Mechanical Properties of Clay/TiO_2 Epoxy Hybrid Nanocomposites

Dissertation submitted in partial fulfillment of the requirement
for the award of degree

MASTER OF ENGINEERING
in
CAD/CAM & Robotics

Submitted by

JATINDER SINGH
Roll No. 801181018

Under Guidance of

Dr. Haripada Bhunia
Associate Professor
Chemical Engg. Department

Dr. Jaswinder Singh Saini
Assistant Professor
Mechannical Engg. Department

MECHANICAL ENGINEERING DEPARTMENT
THAPAR UNIVERSITY
PATIALA-147004, PUNJAB, INDIA

JULY 2013

CERTIFICATE

This is to certify that the dissertation entitled **"Mechanical Properties of Clay/TiO_2 Epoxy Hybrid Nanocomposites"**, is an authentic record of my own work carried out as requirements for the award of degree of Master of Engineering in CAD/CAM & Robotics from Thapar University, Patiala, under the guidance of Dr. Haripada Bhunia (Associate Professor, ChED) and Dr. Jaswinder Singh Saini (Assistant Professor, MED) during July 2012 to July 2013.

Jatinder Singh

Date: 15th July, 2013

JATINDER SINGH

(Roll No: 801181018)

It is certified that the above statement made by the student is correct to the best of our knowledge and belief.

15/7/2013

(Dr. Haripada Bhunia)
Associate Professor
Chemical Engineering Department
Thapar University, Patiala

15/7/13

(Dr. Jaswinder Singh Saini)
Assistant Professor
Mechanical Engineering Department
Thapar University, Patiala

Countersigned by

(Dr. Ajay Batish)
Head, Mechanical Engineering Department
Thapar University, Patiala

(Dr. S. K. Mohapatra)
Dean of Academic Affairs
Thapar University, Patiala

ACKNOWLEDGEMENTS

I am highly grateful to the authorities of Thapar University, Patiala for providing this opportunity to carry out the research work. I would like to express a deep sense of gratitude and thank profusely to my dissertation guides **Dr. Haripada Bhunia**, Associate Professor, Chemical Engineering Department, Thapar University, Patiala and **Dr. Jaswinder Singh Saini**, Assistant Professor, Mechanical Engineering Department, Thapar University, Patiala for their sincere & invaluable guidance, suggestions and attitude which inspired me to submit dissertation report in the present form.

I am highly thankful to **Mr. Toyesh Upreti, Mr. Gaurav Madhu** (Research Scholars in Chemical Engineering Department) and **Mr. Manjeet Singh** (Research Scholar in Mechanical Engineering Department) for his invaluable guidance & continuous support.

I heartily thank to **Mr. Narinder Singh** for helping me in conducting the tests on Micro Hardness Machine.

I am also thankful to other faculty members and all the workshop staff of Mechanical Engineering Department, Thapar Univeristy, Patiala for their intellectual support.

I would also like to thank and acknowledge **Atul India Private Limited, Gujrat** for supplying us generously with Base, Hardener and Accelerator for the present work.

My special thanks are due to my family members and friends who constantly encouraged me to complete this work.

(Jatinder Singh)

ABSTRACT

Composite material is a macroscopic combination of two or more distinct materials, having a recognizable interface between them. The two phases in a composite material are matrix phase and reinforcement phase. When the matrix material used is polymer, then the composites made are called Polymer Nanocomposites. Polymers make ideal materials as they can be processed easily, possess lightweight and desirable mechanical properties. Composites are not only used for their structural properties, but also for electrical, thermal, and environmental applications. Also the high temperature resins are extensively used in aeronautical applications. Modern composite materials are usually optimized to achieve a particular balance of properties for a given range of applications. As there are compromises with properties in the composites, great efforts have been undertaken to modify these materials at the nanoscale to optimize their performance. So, in order to get the more excellent properties composites are filled with Nanomaterials.

In the present work, Clay Epoxy Nanocompsites were developed using Hand Layup technique. These Clay Epoxy Nanocomposites were developed in different compositions on which different mechanical properties were found. The Tensile Strength and the Flexural Strength were evaluated on Universal Testing Machine and the Hardness was evaluated at Vickers' Hardness test apparatus. The best results were found with 2 wt% composition of Nanoclay. Thereafter, TiO_2 was added in different proportions fixing the 2 wt% of Nanoclay. Again the different Mechanical properties were found for the prepared Epoxy Hybrid Nanocomposites.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER-1

INTRODUCTION

1.1 COMPOSITES

Composite materials are engineered materials made from two or more constituent materials with significantly different physical or chemical properties which remain separate and distinct on a macroscopic level within the finished structure.

