CHAPTER 1
INTRODUCTION

1.1 COMPOSITE MATERIALS

Composite materials are materials made from two or more constituent materials with significantly different physical or chemical properties, which when combined, produce a material with characteristics different from those of the individual components. The individual components remain separate and distinct within the finished structure.

1.1.1 Classification:

The composite materials are broadly classified into the following three types:

- Metal matrix composites
- Polymer matrix composites
- Ceramic matrix composites

1.1.1.1 Metal Matrix Composites

A metal matrix composite (MMC) is a composite material with at least two constituent parts, one being a metal. The other material may be a different metal or another material, such as a ceramic or organic compound. When at least three materials are present, it is called a hybrid composite. MMCs are made by dispersing a reinforcing material into a metal matrix. The reinforcement surface can be coated to prevent a chemical reaction with the matrix. For example, carbon fibers are commonly used in aluminum matrix to synthesize composites showing low density and high strength. However, carbon reacts with aluminum to generate a brittle and water-soluble compound Al$_4$C$_3$ on the surface of the fiber. To prevent this reaction, carbon fibers are coated with nickel or titanium boride.

MMC are always more expensive than the more conventional materials they replace. As a result, their improved properties and performance can justify the added cost. Today these applications are found most often in aircraft components, space systems and high-end or "boutique" sports equipment. The scope of applications will certainly increase as manufacturing costs are reduced.
In comparison with the conventional polymer matrix composites, MMCs are resistant to fire, can operate in wider range of temperatures, do not absorb moisture, have better electrical and thermal conductivity, are resistant to radiation damage, and do not display out gassing. But, MMCs tend to be more expensive, the fiber-reinforced materials may be difficult to fabricate, and the available experience in use is limited.

### 1.1.1.2 Polymer Matrix Composites

Composite materials are made up of two or more materials on a macroscopic scale. Polymer matrix composites (PMC) are plastics (resins) within which there are embedded fibers. The plastic is known as the matrix, and the fibers oriented within it are known as the reinforcement. The reinforcement tends to be stiffer and stronger than the matrix providing stiffness and strength. Reinforcement is laid in a particular direction, within the matrix so that the resulting material will have different properties in different directions i.e. composites have anisotropic properties. This characteristic is exploited to optimize the design and provide high mechanical performance where it is needed.

### 1.1.1.3 Ceramic Matrix Composites

Ceramic matrix composites (CMCs) are a subgroup of composite materials as well as a subgroup of technical ceramics. They consist of ceramic fibers embedded in a ceramic matrix, thus forming a ceramic fiber reinforced ceramic (CFRC) material. The matrix and fibers can consist of any ceramic material, hereby carbon and carbon fibers can also be considered a ceramic material.

The motivation to develop CMCs was to overcome the problems associated with the conventional technical ceramics like alumina, silicon carbide, aluminium nitride, silicon nitride or zirconia as they fracture easily under mechanical or thermo-mechanical loads because of cracks initiated by small defects or scratches. The crack resistance like that of glass is very low. To increase the crack resistance or fracture toughness, particles (so-called monocrystalline whiskers or platelets) were embedded into the matrix. However, the improvement was limited, and the products have found application only in some ceramic cutting tools.
Generally, CMC names include a combination of type of fiber/type of matrix. For example, C/C stands for carbon-fiber-reinforced carbon (carbon/carbon), or C/SiC for carbon-fiber-reinforced silicon carbide. Sometimes the manufacturing process is included, and a C/SiC composite manufactured with the liquid polymer infiltration (LPI) process is abbreviated as LPI-C/SiC.

