CHAPTER - 1

INTRODUCTION

1.1 Introduction of Composite materials

The composite material consists of two or more distinct constituent materials which bound together to form an integral unit. In nature, composite materials have been in existence for millions of years. Wood, bamboo and bone are just a few examples of the natural occurring composite materials. Man has learned to fabricate composite materials relatively recently. Perhaps, one of the first evidence of a man-made composite material is the mud blocks reinforced with straw. The composite material fabrication technology has since progressed from straw reinforced mud-blocks to man-made fibre reinforced composite materials such as fibre reinforced polymers, ceramic matrix, metallic matrix and carbon-carbon composite materials [Choo, F.K.S.1990].

An obvious advantage that the fibre reinforced composite materials have over the conventional engineering materials such as copper, steel, aluminium, titanium, etc., is the high specific strength and modulus. High specific strength and specific modulus have important implications on the engineering applications of composite materials [Chung, Deborah D.L.2010]. It means that the composite materials are strong and stiff and yet light weight. Such characteristics are very desirable in aeronautical and aerospace industry. The weight savings are realized by fabricating structural components out of composite materials which is directly translated into fuel savings which in turn makes the operation of an aeroplane or a space vehicle more economical. It was observed that the savings in the operating cost of an aeroplane will be able to pay for a substantial amount of the initial cost of the aeroplane. This factor has been the main impetus on the development of composite materials during the fossil fuel crisis.
The properties of the composite reflect the properties of the reinforcement which greatly contribute to the different properties in different directions. The reinforcement caters to the stiffness and strength of the composites.

1.1.1 Classification of composites

Composite materials consist of a Matrix Phase and Dispersed Phase (commonly referred to fibers). The composite materials are classified based on the above two phases (Figure 1.1).

1.1.1.1 Matrix phase

(i) Polymer Matrix Composites (PMCs)

Polymer matrix composites are composed of a matrix material from thermoset or thermoplastic and embedded in carbon, kevlar or glass fibres in a dispersed phase.

(ii) Metal matrix composites (MMCs)

Metal matrix composites are composed of a metallic matrix (aluminium, copper, magnesium) and dispersed phase of metallic (tungsten, lead, molybdenum). In order to offer high strength, metallic matrix materials require high modulus reinforcements.

(iii) Ceramic Matrix Composites (CMCs)

Ceramic matrix composites are composed of a ceramic matrix and imbedded fibres of other ceramic material in dispersed phase. Ceramic matrices are the obvious choice for high temperature applications.
Figure 1.1 Classification of composites based on matrix

1.1.1.2 Reinforcing phase

The reinforcement in a composite material comes in various forms.

(i) Particle-Reinforced composite

The reinforcement is in the form of particles which are of the order of a few microns in the diameter. The particles are generally added to increase the modulus and decrease the ductility of the matrix materials. In this case, the load is shared by both particles and matrix materials. However, the load shared by the particles is much larger than the matrix material.

(ii) Fiber-Reinforced Composites

Fiber-Reinforced Composites often aim to improve the strength from weight and stiffness to weight ratios (i.e. desire light-weight structures that are strong and stiff). Glass or Metal Fibers are generally embedded in polymeric matrices.
Fibers are available in 3 basic forms:

(a) **Continuous** Fibers - Long, straight and generally laid-up parallel to each other.

(b) **Chopped** Fibers - Short and generally randomly distributed (fiberglass).

(c) **Woven** Fibers - Come in cloth form and provide multidirectional strength.

(iii) **Flake**

Flake is a small, flat, thin piece or layer that is broken from a larger piece. Since these are two dimensional in geometry, they impart almost equal strength in all directions of their planes. Thus, these are very effective reinforcement components. The flakes can be packed more densely when they are laid parallel, even denser than unidirectional fibres and spheres.

(iv) **Whisker**

These are nearly perfect single crystal fibres. These are short, discontinuous and polygonal in cross-section.

1.1.2 **Fibre reinforced composites materials**

Fiber-reinforced composites consist of a polymer matrix and fibers of high strength and modulus. With distinct interfaces (boundary) between them, the fibers, which are the principal load-carrying members are embedded in or bonded to a matrix, which is a load transfer medium between fibers and a fiber protector against environmental damage due to elevated temperatures and humidity [Mallick, P.K.1993].
Probably the most common type of fibre reinforced composite is the ‘laminate’. Laminate Composites are composed of layers of materials held together by matrix. Fibre orientation in each layer and the stacking sequence of various layers can be varied to generate a wide range of physical and mechanical properties.