Composite material is a macroscopic combination of two or more distinct materials, having a recognizable interface between them. Composites are not only used for their structural properties, but also for electrical, thermal, and environmental applications. Modern composite materials are usually optimized to achieve a particular balance of properties for a given range of applications. Given the vast range of materials that may be considered as composites and the broad range of uses for which composite materials may be designed, it is difficult to agree upon a single, simple, and useful definition. However, as a common practical definition, composite materials may be restricted to emphasize those materials that contain a continuous matrix constituent that binds together and provides form to an array of a stronger, stiffer reinforcement constituent. The resulting composite material has a balance of structural properties of constituent materials. The improved structural properties generally result from a load-sharing mechanism. Although composites optimized for other functional properties (besides high structural efficiency) could be produced from completely different constituent combinations that fit this structural definition, it has been found that composites developed for structural applications also provide attractive performance in the other functional areas as well. As a result, this simple definition for structural composites provides a useful definition for most current functional composites. **[1]**

Composites typically have a fiber or particle phase that is stiffer and stronger than the continuous matrix phase. Many types of reinforcements also often have good thermal and electrical conductivity, a Coefficient of Thermal Expansion (CTE) that is less than the matrix, and/ or good wear resistance. There are, however, exceptions that may still be considered composites, such as rubber-modified polymers, where the discontinuous phase is more compliant and more ductile than the polymer, resulting in improved toughness. Similarly, steel wires have been used to reinforce gray cast iron in truck and trailer brake drums.

Composites are made up of individual materials referred to as constituent materials. There are two categories of constituent materials:- matrix and reinforcement. At least one portion of each type is required. The matrix material surrounds and supports the reinforcement materials by maintaining their relative positions. The reinforcements impart their special mechanical and physical properties to enhance the matrix properties. These two categories of constituent materials are also called two phases of composites. These two phases are given below.

1.1.1 MATRIX PHASE

The primary phase, having a continuous character, is called matrix. Matrix is usually more ductile and less hard phase. It holds the dispersed phase and shares a load with it. The various functions of the matrix phase are given below:-

(i) Matrix material holds the fibres together.
(ii) It protects the fibres from environment.
(iii) It distributes the loads evenly between the fibres so that all fibres are subjected to same amount of strain.
(iv) It enhances transverse properties of laminates.
(v) It improves impact and fracture resistance of the component.
(vi) It carries interlaminar shears.

The desired properties of the matrix which are important for a composite are as follows:-

(i) Reduced moisture absorption.
(ii) Low shrinkage.
(iii) Low coefficient of thermal expansion.
(iv) Must be elastic to transfer load to fibres.
(v) Strength at elevated temperatures (depending upon application).
(vi) Excellent chemical resistance.
(vii) Dimensional stability.

1.1.2 DISPERSED (REINFORCING) PHASE

The second phase (or phases) is imbedded in the matrix in a discontinuous form. This secondary phase is called dispersed phase. Dispersed phase is usually stronger than the matrix, therefore it is sometimes called reinforcing phase. The various functions of reinforcement are given below:-

(i) It gives strength to the composite.
(ii) It provides stiffness.
(iii) Gives shape to the composite material.
(iv) Giving the properties that is not available with the matrix material.

The various properties of the reinforcements are given below:-

(i) Dispersed phase is usually stiffer and stronger than the matrix phase.
(ii) Good thermal and electrical conductivity.
(iii) Good wear resistance.
(iv) Low coefficient of thermal expansion (CTE) than matrix.

1.2 CLASSIFICATION

Composites are commonly classified with respect to Matrix and Reinforcement constituents.

1.2.1 Classification made with respect to the Matrix constituent

The classification made with respect to the matrix phase is as follows:-

(i) Organic-matrix composites (OMCs).
(ii) Metal-matrix composites (MMCs).
(iii) Ceramic-matrix composites (CMCs).

The term "Organic-matrix composite" is generally assumed to include two classes of composites: Polymer-Matrix Composites (PMCs) and Carbon-Matrix Composites (commonly referred to as Carbon-Carbon Composites). Carbon-Matrix Composites are typically formed from PMCs by including the extra steps of carbonizing and densifying the original polymer matrix. In the research and development community, Intermetallic-Matrix Composites (IMCs) are sometimes listed as a classification that is distinct from MMCs. However, significant commercial applications of IMCs do not yet exist, and in a practical sense these materials do not provide a radically different set of properties relative to MMCs. In each of these systems, the matrix is typically a continuous phase throughout the component. Composites cannot be made from constituents with divergent linear expansion characteristics. The interface is the area of contact between the reinforcement and the matrix materials. In some cases, the region is a distinct added phase. Whenever there is interphase, there has to be two interphases between each side of the interphase and its adjoint constituent. Some composites provide interphases when surfaces dissimilar constituents interact with each other. Fig. 1.1 shows the classification.

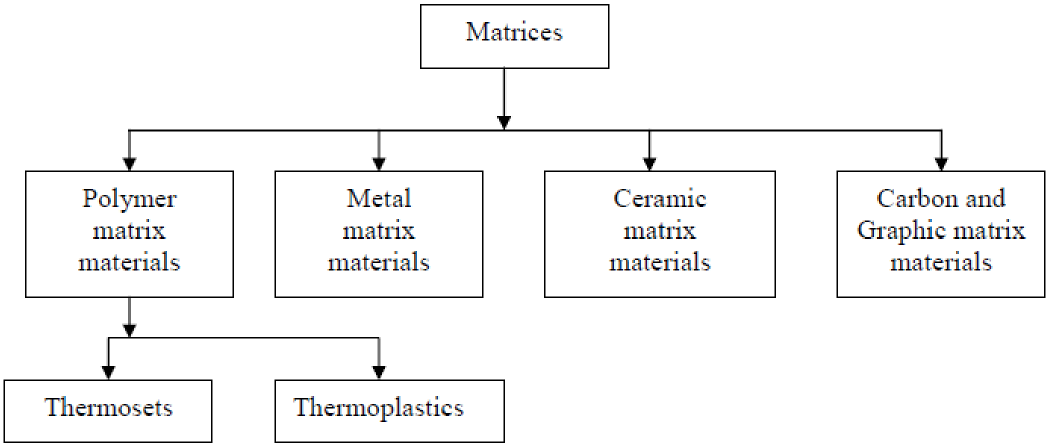


Fig. 1.1 Classification with respect to the Matrix constituent

- **Polymer Matrix Materials**

Polymers make ideal materials as they can be processed easily, possess lightweight, and desirable mechanical properties. Two main kinds of polymers are Thermosets and Thermoplastics:-