The important commercially available CMCs are C/C, C/SiC, SiC/SiC and Al2O3/Al2O3. They differ from conventional ceramics in the following properties, presented in greater detail below:

- Elongation to rupture up to 1%
- Strongly increased fracture toughness
- Extreme thermal shock resistance
- Improved dynamical load capability
- Anisotropic properties following the orientation of fibers

1.2 TYPES OF POLYMER MATRIX COMPOSITES

(i) Thermoplastic Polymer Composites

The composites made from thermoplastic materials are called thermoplastic polymer composites. Thermoplastics consist of linear or branched chain molecules having strong intra molecular bonds but weak intermolecular bonds. They can be reshaped by application of heat and pressure and are either semi crystalline or amorphous in structure. Examples include polyethylene, polypropylene, polystyrene, nylons, polycarbonate, polyacetals, polyamide-imides, polyether ether ketone, polysulfone, polyphenylene sulfide, polyether imide, and so on.

A Thermoplastic, also known as a thermo softening plastic, [1] is a polymer that becomes pliable or moldable above a specific temperature, and returns to a solid state upon cooling. Most thermoplastics have a high molecular weight, whose chains associate with intermolecular forces. This property allows thermoplastics to be remolded because the intermolecular interactions spontaneously reform upon cooling. In this way, thermoplastics differ from thermosetting polymers, which form irreversible chemical bonds during the curing process. Thermoset bonds break down upon melting and do not reform upon cooling.
Thermoplastics are easily recyclable, compared to thermosets, because the polymer chain does not degrade when melted down. This is because the weaker interactions between polymer chains break down at much lower temperatures than the chemical bonds between monomers. This allows thermoplastics to be recycled indefinitely until the polymers are broken down to the point at which the material loses structural integrity.

In real-world recycling, thermoplastics have a limited recyclable lifespan due to the degradation of the polymers and contamination during the recycling process. Contaminants can be inert materials, which act as fillers, or they can be other plastics, which alter the physical properties of the resulting material.

Thermoplastics have a good range of properties and are energy efficient both in their manufacture and processing. Thermoplastic components can be made in very high volume with high precision and low cost. Thermoplastics can replace metals with a considerable weight savings, provided proper care is taken in design. Most thermoplastics have better fatigue properties than metals and will tolerate larger deflections than metals without deforming.

Thermoplastics have a few disadvantages some degrade in direct sunlight or under high U.V. light levels. Many materials have poor resistance to hydrocarbons, organic solvents, and highly polar solvents but others have excellent resistance to these materials. Thermoplastics suffer from creep, a relaxation of the material under long term loading. Many thermoplastic materials, especially composites, tend to fracture rather than deform under high stress levels.

(ii) Thermosetting Polymer

The composites made from thermosetting plastic materials are called thermoplastic polymer composites. Thermosets have cross-linked or network structures with covalent bonds with all molecules. They do not soften but decompose on heating. Once solidified by cross-linking process, they cannot be reshaped. Common examples are epoxies, polyesters, phenolics, ureas, melamine, silicone and polyimides.
A thermosetting plastic, also known as a thermoset, is a polymer material that irreversibly cures. The cure may be done through heat (generally above 200 °C (392 °F)), through a chemical reaction (two-part epoxy, for example), or irradiation such as electron beam processing.

Thermoset materials are usually liquid or malleable prior to curing and designed to be molded into their final form, or used as adhesives. Others are solids like that of the molding compound used in semiconductors and integrated circuits (IC). Once hardened, a thermoset resin cannot be reheated and melted back to a liquid form.

According to IUPAC recommendation, a thermosetting polymer is a prepolymer in a soft solid or viscous state that changes irreversibly into an infusible, insoluble polymer network by curing. Curing can be induced by the action of heat or suitable radiation, or both. A cured thermosetting polymer is called a thermoset [2].

The curing process transforms the resin into a plastic or rubber by a cross-linking process. Energy and/or catalysts are added that cause the molecular chains to react at chemically active sites (unsaturated or epoxy sites, for example), linking into a rigid, 3-D structure. The cross-linking process forms a molecule with a larger molecular weight, resulting in a material with a higher melting point. During the reaction, the molecular weight has increased to a point at which the melting point is higher than the surrounding ambient temperature and the material becomes solid.