1.1.2.1 Fiber factors contribute to the mechanical performance

Four fiber factors contribute to the mechanical performance of a composite:

- **Length**: The fibers can be long or short. Long, continuous fibers are easy to orient and process, but short fibers cannot be controlled fully for proper orientation. Long fibers provide many benefits over short fibers. These include impact resistance, low shrinkage, improved surface finish, and dimensional stability [Autar K, Kaw. 2006]. However, short fibers provide low cost, are easy to work with and have fast cycle time fabrication procedures. Short fibers have fewer flaws and therefore have higher strength.

- **Orientation**: Fibers oriented in one direction give very high stiffness and strength in that direction. If the fibers are oriented in more than one direction, such as, in a mat, there will be high stiffness and strength. However, for the same volume of fibers per unit volume of the composite, it cannot match the stiffness and strength of unidirectional composites.

- **Shape**: The most common shape of fibers is circular because handling and manufacturing them is easy. Hexagon and square shaped fibers are possible, but their advantages of strength and high packing factors do not outweigh the difficulty in handling and processing.

- **Material**: The material of the fiber directly influences the mechanical performance of a composite. Fibers are generally expected to have
high elastic moduli and strengths. This expectation and cost have been key factors in the graphite, aramids, and glass dominating the fiber market for composites. The applications of fibre reinforced materials are listed in Table 1.1.

**Table 1.1 Fibre reinforced materials and applications**

<table>
<thead>
<tr>
<th>Materials</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Borsic aluminum</td>
<td>Fan blades in engine, other aircraft and aerospace application.</td>
</tr>
<tr>
<td>Kevlar-epoxy</td>
<td>Aircraft, aerospace application (including space shuttle), boat hulls, sporting.</td>
</tr>
<tr>
<td>Graphite-polymer</td>
<td>Aerospace and automotive application, sporting goods.</td>
</tr>
<tr>
<td>Silicones</td>
<td>Electrical application (Printed circuit board)</td>
</tr>
<tr>
<td>Glass-polymer</td>
<td>Light weight automotive application, water and marine application, corrosion resistant application, sporting goods, aircraft and aerospace components.</td>
</tr>
</tbody>
</table>

1.2 Introduction of Nanoparticles

The transition from microparticles to nanoparticles yields dramatic changes in physical properties. Nanoscale materials have a large surface area for a given volume. Since many important chemical and physical interactions are governed by surfaces and surface properties, a nanostructured material can have substantially different properties from a larger-dimensional material of the same composition. In the case of particles and fibers, the surface area per unit volume is inversely proportional to the material’s diameter, thus, the smaller the diameter, the greater the surface area per unit volume [Luo, J.J.et al, 2003].

Polymer nanocomposite is a new class of material in which resin materials is usually tailored by inorganic nanoparticles to exhibit improved mechanical, thermal and fire resistance properties [Alexander, M. et al, 2000 and Wang and Pinnavaia 1998]. Such enhancement in the properties of nanocomposites occurs mostly due to their unique phase morphology and improved interfacial
properties [Novak, B.M. 1993]. The types of nanomaterials that are most widely used for this purpose include: nanotubes, nanoclays, silica particles and electro-spun polymeric nanofibers.

### 1.2.1 Carbon nanotubes

In 1991, long and thin cylinders of carbon nanotubes (CNT) were discovered by Iijima, S. There has been a phenomenal growth in the synthesis of various composites using these carbon nanotubes. The morphology of a carbon nanotube is defined by the orientation and magnitude of the chiral vector in a graphene sheet, which is ‘‘wrapped up’’ to form the single-walled carbon nanotube (SWCNT) [Thostenson, E.T. et al, 2005]. The two limiting configurations are armchair and zigzag nanotubes (Figure 1.2).