(a) Thermosets

Thermosets have qualities such as a well-bonded three-dimensional molecular structure after curing. They decompose instead of melting on hardening. Merely changing the basic composition of the resin is enough to alter the conditions suitably for curing and determine its other characteristics. They can be retained in a partially cured condition too, over prolonged periods of time, rendering thermosets very flexible. Thus, they are most suited as matrix bases for advanced conditions fiber reinforced composites. Thermosets find wide ranging applications in the chopped fiber composites form particularly when a premixed or moulding compound with fibers of specific quality and aspect ratio happens to be starting material as in epoxy, polymer and phenolic polyamide resins.

Thermosets are the most popular of the fiber composite matrices without which, research and development in structural engineering field could get truncated. Aerospace components, automobile parts, defense systems etc., use a great deal of this type of fiber composites. Epoxy matrix materials are used in printed circuit boards and similar areas. Fig.1.2 shows various types of thermosets.

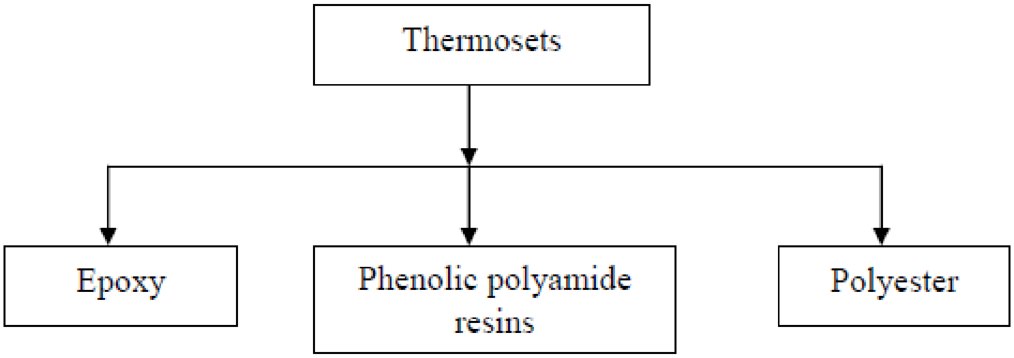


Fig. 1.2 Various types of Thermosets

Polyesters Phenolic and Epoxies are the two important classes of thermoset resins. Epoxy resins are widely used in filament-wound composites and are suitable for moulding prepress. They are reasonably stable to chemical attacks and are excellent adherents having slow shrinkage during curing and no emission of volatile gases. These advantages, however, make the use of epoxies rather expensive. Also, they cannot be expected beyond a temperature of 140ºC. Their use in high technology areas where service temperatures are higher, as a result, is ruled out.

Polyester resins on the other hand are quite easily accessible, cheap and find use in a wide range of fields. Liquid polyesters are stored at room temperature for months, sometimes for years and the mere addition of a catalyst can cure the matrix material within a short time. They are used in automobile and structural applications. The cured polyester is usually rigid or flexible as the case may be and transparent. Polyesters withstand the variations of environment and stable against chemicals. Depending on the formulation of the resin or service requirement of application, they can be used up to about 75ºC or higher. Other advantages of polyesters include easy compatibility with few glass fibers and can be used with verify of reinforced plastic accountrey. Aromatic Polyamides are the most sought after candidates as the matrices of advanced fiber composites for structural applications demanding long duration exposure for continuous service at around 200-250ºC.

(b) Thermoplastics

Thermoplastics have one or two dimensional molecular structure and they tend to at an elevated temperature and show exaggerated melting point. Another advantage is that the process of softening at elevated temperatures can reversed to regain its properties during cooling, facilitating applications of conventional compress techniques to mould the compounds.

Resins reinforced with thermoplastics now comprised an emerging group of composites. The theme of most experiments in this area to improve the base properties of the resins and extract the greatest functional advantages from them in new avenues, including attempts to replace metals in die-casting processes. In crystalline thermoplastics, the reinforcement affects the morphology to a considerable extent, prompting the reinforcement to empower nucleation. Whenever crystalline or amorphous, these resins possess the facility to alter their creep over an extensive range of temperature. But this range includes the point at which the usage of resins is constrained, and the reinforcement in such systems can increase the failure load as well as creep resistance. Fig.1.3 shows the types of thermoplastics.