Uncontrolled reheating of the material results in reaching the decomposition temperature before the melting point is obtained. Therefore, a thermoset material cannot be melted and re-shaped after it is cured. This implies that thermosets cannot be recycled, except as filler material [3].

Thermoset materials are generally stronger than thermoplastic materials due to this three dimensional network of bonds (cross-linking), and are also better suited to high-temperature applications up to the decomposition temperature. However, they are more brittle. Since they are "set" (non-reformable), they tend not to be recyclable.
1.2.1 Advantages of polymer composite

PMCs are very popular due to their low cost and simple fabrication methods. Use of non-reinforced polymers as structure materials is limited by the low level of their mechanical properties, namely strength, modulus, and impact resistance. Reinforcement of polymers by strong fibrous network permits fabrication of PMCs, which is characterized by the following:

- High specific strength
- High specific stiffness
- High fracture resistance
- Good abrasion resistance
- Good impact resistance
- Good corrosion resistance
- Good fatigue resistance
- Low cost

1.2.2 Limitations of polymer Composites

The main disadvantages of PMCs are:

- Low thermal resistance and
- High coefficient of thermal expansion.

1.2.3 Applications of polymer Composites

Polymer Composites are used for manufacturing

- Aerospace structures: The military aircraft industry has mainly led the use of polymer composites. In commercial airlines, the use of composites is gradually increasing. Space shuttle and satellite systems use graphite / epoxy for many structural parts.
- Marine: Boat bodies, canoes, kayaks, and so on.
- Automotive: Body panels, leaf springs, drive shaft, bumpers, doors, racing car bodies, and so on.
- Sports goods: Golf clubs, skis, fishing rods, tennis rackets, and so on.
- Bullet proof vests and other armor parts.
- Chemical storage tanks, pressure vessels, piping, pump body, valves, and so on.
- Biomedical applications: Medical implants, orthopedic devices, X-ray tables.
- Bridges made of polymer composite materials are gaining wide acceptance due to their lower weight, corrosion resistance, longer life cycle, and limited earthquake damage.
- Electrical: Panels, housing, switchgear, insulators, and connectors.

### 1.3 RESINS

Typically, most commonly used resins in thermosetting composite materials, include the following:

**Polyester resin** tends to have yellowish tint, and is suitable for most backyard projects. Its weaknesses are that it is UV sensitive and can tend to degrade over time, and thus generally it is also coated to help preserve it. It is often used in the making of surfboards and for marine applications. Its hardener is a peroxide, often MEKP (methyl ethyl ketone peroxide). When the peroxide is mixed with the resin, it decomposes to generate free radicals, which initiate the curing reaction. Hardeners in these systems are commonly called catalysts, but since they do not re-appear unchanged at the end of the reaction, they do not fit the strictest chemical definition of a catalyst.

**Vinyl ester resin** tends to have a purplish to bluish to greenish tint. This resin has lower viscosity than polyester resin, and is more transparent. This resin is often billed as being fuel resistant, but will melt in contact with gasoline. This resin tends to be more resistant over time to degradation than polyester resin, and is more flexible. It uses the same hardeners as polyester resin (at a similar mix ratio) and the cost is approximately the same.

**Epoxy resin** is almost totally transparent when cured. In the aerospace industry, epoxy is used as a structural matrix material or as structural glue.

**Shape memory polymer (SMP) resins** have varying visual characteristics depending on their formulation. These resins may be epoxy-based, which can be
used for auto body and outdoor equipment repairs; cyanate-ester-based, which are used in space applications; and acrylate-based, which can be used in very cold temperature applications, such as sensors that indicate whether perishable goods have warmed above a certain maximum temperature. These resins are unique in that their shape can be repeatedly changed by heating above their glass transition temperature ($T_g$). When heated, they become flexible and elastic, allowing for easy configuration. Once they are cooled, they will maintain their new shape. The resins will return to their original shapes when they are reheated above their $T_g$. The advantage of shape memory polymer resins is that they can be shaped and reshaped repeatedly without losing their material properties. These resins can be used in fabricating shape memory composites.

