhesive strength, chemical and moisture resistance, heat resistance, and other characteristics. The resin must be simple to employ in the chosen fabrication method and withstand the conditions required for the product. The polymer matrix should have the ability to soak and permeating into the reinforcement, substituting any voids and providing mechanical and physical properties that improve fiber performance.

In the matter of PMCs, the polymer resin primarily determines the composite's shear, chemical, and electrical characteristics. The usefulness of the composites in the face of a erosive conditions and elevated temperature is, once again, determined by the resin type. Some of the physical properties like density and material properties like tensile strength, modulus can be determined by rule of mixing.

Based on the reinforcement phase, the composites can be classified as the following:

1.2 Classification of Composite materials based on Reinforcement

1.2.1 Fiber reinforced composites (FRC)

Fiber-reinforced composites composed of reinforcement where the cross-sectional area of the reinforcement is negligible when compared to the length. Fibrous reinforcement involves physical modification of material instead of chemical to fulfill different technical purposes. Owing to their innate stiffness and high strength to weight ratio, FRC are widely employed in a range of industrial applications. These types of composites are gaining traction in structural and tribological applications due to their outstanding structural performance. The leading load-carrying candidates are fibers, which are kept in the proper position and orientation by the surrounding matrix [4,5]. Continuous (long) FRC and discontinuous (short) FRC are the two major types of FRC.

1.2.1.1 Short or discontinuous fiber composites

A discontinuous fiber composite, also known as a short fiber composite, consists of a matrix that is strengthened by a scattered phase consisting of short or discontinuous fiber. Aspect ratio is also considered as a distinguishing factor for fibers. Short fiber is defined as having an aspect ratio between 8 and 12. Short or discontinuous fiber composites are preferred over other types of composites for industrial scale production due to their low cost, simplicity of producing complicated components, and isotropic nature. Short or discontinuous fiber reinforced composite can be classified as (a) biassed or preferred oriented fiber composite and (b) randomly oriented fiber composite. The fibers in the former are orientated in specified orientations, while the fibers in the latter are arranged randomly.

1.2.1.2 Long or continuous fiber composites

A continuous fiber composite, also known as a long fiber composite, consists of a matrix that is strengthened by a scattered phase consisting of long or continuous fiber. These type of composites are characterized by having high length to diameter ration of the fibers. Long fiber is defined as fiber with an aspect ratio greater than 12. They are often stiffer and sturdier than bulk material. It is further separated into three groups based on how fibers are placed within the matrix: (a) unidirectional fiber arrangement, (b) bidirectional fiber arrangement, and (c) woven fiber arrangement. The fibers in the unidirectional arrangement are only orientated in one particular direction, however if the fibers are aligned at right angle or any angle then it is known as bidirectional arrangement. Numerous threads are weaved on a warp and a weft to form woven fabrics, which are frequently produced on a loom. Woven fabric is technically any fabric created by weaving together two or more threads at right angles.

Natural and synthetic fibers can both be used to make woven fabrics, and these two types of fibers are frequently combined. The composites prepared with long fiber arrangement has some degree of anisotropy in its overall characteristics.

1.2.2 Particulate reinforced composites (PRC)

Particulate reinforced composites are composites in which the reinforcement is a particle with nearly identical dimensions. Composites reinforced with particulate fillers have higher temperature resistance, lesser voids and improved tribological performance. Unreinforced concrete can be considered as a particle reinforced composites, where the sand acts as a filler/particulate and carries maximum amount of load (typically lesser than fiber) where as the cements performs the role of matrix and is responsible for holding the sands together. As a result, PRC are primarily used for high stiffness applications instead of strength. Particles, in general, are not particularly good at enhancing fracture resistance, although they do improve composites' stiffness to an appreciable level. Particulate composites are utilized in conjunction with all the types of matrix materials available: polymers, ceramics, and metals.

1.3 Natural fiber Reinforced Composites

Increasing social, environmental, and economic awareness, as well as the rapid dwindling of petroleum assets, sustainability concept and new G20 legislation, have sparked the advancement of environmentally sustainable composite materials to reduce global greenhouse gas emissions. Due to benefits such as low weight and high strength, better specific properties, ease of availability, non-carcinogenicity, and bio-degradability, research and engineering interests are turning away from standard synthetic fiber composites and toward lignocellulosic natural fiber composites [6-7].

Because of their excellent stiffness and tensile qualities, man-made fibers such as aramid, glass, rayon and carbon fibers are usually employed in polymer composites [8]. However, the allure of employing man-made fibers in composite industries are diminishing due to the underneath factors: they can be hazardous, corrosive, costly, difficult to degrade and can also cause damage to the processing equipment [9].

Plant based cellulosic fibers and waste from agro industries are among the bio-based materials quickly expanding in terms of commercial uses and basic research. They are an appealing ecological option to substitute synthetic fibers used in the manufacturing of composite materials. Natural fibers are primarily derived from three sources like plant based cellulosic fibers, animal based protein fibers and mineral fibers. However, in the composites sector, majority of the applications require plant based cellulosic fibers. These fibers contribute significantly to plant structural performance and can offer considerable reinforcement when utilized in plastic composites. Wood is a plant based material consists of cellulose which has a higher percentage of crystalline content. Cellulose fibers have relatively higher load carrying capacity for lesser weight. The cellulose that is packed closer together has a higher density and strength. The fundamental weight carrying components of trees are the walls of these hollow elongated cells. The cellulose present in cell walls of the plant is affected by the load acting on that part of the plant and over a period of time this will strengthen the cellulose of the cell walls. Plant-based natural fiber geometry and characteristics are influenced by a variety of factors including species, growth circumstances, time of harvesting, age, etc. As these plant fibers can exhibit a broad range of weak and strong attachments to the resin, depending on the type of fiber, matrix and fabrication techniques, the best interface is often found somewhere in the middle. Because stress-concentrating faults are unavoidable, there is also a problem with excessively strong fiber-matrix bonding as it will make the composite excessively brittle which may result in poor strength and highly noth-sensitive material.