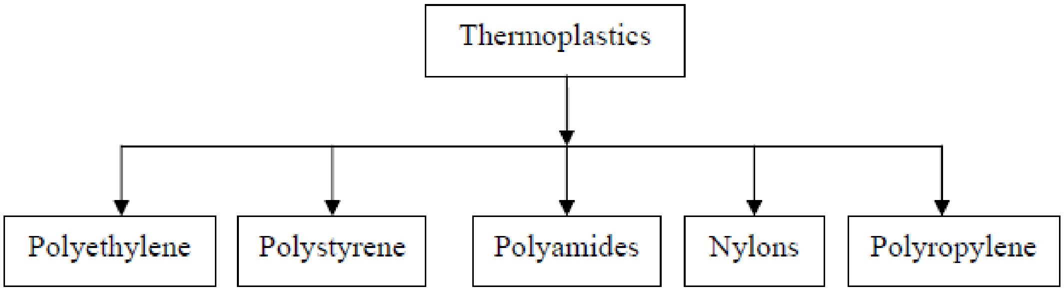


Fig. 1.3 Types of Thermoplastics

A small quantum of shrinkage and the tendency of the shape to retain its original form are also to be accounted for. But reinforcements can change this condition too. The advantage of thermoplastics systems over thermosets are that there are no chemical reactions involved, which often result in the release of gases or heat. Manufacturing is limited by the time required for heating, shaping and cooling the structures.

- **Carbon Matrices**

Carbon and graphite have a special place in composite materials options, both being highly superior, high temperature materials with strengths and rigidity that are not affected by temperature up to 2300ºC. This carbon-carbon composite is fabricated through compaction of carbon or multiple impregnations of porous frames with liquid carboniser precursors and subsequent pyrolization. They can also be manufactured through chemical vapour deposition of pyrolytic carbon. Carbon-carbon composites are not be applied in elevated temperatures, as many composites have proved to be far superior at these temperatures. However, their capacity to retain their properties at room temperature as well as at temperature in the range of 2400ºC and their dimensional stability make them the oblivious choice in a garnut of applications related to aeronautics, military, industry and space. Components, that are exposed to higher temperature and on which the demands for high standard performance are many, are most likely to have carbon-carbon composites used in them.

- **Glass Matrices**

In comparison to ceramics and even considered on their own merit, glass matrices are found to be more reinforcement-friendly. The various manufacturing methods of polymers can be used for glass matrices. Glasses are meant to improve upon performance of several applications. Glass matrix composite with high strength and modulus can be obtained and they can be maintained upto temperature of the order of 650ºC.

Composites with glass matrices are considered superior in dimensions to polymer or metal system, due to the low thermal expansion behaviour. This property allows fabrication of many components in intricate shapes and their tribological characters are considered very special. Since the elastic modulus of glass is far lower than of any prospective reinforcement materials, application of stress usually results in high elasticity modulus fiber that the tensile strength of the composite its considerably enhanced than that of the constituents, which is not case in ceramic matrices.

1.2.2 Classification made with respect to Reinforcement constituent

Reinforcements for the composites can be fibers, fabrics particles or whiskers. Fibers are essentially characterized by one very long axis with other two axes either often circular or near circular, when the fiber is in the woven form that is called fabric. Particles have no preferred orientation and so does their shape. Whiskers have a preferred shape but are small both in diameter and length as compared to fibers. Reinforcing constituents in composites, as the word indicates, provide the strength that makes the composite what it is. But they also serve certain additional purposes of heat resistance or conduction, resistance to corrosion and provide rigidity. Reinforcement can be made to perform all or one of these functions as per the requirements.

A reinforcement that embellishes the matrix strength must be stronger and stiffer than the matrix and capable of changing failure mechanism to the advantage of the composite. This means that the ductility should be minimum or even nil the composite must behave as brittle as possible. Fig. 1.4 shows types of reinforcements in composites.

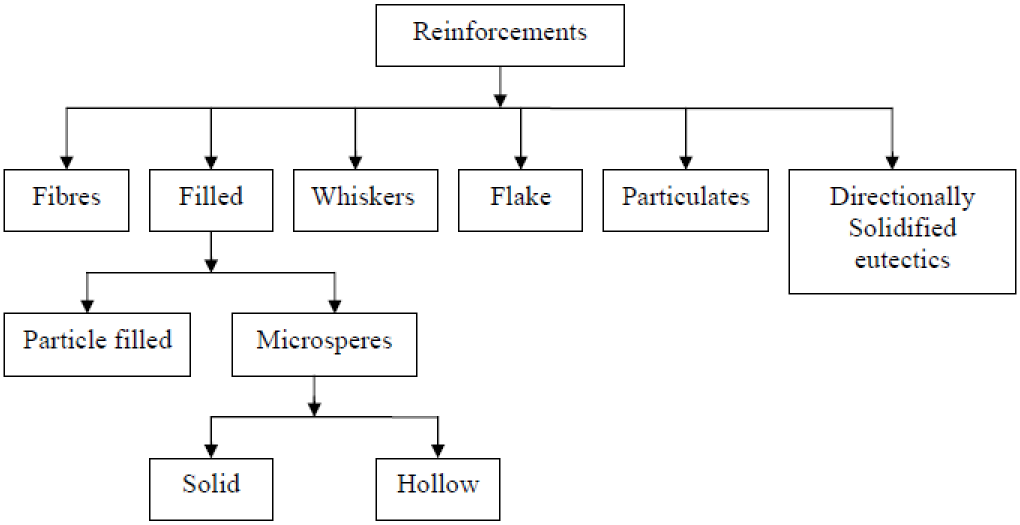


Fig. 1.4 Classification with respect to Reinforcement constituent

(i) Fiber Reinforcement

Fibers are the important class of reinforcements, as they satisfy the desired conditions and transfer strength to the matrix constituent influencing and enhancing their properties as desired.