1.4 FIBERS

Reinforcement usually adds rigidity and greatly impedes crack propagation. Thin fibers can have very high strength, and provided if they are mechanically well attached to the matrix, they can greatly improve the composite's overall properties [9].

Fiber-reinforced composite materials can be divided into two main categories normally referred to as short fiber-reinforced materials and continuous fiber-reinforced materials. Continuous fiber reinforced materials will often constitute a layered or laminated structure. The woven and continuous fiber styles are typically available in a variety of forms, pre-impregnated with the given matrix (resin), dry, uni-directional tapes of various widths, plain weave, harness satins, braided, and stitched.

The short and long fibers are typically employed in compression moulding and sheet moulding operations. These come in the form of flakes, chips, and random mate (which can also be made from a continuous fiber laid in random fashion until the desired thickness of the ply / laminate is achieved).

Common fibers used for reinforcement include glass fibers, carbon fibers, cellulose (wood/paper fiber and straw) and high strength polymers, for example aramid.
1.4.1 Natural Fibers

(i) Plant fiber

Natural fibers are made from plant, animal and mineral sources. Natural fibers can be classified according to their origin as shown in Table 1.1.

**Table 1.1. Classification of natural fibers according to their origin**

<table>
<thead>
<tr>
<th>Category</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seed fiber</td>
<td>Fibers collected from seeds or seed cases. E.g. cotton and kapok</td>
</tr>
<tr>
<td>Leaf fiber</td>
<td>Fibers collected from leaves. E.g., sansevieria, fique, sisal, banana and agave.</td>
</tr>
<tr>
<td>Bast fiber</td>
<td>Fibers are collected from the skin or bast surrounding the stem of their respective plant. These fibers have higher tensile strength than other fibers. Therefore, these fibers are used for durable yarn, fabric, packaging, and paper. Some examples are flax, jute, kenaf, industrial hemp, ramie, rattan, and vine fibers.</td>
</tr>
<tr>
<td>Skin fiber</td>
<td>Fibers are collected from the fruits of the plant, e.g. coconut (coir) fiber.</td>
</tr>
<tr>
<td>Fruit fiber</td>
<td>Fibers are actually the stalks of the plant. E.g. straws of wheat, rice, barley, and other crops including bamboo and grass. Tree wood is also such a fiber.</td>
</tr>
</tbody>
</table>

The most used plant fibers are cotton, flax and hemp, although sisal, jute, kenaf, bamboo and coconut are also widely used.

Hemp fibers are mainly used for ropes and aero foils because of their high suppleness and resistance within an aggressive environment. Hemp fibers are, for example, currently used as a seal within the heating and sanitary industries.

(ii) Animal fibers

Animal fibers generally comprise proteins such as collagen, keratin and fibroin; examples include silk, sinew, wool, catgut, angora, mohair and alpaca.

Animal hair (wool or hair): Fiber or wool taken from animals or hairy mammals. E.g. sheep's wool, goat hair (cashmere, mohair), alpaca hair, horse hair, etc.
Silk fiber: Fiber secreted by glands (often located near the mouth) of insects during the preparation of cocoons.

Avian fiber: Fibers from birds, e.g. feathers and feather fiber.

### 1.4.2 Synthetic fiber

Synthetic fibers are the result of extensive research by scientists to improve on naturally occurring animal and plant fibers. In general, synthetic fibers are created by forcing, usually through extrusion, fiber-forming materials through holes (called spinnerets) into the air, forming a thread. Before the development of synthetic fibers, artificially manufactured fibers were made from cellulose, which comes from plants. These fibers are called cellulose fibers.