![Atomic structures of (a) armchair and (b) zig-zag carbon nanotubes](Thostenson, E.T, 2001)

The exceptional properties of carbon nanotube excerpted from Collins and Avouris [2001]. The density of a SWCNT is about 1.33–1.40 g/cm³, which is just one-half of the density of aluminum. The elastic modulus of SWCNT is comparable to that of diamond (1.2 TPa). The reported tensile strength of SWCNT is much higher than that of high-strength steel (2 GPa). The tremendous resilience of SWCNT in sustaining bending to large angles and restraightening without damage is distinctively different from the plastic deformation of metals and brittle
fracture of carbon fibers at much lower strain when subjected to the same type of deformation. The electric current carrying capability is estimated to be $1 \times 10^9$ amp/cm$^2$, whereas copper wires burn out at about $1 \times 10^6$ amp/cm$^2$. The thermal conductivity of SWCNT is predicted to be 6000 W/m K at room temperature; this is nearly double the thermal conductivity of diamond of 3320 W/m K. SWCNTs are stable up to 2800 °C in vacuum and 750 °C in air, whereas metal wires in microchips melt at 600–1000 °C. SWCNTs have great potential in field emission applications because they can activate phosphors at 1–3 V if electrodes are spaced 1 µm apart. Traditional Mo tips require fields of 10–100 V/µm and have very limited lifetimes. Carbon nanotubes possess excellent mechanical properties such as reinforcement, for imparting strength, toughness and very large aspect ratios have stimulated the development of nanotube-reinforced composites for both structural and functional applications [Vaia, R.A. et al, 2004 and Curtin, W.A. et al, 2004]. These carbon nanotubes can be dispersed to develop nano-enhanced composites using two methods. They are by physical mixing or ultrasonic dispersion techniques [Morinobu, E. et al, 2006].

### 1.2.2 Nanoclay

The essential nanoclay raw material is montmorillonite a 2-to-1 layered smectite clay mineral with a platey structure. Individual platelet thicknesses are just one nanometer. One gram of powdered material can have billions of nanoparticles with a surface area of many square meters [Guggenheim. et al, 1995]. Organo treated montmorillonite clay is widely used as nanofiller in the polymer due to its superior compatibility with organic matrix, specific surface area, aspect ratio and nano dispersible characteristics. Nanoclay increases strength, stiffness and heat resistance but decreases moisture absorption, flammability and permeability to gas and water. This in turn can result in significant weight reduction, which is of obvious importance in aerospace and marine applications [Abdulakh, k. et al, 2006].

In polymer nanocomposites (PCNs), montmorillonite based layered silicate clay is commonly used as reinforcement in polymer matrix
Its crystal lattice consists of two-dimensional layers where a central octahedral sheet of alumina or magnesia is fused into two external silica tetrahedron by the tip, so that the oxygen ions of the octahedral sheet also belong to tetrahedral sheets (Figure 1.3) [Pinnavaia, T.J. et al, 2000].

![Figure 1.3 Structure of layered clay](image)

The layer thickness (which constitutes two silica tetrahedron and an octahedral site) is around 1nm and the lateral dimensions of these layers vary from 300 Å to several microns, with a regular gap in between them called the interlayer or the gallery. In montmorillonite (MMT) clay, Mg\(^{2+}\) is situated at the octahedral site instead of Al\(^{3+}\). As a result of this, a negative charge is generated within the crystal layer. To counterbalance the charge, the Na\(^+\) ion is present at the interlayer region and hence becomes neutral [Alaxandre, M. et al, 2000 and Giannelis, E. P. et al, 1999]. To disperse nanolayers in the polymer matrix, unmodified MMT clay is given surface treatment so that they become hydrophobic.

The commonly used surfactants are alkyl ammonium ions (R-NH\(^3+\), where R is an alkyl group). The process of such treatment is called “cation exchange process”. In this process the existing Na\(^+\) ions of MMT are replaced by alkyl ammonium ions in the interlayer region.

The advantage of using alkyl ammonium ions is that they have same charge as Na\(^+\), which does not create charge misbalance. In addition to this, alkyl
ammonium ions attract the matrix polymer due to their organophilic nature. As a result, individual nanolayers can disperse in the polymer matrix leading to the formation of nanolayer dispersed nanocomposites [Vaia, R. A. et al, 1994].