Fibers fall short of ideal performance due to several factors. The performance of a fiber composite is judged by its length, shape, orientation, composition of the fibers and the mechanical properties of the matrix. The orientation of the fiber in the matrix is an indication of the strength of the composite and the strength is greatest along the longitudinal directional of fiber. Optimum performance from longitudinal fibers can be obtained if the load is applied along its direction. The slightest shift in the angle of loading may drastically reduce the strength of the composite.

Unidirectional loading is found in few structures and hence it is prudent to give a mix of orientations for fibers in composites particularly where the load is expected to be the heaviest. The strength of the fiber in any one of the three axes would, therefore be one-third the unidirectional fiber composite, assuming that the volume percentage is equal in all three axes. However, orientation of short fibers by different methods is also possible like random orientations by sprinkling on to given plane or addition of matrix in liquid or solid state before or after the fiber deposition. Even three-dimensional orientations can be achieved in this way.

There are several methods of random fiber orientations, which in a two-dimensional one, yield composites with one-third the strength of a unidirectional fiber-stressed composite, in the direction of fibers. In 3D, it would result in a composite with a comparable ratio, about less than one-fifth. Shorter fibers with proper orientation composites that use glass, ceramic or multi-purpose fibers can be endowed with considerably higher strength than those that use continuous fibers. Short fibers are also known to their theoretical strength. The continuous fiber constituent of a composite is often joined by the filament winding process in which the matrix impregnated fiber wrapped around a mandrel shaped like the part over which the composite is to be placed, and equitable load distribution and favorable orientation of the fiber is possible in the finished product. However, winding is mostly confined to fabrication of bodies of revolution and the occasional irregular, flat surface. Most fibers in use currently are solids which are easy to produce and handle, having a circular cross-section, although a few non-conventional shaped and hollow fibers show signs of capabilities that can improve the mechanical qualities of the composites. Given the fact that the vast difference in length and effective diameter of the fiber are assets to a fiber composite, it follows that greater strength in the fiber can be achieved by smaller diameters due to minimization or total elimination of surface defects.

Various types of organic and inorganic fibers are used to reinforce composite materials. Organic fibers have low density, flexibility and elasticity where as inorganic fibers are of high modulus, high thermal stability and possess greater rigidity than organic fibers.

(ii) Laminar Composites

Laminar composites are found in as many combinations as the number of materials. They can be described as materials comprising of layers of materials bonded together. These may be of several layers of two or more metal materials occurring alternately or in a determined order more than once, and in as many numbers as required for a specific purpose.

Powder metallurgical processes like roll bonding, hot pressing, diffusion bonding, brazing and so on can be employed for the fabrication of different alloys of sheet, foil, powder or sprayed materials. It is not possible to achieve high strength materials unlike the fiber version. But sheets and foils can be made isotropic in two dimensions more easily than fibers. Foils and sheets are also made to exhibit high percentages of which they are put. For instance, a strong sheet may use over 92% in laminar structure, while it is difficult to make fibers of such compositions. The main functional types of metal-metal laminates that do not posses high strength or stiffness are single layered ones that endow the composites with special properties, apart from being cost-effective. They are usually made by pre-coating or cladding methods. Pre-coated metals are formed by forming a layer on a substrate, in the form of a thin continuous film. This is achieved by hot dipping and occasionally by chemical plating and electroplating. Clad metals are found to be suitable for more intensive environments where denser faces are required.

There are many combinations of sheet and foil which function as adhesives at low temperatures. Such materials, plastics or metals, may be clubbed together with a third constituent. Pre-painted or pre-finished metal whose primary advantage is elimination of final finishing by the user is the best known metal-organic laminate. Several combinations of metal-plastic, vinyl-metal laminates, organic films and metals, account for up to 95% of metal-plastic laminates known. They are made by adhesive bonding processes.

(iii) Flake Composites

Flakes are often used in place of fibers as can be densely packed. Metal flakes that are in close contact with each other in polymer matrices can conduct electricity or heat, while mica flakes and glass can resist both. Flakes are not expensive to produce and usually cost less than fibers. But they fall short of expectations in aspects like control of size, shape and show defects in the end product. Glass flakes tend to have notches or cracks around the edges, which weaken the final product. They are also resistant to be lined up parallel to each other in a matrix, causing uneven strength. They are usually set in matrices, or more simply, held together by a matrix with a glue-type binder. Depending on the end-use of the product, flakes are present in small quantities or occupy the whole composite.

Flakes have various advantages over fibers in structural applications. Parallel flakes filled composites provide uniform mechanical properties in the same plane as the flakes. While angle-plying is difficult in continuous fibers which need to approach isotropic properties, it is not so in flakes. Flake composites have a higher theoretical modulus of elasticity than fiber reinforced composites. They are relatively cheaper to produce and be handled in small quantities.