Natural fibers are confined to applications where lesser strength is required like packaging industries in comparision to synthetic fibers which found application in aerospace, automobiles, etc notwithstanding their interest and ecological appeal. Structural designs, fiber surface modification, and improved placement, in the way of arranging the these natural fibers in precise regions for maximum strength properties, can overcome the drawback (poor strength and stiffness) of these natural fiber composites.

1.4. Usage of natural fiber-reinforced polymer composites (NFRPC)

Fibers derived from natural sources, when employed to substitute synthetic fiber reinforcements in polymer composites, offer a great deal of promise to reduce CO_2 emissions while simultaneously conserving non-renewable resources. Glass fibers primarily found application as a building insulation material and as a reinforcement for polymer composites employed in the automotive industry. Moreover, because of considerable energy consumption and associated health concerns during manufacture and handling, the environmental performance of glass fiber composites has numerous limitations. Glass fibers are responsible for causing abrasion to the processing machines, and these type of composites may cause injuries to the passengers from the sharp splints after an accident.

Natural fibers, on the other hand, are being studied more thoroughly by research institutes and vehicle manufacturers as an environmentally acceptable alternative to glass fibers. The majority of the bast fibers researched come from naturally occuring plants like jute, ramie, bamboo, flax, kenaf, sisal, and hemp plants. Floor panels, seatback linings, and door cladding are made from composites of flax, sisal, and hemp. Head restraints, back cushions, and seat bottoms are produced from coir fiber, while soundproofing is provided by cotton, and seatback cushions are made of wood fiber [10]. The application of various natural fibers and their composites are represented in Table 1.2.

However, the usage of these type of bio-composites are not confined to the automobile sector. Wood is also used as a reinforcing ingredient in polymers by window and door profile producers [11]. Other documented natural fiber composite uses include packaging industries, floors, walls, louvres, and indoor and furniture.

Regrettably, the present generation of NFRPC lacks the mechanical characteristics required for usage in increasingly demanding sophisticated structural and load-bearing applications. In addition to the poor mechanical properties, concerns regarding thermal behaviour and water retention rate of these NFRPCs must be resolved before these NFRPCs can be exploited to their full potential in the industry.

Table 1.2 Applications of natural fibers and their composites [1,5,6,8]

Applications	Natural fibers
Door panels	Kenaf/Hemp
Glove box	Flax/Sisal
Insulation	Cotton
Seat surface	Coconut/Flax
Spare wheel pan	Abaca
Bearing	Linen/Jute
Clutch	Banana/Kenaf
Brake pad	Rice straw dust/Rice husk
Dental	Sea shell nano powder

1.5 Organization of Thesis

Retention of moisture from the atmosphere is an important drawback of lignocellulosic fibers. The elimination of these water particles from the fiber is a necessary footstep in reducing its water absorption character and improving its mechanical interlocking with the matrix. Although many researchers and scientists have employed various tools (both chemical and physical) to improve the fiber's compatibility with the polymer matrix. However, most of these surface modification techniques are harmful to the environment and will negate the very purpose of using natural fibers as reinforcement. Hence, the present research work has been undertaken to modify the fiber surface with various eco-friendly chemicals in order to minimize hydrophilicity and enhance the strength, crystallinity, and surface roughness of the fibers so that the fibers can have efficient bonding with the matrix made up off polymer.

Other than the use of various eco-friendly chemicals, the fiber surfaces were also coated with environmentally-safe plant based polymers like Polylactic acid (PLA) and Polyhydroxybutyrate (PHB) to enhance the natural fiber's compatibility with the polymer matrix. Scanning electron microscopy (SEM), X-Ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and Thermogravimetric analysis (TGA)/Differential scanning calorimetry (DSC) is used to study morphology, surface chemistry, and thermal stability of the modified and untreated fibers, and these investigations are connected to the mechanical and tribological characteristics of the NFRPC. The water retention performance of the unmodified NFRPC and modified NFRPC was also investigated. Dry sliding wear experiments were performed under simulated laboratory settings to evaluate the composites' potential for tribological applications. Tensile and flexural fractured surface and worn-out surface of tribotested specimens were examined using a Scanning Electron Microscope (SEM) to get insight into the composite's fractured behavior.

The present thesis is organised into six chapters

Chapter - 1: The opening chapter of the thesis proposes different forms of composite materials and their matrix materials, as well as the varieties of natural fibers available and the advantages of employing them as a reinforcing material in polymer composites.

Chapter - 2: This chapter offers a literature review to provide an overview of the existing set of information on the topics of interest. It offers previous investigators' scientific work on NFRPC, with a focus on the physical, thermal, water absorption, mechanical, and tribological properties of natural fiber and NFRPC.

Chapter - 3: Type of materials utilized in this research and the various experimental test methods employed in this study are described in this chapter. This chapter also provides information on the types of characterization techniques and fabrication methods of the investigated natural fibers and NFRPC, as well as specifics on various fiber surface modification techniques.

Chapter - 4: This chapter describes the test findings for the physical (XRD, FTIR, and XRD) and thermal (TGA/DSC) characterization of the natural fibers under consideration.

Chapter -5: This chapter describes the test findings for the water absorption, mechanical, and tribological properties of the NFRPC under consideration.

Chapter -6: This chapter summarizes the research outcomes and describes particular inferences gained from the experimental data, proposed applications, and future research possibilities.

The next chapter presents the reviews of research papers that are currently accessible on a variety of subjects related to NFRPC, with a focus on their physical, thermal, mechanical and tribological properties.