1.2.3 Silica and Alumina Nanoparticles

One of the nanoparticles which have been used for improving the mechanical properties of polymers is nanosilica (SiO$_2$). Researchers claim that nanosilica particles impact higher stiffness, tensile strength, modulus, impact strength, toughening, crystallinity, viscosity, and creep resistance in polyethylene, polypropylene, and thermoplastic elastomeric nanocomposites, depending on surface properties of such nano-silica particles [Parvinzadeh Gashti, M. et al, 2012]. Nanosilica is used to improve the mechanical properties of thermoset polymer. Silica particles, with a mean diameter ranged between 30 and 50 µm, particles surface area 150 m$^2$/g and the average pore radius, $r_p$, 30 nm, were used as inorganic substrate material.

Aluminium oxide (Al$_2$O$_3$) nanopowder with an average particle size of 40 nm to 50 nm holds a specific surface area of 35m$^2$/g to 45m$^2$/g [Azom, 2007]. They have high-temperature strength, high oxidation ability, excellent dielectric and thermal properties. Aluminium oxide is widely used in refractories, ceramics, abrasive and biomedical applications.

1.2.4 Nanofibers

When the diameters of polymer fiber materials are shrunk from micrometers (e.g. 10–100 µm) to sub microns or nanometers (e.g. 10x10$^{-3}$–100x10$^{-3}$ µm), there appear several amazing characteristics such as very large surface area to volume ratio (this ratio for a nanofiber can be as large as 10$^3$ times of that of a microfiber), flexibility in surface functionalities and superior mechanical performance (e.g. stiffness and tensile strength) compared with any other known form of the material [Zheng-Ming Huang, Y.Z. et al, 2003].
The polymer nanofibers are produced by various techniques of electrospinning, template synthesis and phase separation. For instance, [Fong, H.et al, 1999(a)] electrospinning of aqueous poly ethylene oxide (PEO) dissolved in ethanol-to-water solutions, with viscosities in the range of 1–20 poises and surface tension between 35 and 55 dynes/cm were suitable for fiber formation. As long as a polymer can be electrospun into nanofibers, ideal targets would be (1) the diameters of the fibers are consistent and controllable, (2) the fiber surface is defect-free or defect-controllable and (3) continuous single nanofibers are collectable. A schematic diagram to interpret electrospinning of polymer nanofibers is shown in Figure 1.4. There are basically three components to fulfill the process: a high voltage supplier, a capillary tube with a pipette or needle of small diameter, and a metal collecting screen. In the electrospinning process a high voltage is used to create an electrically charged jet of polymer solution or melt out of the pipette. Before reaching the collecting screen, the solution jet evaporates or solidifies, and is collected as an interconnected web of small fibers [Fong and Reneker, 1999(b)].

![Figure 1.4 (a) Polymer nanofibers by electrospinning and (b) PLLA nanofibers [Bognitzki, M. et al, 2001](image)](image)

The outstanding properties make the polymer nanofibers to be optimal material for many important applications. This is because nanofibers can have even better mechanical properties than micro fibers of the same materials. Hence, the
superior structural properties of nanocomposites can be anticipated. Moreover, nanofiber reinforced composites may possess some additional merits which cannot be shared by traditional (microfiber) composites [Larrondo and Manley, 1981].

1.2.5 Nanomaterials demand and Applications

A detailed market survey was carried out to assess the growing demand for nanocomposites. It was observed that a conducive environment for nanocomposites exists because of its low cost and its innumerable varieties of applications. Nylon-6 was the first polymer to be used in the development of nanocomposites over 15 years ago. The use of organoclay as precursors to nanocomposite formation has been extended into various polymer systems [LeBaron, P.C. et al, 1999], which include epoxies, polyurethanes, polyimides, nitrile rubber, polyesters, polypropylene, polystyrene and polysiloxanes. The development activities have spread to all regions of the world. Some of the programs are focused on polypropylene, polyester, polyvinyl chloride, acrylics, polystyrene and a range of elastomers as well as traditional thermosets.