(iv) Filled Composites

Filled composites result from addition of filer materials to plastic matrices to replace a portion of the matrix, enhance or change the properties of the composites. The fillers also enhance strength and reduce weight. Another type of filled composite is the product of structure infiltrated with a second-phase filler material. The skeleton could be a group of cells, honeycomb structures, like a network of open pores. The infiltrant could also be independent of the matrix and yet bind the components like powders or fibers, or they could just be used to fill voids. Fillers produced from powders are also considered as particulate composite. In the open matrices of a porous or spongy composite, the formation is the natural result of processing and such matrices can be strengthened with different materials. Metal impregnates are used to improve strength or tolerance of the matrix. Metal casting, graphite, powder metallurgy parts and ceramics belong to this class of filled composites. In the honeycomb structure, the matrix is not naturally formed, but specifically designed to a predetermined shape. Sheet materials in the hexagonal shapes are impregnated with resin or foam and are used as a core material in sandwich composites.

Fillers may be the main ingredient or an additional one in a composite. The filler particles may be irregular structures, or have precise geometrical shapes like polyhedrons, short fibers or spheres. While their purpose is far from adding visual embellishment to the composites, they occasionally impart color or opacity to the composite which they fill. The final composite properties can be affected by the shape, surface treatment, blend of particle types, size of the particle in the filler material and the size distribution.

Filled plastics tend to behave like two different constituents. They do not alloy and accept the bonding. They are meant to develop mutually; they desist from interacting chemically with each other. It is vital that the constituents remain in co-ordination and do not destroy each other's desired properties. The benefits offered by fillers include increase stiffness, thermal resistance, stability, strength and abrasion resistance, porosity and a favorable coefficient of thermal expansion. However, the methods of fabrication are very limited and the curing of some resins is greatly inhibited. They also shorten the life span of some resins and are known to weaken a few composites.

(v) Particulate Reinforced Composites

Microstructures of metal and ceramics composites, which show particles of one phase strewn in the other, are known as particle reinforced composites. Square, triangular and round shapes of reinforcement are known, but the dimensions of all their sides are observed to be more or less equal. The size and volume concentration of the dispersoid distinguishes it from dispersion hardened materials.

The dispersed size in particulate composites is of the order of a few microns and volume concentration is greater than 28%. The difference between particulate composite and dispersion strengthened ones is, thus, oblivious. The mechanism used to strengthen each of them is also different. The dispersed in the dispersion-strengthen materials reinforces the matrix alloy by arresting motion of dislocations and needs large forces to fracture the restriction created by dispersion.

Three-dimensional reinforcement in composites offers isotropic properties, because of the three systematical orthogonal planes. Since it is not homogeneous, the material properties acquire sensitivity to the constituent properties, as well as the interfacial properties and geometric shapes of the array. The composite's strength usually depends on the diameter of the particles, the inter-particle spacing, and the volume fraction of the reinforcement. The matrix properties influence the behaviour of particulate composite too.

1.3 NANOCOMPOSITES

A Nanocomposite is defined such that the size of the matrix or reinforcement falls within the nanoscale. The physical properties and performance of the nanocomposite will greatly differ from those of the component materials. According to the type of matrix, nanocomposites can be classified into ceramic matrix nanocomposites, metal matrix nanocomposites, and polymer matrix nanocomposites. **[2]**

These days' polymer composites are undergoing extensive research because for many fields of the modern industry, the appreciable improvement of physiomechanical properties of polymeric materials is required. Nowadays, the most perspective decision of this problem is a modification polymer with nanostructure modifiers – creation of polymeric nanocomposites. Polymer Nanocomposites (PNC) are polymers (thermoplastics, thermo sets, elastomers) that have been reinforced with small quantities (less than 5% by weight) of nanosized particles. Molecular interaction between polymer and nanofillers do not posses. Uniform dispersion of nanoparticles in polymer matrix produces ultra- large interfacial area per volume between the nanoparticle and the host polymer. This immense internal interfacial area and the nanoscopic dimension between nanoparticle fundamentally differentiate PNCs from traditional composites and filled plastics. Introduction of nanoparticles to polymer matrix ensure significant property improvements with very low loading levels. Traditional micro particles additives require much higher filler concentration to achieve similar results. The most commonly used nano fillers are:

(i) Manomorillonite Organoclays (MMT)
(ii) Carbon Nanofiber (CNFs)
(iii) Carbon Nanotubes (CNTs)
(iv) Metallic Nanoparticles

The value of PNC technology comes from providing value added properties not present in the neat polymer, without sacrificing the inherent processibility and mechanical properties of the polymer. Some of the major advantages of the polymer nanocomposites are:

Mechanical properties

- High adhesion of nanoparticles to polymer matrix result in the enhanced strength of nanocomposites relative to conventional composite.
- Small size of nanoparticles ensures small size of pores in the case of exfoliation of a matrix from filler particles. It results in the strength increase too.
- Introduction of small amount of nanoparticles to polymer significantly enhance the adhesion of polymer to different substance.

Optical properties

- Nanocomposites are optically more transparent in comparison to conventional composites.
- Special optical effects.
- Optical clarity in comparison to conventionally filled polymers.

Magnetic properties

- In some cases composites with magnetic nanoparticles have the magneto resistance and magnetic permeability much higher than in the case of conventional composites.
- It is possible to make composites with magnetic threshold concentration smaller than electrical percolation threshold.