Synthetic fibers are made from synthesized polymers or small molecules. The compounds that are used to make these fibers come from raw materials such as petroleum-based chemicals or petrochemicals. These materials are polymerized into a long, linear chemical that bond two adjacent carbon atoms. Differing chemical compounds will be used to produce different types of fibers. Although there are several different synthetic fibers, they generally have the same common properties. Generally, they are known for the following characteristics:

- Heat-sensitive
- Resistant to most chemicals
- Resistant to insects, fungi and rot when damp and warm may attract them
- Low moisture absorbency
- Electrostatic
- Flame resistant
- Density or specific gravity
- Pilling
- Low melting temperature
- Extremely hazardous to the environment.
- Can shrink, wrap and suffocate the user.
- Can get overheated
- Do not depend either on an agricultural crop or on animal farming.
Generally cheaper than natural fiber.
Possess unique characteristics which make them popular dress material.
Dry up quickly, are durable, readily available and easy to maintain.
Can make you get cold when wet

1.4.3 Metallic fibers

Metallic fibers can be drawn from ductile metals such as copper, gold or silver and extruded or deposited from more brittle ones, such as nickel, aluminum or iron.

1.4.4 Carbon fiber

Carbon fibers are often based on oxidized and via pyrolysis carbonized polymers like PAN, but the end product is almost pure carbon.

1.4.5 Silicon carbide fiber

Silicon carbide fibers, where the basic polymers are not hydrocarbons but polymers, where about 50% of the carbon atoms are replaced by silicon atoms, so-called poly-carbo-silanes. The pyrolysis yields an amorphous silicon carbide, including mostly other elements like oxygen, titanium, or aluminium, but with mechanical properties very similar to those of carbon fibers.

1.4.6 Fiberglass

Fiberglass, made from specific glass, and optical fiber, made from purified natural quartz, are also man-made fibers that come from natural raw materials, silica fiber, made from sodium silicate (water glass) and basalt fiber made from melted basalt.

1.4.7 Mineral fibers

Mineral fibers can be particularly strong because they are formed with a low number of surface defects, and asbestos is a common one [4].
1.4.8 Cellulose fibers

Cellulose fibers are a subset of man-made fibers, regenerated from natural cellulose. The cellulose comes from various sources. Modal is made from beech trees, bamboo fiber is a cellulose fiber made from bamboo, and sea cell is made from seaweed.

1.5 FILLER MATERIALS

Fillers are particles added to materials (plastics, composite material, and concrete) to lower the consumption of more expensive binder material or to better some properties of the mixture material. Worldwide, more than 53 million tons of fillers with a total sum of approximately EUR16 billion are used every year in the different application areas, such as paper, plastics, rubber, paints, coatings, adhesives and sealants. As such, fillers, produced by more than 700 companies, rank among the world's major raw materials and found in a variety of goods for daily consumer needs.

Types of fillers:

Formerly, fillers were used predominantly to cheapen end products, in which case they are called extenders. Among the 21 most important fillers, calcium carbonate holds the largest market volume and is mainly used in the plastics sector [5]. While the plastic industry mostly consumes ground calcium carbonate, the paper industry primarily uses precipitated calcium carbonate that is derived from natural minerals.

In some cases, fillers also enhance the properties of the products, e.g. in composites. In such cases, a beneficial chemical interaction develops between the host material and the filler. As a result, a number of optimized types of fillers, nano-fillers or surface treated goods have been developed.

1.6 MECHANICAL CHARACTERIZATION

A materials property is an intensive, often quantitative, property of a solid or quasi-solid. Quantitative properties may be used as a metric by which the
benefits of one material versus another can be assessed, thereby aiding in materials selection.

A property may be a constant or may be a function of one or more independent variables, such as temperature. Materials properties often vary to some degree according to the direction in which they are measured, a condition referred to as anisotropy. Material properties that relate two different physical phenomena often behave linearly (or approximately so) in a given operating range, and may, then, be modeled as a constant for that range. This linearization can significantly simplify the differential constitutive equations that the property describes.