Nanomaterials are being applied across a raft of industries and technologies due to their outstanding, mechanical, magnetic, optical, catalytic and electronic properties, which depend greatly on their size, structure, and shape. The Global Market for Nanomaterials 2002-2016 is the most comprehensive study ever conducted on the nanomaterials market, which will greatly impact all industries in the coming years. Future Markets conservatively estimates the 2012 worldwide production of nanomaterials to be more than 270,000 tons, a tenfold increase from 2002. Optimistic market estimates are also covered in the report. The production volume in 2016 is conservatively estimated to reach more than 350,000 tons, driven by demand from applications in electronics, energy, medicine, chemicals, coating and catalysts. The forecast demands of nanomaterials are presented in Figure 1.5 [Frank, M. 2006].

Reports from a market research firm Business Communications Co. Inc. (BCC), Norwalk, say that the total worldwide markets for nanocomposites were
around 26 million kgs during the recent year which is valued at US$ 90.8 million. The firm projects the market to grow at an average annual rate of 18.4% to reach USD 211.1 million by 2011. Even if these nano-developments hit some technical hitches, BCC also says that some of the applications like construction, packaging and automotives will grow more than 20% each year [Mc Williams, A. 2007].

![Graph showing nanomaterials demand for making integrated circuits](image1)

**Figure 1.5 Nanomaterials demand for making integrated circuits**

[Frank, M. 2006]

![Graph showing expected demand of different types of nanocomposites in the market 2011](image2)

**Figure 1.6 Share of different types of nanocomposites in the market 2011**

[Research Report, 2007 and 2008]
Nanoclay composites accounted for nearly one quarter (24%) of total nanocomposite consumption by value in 2005 followed by metal and metal oxide nanocomposites (19%) and carbon nanotube composites (15%). According to BCC, the consumption of nanoclay composites is projected to increase their market share to 44% by the year 2011 (Figure 1.6). Apart from that, other market share gainers include metal/metal oxide nanocomposites and ceramic nanocomposites, which are projected to attain market shares of 20% and 11.5% respectively between 2009 and 2011, whereas nanocarbon composites are expected to lose market share down to 7.5% [Research Report, 2007].

The major applications of nanocomposites will be automotive components, packaging, appliances, electrical/electronic parts, and building and construction products. The major players in the field of polymer/clay nanocomposites currently include Bayer, Honeywell Polymer, RTP Company, Toyota Motors, Ube, Unitika, Basell, General Motors, Southern Clay Products, Mitsubishi Gas Chemical Company, Noble Polymer, Nanocor, Elementis Specialties, PolyOne Corporation, Clariant Corporation, Sud-Chemie [Nanocompositech.com]. There are many more polymer, clay and specialty material producers poised to enter into this emerging field.

Layered-silicate based polymer nanocomposites are attractive not only for their obvious potential as technological materials, but also for providing a convenient macroscopic system to study fundamental scientific issues concerning confined and tethered polymers. Studying the formation, structure and dynamics of nanocomposites can lead to better understanding of organic-inorganic hybrids and polymers in a confined environment or at a solid interface.

1.3 Nanocomposites

Polymer-clay nanocomposites have their origin in the pioneering research conducted at Toyota Central Research Laboratories in 80s [Giese, R.F.et al, 2002] where these two divergent organic and mineral materials were successfully
integrated. The first practical application of nanocomposites was in the use of nylon-montmorillonite clay nanocomposite as a timing belt cover on a Toyota Camry automobile. This nanocomposite exhibited large increase in tensile strength, modulus, and heat distortion temperature without loss of impact resistance. It was shown [Kojima, Y. et al, 1993] that at a loading of only 4.2 wt% clay, the modulus of nylon-6 doubled, the strength increased more than 50%, and the heat distortion temperature increased by 80°C. It was further demonstrated that nanoclay greatly improved the dimensional stability, the barrier property and even flame-retardant property. The composite had lower water sensitivity, lower permeability to gases, and lower coefficient of thermal expansion.

The pioneering work at Toyota Central Research Laboratories provided an optimism and motivation for the scientists in the field of nanocomposite materials. The nanocomposite research has drawn the attention, imagination and close scrutiny of scientists and engineers. This is based on the premise that using building blocks with dimensions in the nanosize range makes it possible to create new materials with unprecedented improvements in physical properties.