1.4 APPLICATIONS

Nanocomposites have wide range of applications, **[2]** the main areas in which nanocomposites used are

(i) Land transportation and Marine engineering.
(ii) Commercial and industrial applications.
(iii) Composite bio materials.
(iv) Scientific applications of composites.
(v) Construction.
(vi) Sporting and goods industry.
(vii) Aerospace equipment and instrument structure.

CHAPTER-2

LITERATURE REVIEW

Polymer Composites have been extensively used in structural components as well as in aeronautical, automotive, marine and sporting industries for a wide range of applications because of their attractive properties, fatigue and corrosion resistance combined with lightweight, high specific stiffness and strength. Extensive literature review has been carried out for defining the research problem. Most of the work carried out is on the characterization of composites made by adding nanofillers to matrix system. A review of the literature is presented in the following section.

2.1 LITERATURE REVIEW

Myskove *et al.* (2003) investigated the influence of montmorillonite concentration and the temperature regime on the cure rate and mechanical properties of the composite material obtained. The addition of the modified clay to the epoxy-amine hardener system influenced the rate of curing reaction. The presence of clay increased the modulus both in the glassy state and in the rubber region. The clay brings about the development of a secondary maximum at higher temperatures, which was caused by the formation of a polymer phase with a limited mobility on the surface of clay particles. The addition of clay considerably improved the tensile mechanical properties of epoxy systems.

Brunner *et al.* (2006) investigated whether a nano-modified epoxy matrix yields improved delamination resistance in a fiber-reinforced laminate compared to a laminate with neat epoxy as matrix material. An increase between about 40-50% in fracture toughness and around 10-20% in energy release has been observed relative to the neat epoxy for nano-modified epoxy prepared by addition of 10 wt% of functionalized organosilicate clay, along with various other properties are improved in the nano-modified epoxy, *e.g.* a considerable increase in tensile and compressive modulus by more than 50% is observed. The most noteworthy exceptions known to date are ultimate tensile strength, elongation at break, and glass transition temperature, which were all reduced.

Chowdhury *et al.* (2006) fabricated Woven carbon/epoxy laminates with the epoxy modified using Nanomer I-28E nanoclay, organically modified clay at different weight percentages. Thermomechanical and flexural properties of the nanophased composites were determined and compared with those of control samples. The microstructural characterization was carried out through Scanning Electron Microscopy. The results showed that the flexural test results of thermally post-cured samples indicated a maximum improvement in strength and modulus of about 31% and 21%

respectively. From DMA results, it was seen that storage modulus increased by significant amount while glass transition temperature remained almost unchanged for different weight percentages of Nanoclay samples. Therefore, the changes in mechanical properties were due to the physical presence of the Nanoclay as opposed to changes in the polymeric network structure. Also, 2 wt% Nanoclay seems to be an optimum loading for carbon/SC-15 epoxy composites in terms of mechanical and thermal properties. Micro-structural studies revealed that Nanoclay promotes good adhesion of fiber and matrix thereby increasing the mechanical properties.

Li *et al.* (2007) modified epoxy resin with Nano-SiO_2, standard SiO_2 particles with diameter 30-40 nm and 3 μm, respectively, and γ-glycidoxypropyltrimethoxy silane. The bonded stationary phase was formed with γ-glycidoxypropyltrimethoxy silane between Nano-SiO_2 and epoxy resin which is indicated by IR spectra. Thermogravimetric analysis, impact strength and bulk resistivity tests showed that initial decomposition temperature, impact strength and bulk resistivity of epoxy resin-based composite increased and then decreased after Nano-SiO_2 content reached 4 wt%, optimal values were 323 °C, 89.2 kJ m^{-2} and 3.56×1014 Ω cm, respectively and similar behavior had been also observed on standard SiO_2/epoxy resin-based composites, optimal values were 308 °C, 17.13 kJm^{-2} and 2.80×1014Ωcm, respectively. SEM analysis was also done which showed that toughness of Nano-SiO_2/Epoxy resin-based composite and standard SiO_2/epoxy resin-based composite also increased and then decreased after Nano-SiO_2 and standard SiO_2 content reached 4 wt%.

Kim *et al.* (2008) mixed nano-particle additives such as carbon black and Nanoclay with epoxy resin in order to improve the fracture toughness of epoxy resin. The fracture toughness was measured using the single edge notched bend specimen at the room (25^{o}C) and cryogenic temperature (-150^{o}C). The results showed that reinforcement with nano-particles improved the fracture toughness at the room temperature, but decreased the fracture toughness at the cryogenic temperature in spite of their toughening effect. If the nano-particle reinforced matrix is used for a composite laminate, the interlaminar fracture toughness and the impact characteristic can be improved at the room temperature where as at the cryogenic temperature, un-reinforced epoxy may be able to provide better structural characteristics.

Fu *et al.* (2008) reviewed and discussed the effects of particle size, particle/matrix interface adhesion and particle loading on the stiffness, strength and toughness of such particulate–polymer composites. The basic understanding of the stiffening, strengthening and toughening mechanisms of the composites which is necessary to develop high performance particulate composites was discussed. The experimental results were compared with theoretical models and were critically evaluated.