Some material properties are used in relevant equations to predict the attributes of a system a priori. For example, if a material of a known specific heat gains or loses a known amount of heat, the temperature change of that material can be determined. Material properties are most reliably measured by standardized test methods. Many such test methods have been documented by their respective user communities and published through ASTM International.

1.6.1 Tensile Properties

Tensile testing, also known as tension testing [6], is a fundamental materials science test in which a sample is subjected to a controlled tension until failure. The results from the test are commonly used to select a material for an application, for quality control, and to predict how a material will react under other types of forces. Properties that are directly measured via a tensile test are ultimate tensile strength, maximum elongation and reduction in area [7]. From these measurements the following properties can also be determined: Young's modulus, Poisson's ratio, yield strength, and strain-hardening characteristics. Uniaxial tensile testing is the most commonly used for obtaining the mechanical characteristics of isotropic materials.

1.6.2 Flexural properties

Flexural strength, also known as modulus of rupture, bend strength, or fracture strength, a mechanical parameter for brittle material, is defined as a
material's ability to resist deformation under load. The transverse bending test is most frequently employed, in which a rod specimen having either a circular or rectangular cross-section is bent until fracture using a three point flexural test technique. The flexural strength represents the highest stress experienced within the material at its moment of rupture. It is measured in terms of stress, here given the symbol $\sigma$.

1.6.3 Impact Property

The impact test, also known as the V-notch test, is a standardized high strain-rate test which determines the amount of energy absorbed by a material during fracture. This absorbed energy is a measure of a given material's notch toughness and acts as a tool to study temperature-dependent ductile-brittle transition. It is widely applied in industry, since it is easy to prepare and conduct and results can be obtained quickly and cheaply. A disadvantage is that some results are only comparative [8].

1.6.4 Hardness Property

Hardness is a measure of how resistant solid matter is to various kinds of permanent shape change when a force is applied. Macroscopic hardness is generally characterized by strong intermolecular bonds, but the behavior of solid materials under force is complex. Therefore, there are different measurements of hardness such as scratch hardness, indentation hardness, and rebound hardness. Hardness is dependent on ductility, elastic stiffness, plasticity, strain, strength, toughness, viscoelasticity, and viscosity. Common examples of hard matter are ceramics, concrete, certain metals, and super hard materials, which can be contrasted with soft matter.

1.6.5 Water Absorption Test

Water absorption data may be obtained by immersion of specimens for 24 hours or longer in water at 73.4° F. Upon removal, specimens are dried and weighed immediately. The increase in weight is reported as the percentage gained.

Various plastic absorb varying amount of water and the presence of absorbed water may affect plastics in different ways. Electrical properties change most noticeably with water absorption and this is one of the reasons why polyethylene, is highly favored as a dielectric, Plastics which absorb relatively larger amount of water
tend to change dimension in the process. When dimensional stability is required in products made of such plastics, grades with fewer tendencies to absorb water are chosen. The water absorption rate of acetal type plastics is low as to have a negligible effect on properties.

1.7 SEM

A scanning electron microscope (SEM) is a type of electron microscope that produces the images of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that can be detected and that contain information about the sample's surface topography and composition. The electron beam is generally scanned in a raster scan pattern, and the beam's position is combined with the detected signal to produce an image. SEM can achieve resolution better than 1 nanometer. Specimens can be observed in high vacuum, low vacuum and in environmental SEM specimens can be observed in wet conditions.

The most common mode of detection is by the secondary electrons emitted by atoms excited by the electron beam. The number of secondary electrons is a function of the tilt of the surface. On a flat surface, the plume of secondary electrons is mostly contained by the sample, but on a tilted surface, the plume is partially exposed and more electrons are emitted. By scanning the sample and detecting the secondary electrons, an image displaying the tilt of the surface is created.