Nanocomposites are a special class of composites, in which the dispersed phase is made of nanoparticles. Nanoparticles have one dimension of the order of 1 nm \( (10^{-9} \text{ m}) \). The term nanocomposite refers to the combination of two or more component phases where at least one phase dimension is in the nanometer range [Goldstein, N. 1997]. These materials exhibit behavior different from conventional composite materials with microscale structure, due to the small size of the reinforcing unit and the high surface-to-volume ratio.

1.4 Statement of Problem

Polymer matrix composites (PMCs) are thus a versatile class of materials offering a broad range of properties. Fibre reinforced composite material is a lightweight engineered material that consists of glass fibre incorporated in polymer
matrix. The organic matrix fiber-reinforced composite laminates are very susceptible to low-velocity impact. It has been indicated by many researchers that low-velocity impact could cause various damages such as matrix cracks, delamination and fiber breakage [Abrate, S. 1994 and Li CF, et al, 2002]. Such impact may occur during fabrication, normal maintenance operations or during service conditions. These damages are very difficult to detect by naked eyes and can cause significant reduction in the strength and stiffness of the materials.

The resultant damage may cause a considerable reduction in strength and performance of the composites materials. Thus, it is appropriate to investigate the effects of low velocity impact on structural composite materials. There remains considerable need for improvement of damage tolerance and arresting matrix cracking, delamination and fibre pullout can be improvised by incorporating high stiffer nanoclay into the glass fibre reinforced polymer matrix.

This is done as the surface contact area of such nanoclay in the matrix acts as good interface material which in turn improves the impact performance and control damages. The addition of nanoclay lowers the raw material cost and at the same time reduces the shrinkage of the resin after solidification. It also improves the mechanical properties without any noticeable influence on the other properties. Hence, the resulting nanocomposites have high strength, higher load bearing capacity, more energy absorption and good damage resistance. The growth of aerospace structural applications of these nanocomposites laminates would benefit from this investigation.
1.5 Objectives of the Present Study

The objectives of the present study is to,

[i] Develop a Design of Experiment (DOE) based methodology to optimize the process parameters of nanocomposites.

[ii] Prepare a glass fibre reinforced epoxy nanocomposite, with varying percentage of nanoclay (1 wt%, 3 wt% and 5wt %) using high shear mechanical mixing process. To prepare three different configurations of Chopped strand mat (CSM), Woven roving mat (WRM) and Mixed glass/epoxy nanocomposite using hand lay-up techniques.

[iii] To study the structure characterizations of epoxy/clay nanocomposites by means of X-ray diffraction (XRD), atomic force microscopy (AFM) and scanning electron microscopy (SEM).

[iv] Evaluate mechanical properties (tensile, flexural and interlaminar shear strength) and to understand the influence of nanoclay in polymer system.

[v] Characterize the low velocity impact properties of glass fibre reinforced epoxy nanocomposite in terms of maximum load and energy absorption. To analyze various modes of impact damages using scanning electron microscopy (SEM).

This work is also expected to introduce a new class of polymer nanocomposite material that might find many applications especially in the fields of aerospace, marine and structural.
1.6 Research Work Plan

![Flow chart of research work plan](image)

**Figure 1.7** Flow chart of research work plan
1.7 Thesis Outline

The structure of the thesis is presented in the following eight chapters:

Chapter 1 Deals with general introduction of composites materials, fibre reinforced composites and types of nanomaterials, statement of the problem and objectives of the present investigation.

Chapter 2 Provides a review of relevant literature on polymer nanocomposites. This chapter deals with the work reported regarding the effect of nanoclay on mechanical and impact properties.

Chapter 3 Presents the Design of experiment (DOE), optimization of process parameters and optimal values of nanoclay concentration, stirrer speed and stirring time which are to be used in preparation of epoxy/clay nanocomposites.

Chapter 4 Presents the materials, preparation and characterization methods of E-glass fibre/epoxy nanocomposites. X-ray diffraction pattern of nanocomposites also discussed.

Chapter 5 Deals with the experimental setup, experimental details, methods and standard used to determine the mechanical and impact properties.

Chapter 6 Presents the results and discusses regarding the effect of nanoclay on CSM/WRM/Mixed epoxy nanocomposites. Study of structure properties correlation also carried out through XRD, SEM and AFM are also reported.

Chapter 7&8 Summarizes the conclusions drawn from this research and offers recommendations for future scope of the work.