Uddin and Sun (2008) developed a technique to improve the strength of unidirectional composites by enhancing the matrix properties through nanoparticles infusion. To make fiber composites a commercially available standard DGEBA epoxy with silica nanoparticles (Nanopox F 400) was used as the matrix and the silica nanoparticles in Nanopox were grown in situ via a sol-gel process resulting in a concentration of 40 wt% which was later diluted to 15 wt% particle loading. After the experimentation the TEM images showed very uniform dispersion of silica nanoparticles with a size distribution of about 20 nm. Compression test revealed a substantial improvement (40%) in elastic modulus of the modified epoxy. To fabricate unidirectional E-glass fiber reinforced silica/epoxy nanocomposites a modified vacuum assisted resin transfer molding process was used and inclusion of silica nanoparticles dramatically increased the longitudinal compressive strength and moderately increased the longitudinal and transverse tensile strengths. In the end the compression testing results are verified by microbuckling model.

Xu and Hoa (2008) fabricated Epoxy/Clay Nanocomposites (ENCs) from TGDDM epoxy and montmorillonite Nanoclay and manufactured carbon fiber reinforced epoxy/clay nanocomposites (CFRENCs) through hot melt lay-up plus autoclave process. The CFRENCs have uniform fiber volume fraction, very few dry spots, and very few resin rich areas. The interlaminar fracture toughness of CFRENCs was increased by 85% with the introduction of 4 phr nanoclay in epoxy. Small amount of Nanoclay (2 phr) added into the epoxy of carbon/epoxy composites can enhance the flexural strength by 38% but adding more clay does not further improve the flexural properties.

Sundaram *et al.* (2008) prepared FRP with nanocomposites in the combination of polyester resin, E-glass fiber, and nano-montmorillonite (nano clay) and the mechanical properties of the nanocomposites were studied. The tensile behavior of an experimentally produced nano-FRP in various combinations was investigated at room temperature in 0.833 strain rates. This results in increase of tensile strength, percent elongation and yield strength, moderate increase in Poisson ratio, and reduced area. The nano-FRP has sufficiently high ultimate tensile strength and 50% improvement of UTS at 5 wt% increment of nanopowder. Elongation increases with the addition of nanopowder 0.5 wt%, improvement in elongation was observed with the addition of 5% NP. Moreover, 3.9% improvement in elongation was observed with the addition of 10% NP. Yield strength increases into 7.24 N/mm2 with the addition of 5% NP. Poisson ratio moderately increases with an addition of nanopowder wt%. A 50% improvement in Poisson ratio was observed at 5 wt% increment of nanopowder. Reduction in area greatly reduced to 3.115 with the addition of 5% NP.

Schilde *et al.* (2010) studied that fiber reinforced composites are indispensable in the field of modern lightweight structures, such as aerospace, automotive industry etc because these materials provide high weight savings which in turn increase the efficiency of a structure. The intensity and the frequency of the stress transferred by the dispersing machines, the surface modification, the fluid properties and at least the stabilization method have a great influence on the energy efficiency and the obtained product fineness of the dispersing process. Usually, an increase of the viscosity and mass fraction of the product leads to an increase of the energetically efficiency of the dispersion process in the stirred media mill and three-roll-mill. The effect of wall gliding of the suspension between the rolls leads to lower stress intensities and thus to coarser product quality in the three-roll-mill. By measuring the contact angle and the rheological properties, the level of optimization was indicated. With increasing alumina solid content in the cured alumina epoxy resin composites the Young’s modulus and the fracture strength rise, while the fracture strain decreases and at high solid contents the ceramic nano-particles lead to an embrittlement of the elastic resin matrix.

Kuilla *et al.* (2010) reviewed the advances in the modification of graphene and the fabrication of graphene-based polymer nanocomposites. From the review, it was shown that graphene produced a dramatic improvement in properties at very low filler content. The modification of graphene/graphene oxide and the utilization of these materials in the fabrication of nanocomposites with different polymer matrixes were explored. The different organic polymers were used and graphene filled polymer nanocomposites were fabricated by a range of methods. It was seen that in the case of modified graphene-based polymer nanocomposites, the percolation threshold was achieved at a very lower filler loading. The structure, preparation and properties of polymer/graphene nanocomposites were also discussed in general with help of detailed examples drawn from the scientific literature.

Mirmohseni and Zavareh (2010) developed an epoxy-based nanocomposites toughened by the combination of thermoplastic, layered and particulate nano-fillers, the main objective of which is to incorporate poly(acrylonitrile-co-butadiene-co-styrene) (ABS), clay (layered nano-filler) and nano-TiO2 (particulate nano-filler) into epoxy matrix with the aim of obtaining the quaternary nanocomposite with higher impact strength and lower cost without attenuating the other desired mechanical properties such as tensile strength. Taguchi method was applied for optimization of the nanocomposite composition and the findings show that the quaternary nanocomposite with optimum composition exhibited maximum impact and tensile strengths with improvements of 168% and 64%, respectively and the synergistic effect was observed for the impact strength with the addition of three type modifiers to epoxy. The results showed that ABS had higher effect on mechanical properties of the quaternary nanocomposite compared to Clay and TiO_2 nanofillers. By XRD and SEM techniques a dispersion of clay nano-platelets, TiO_2 and ABS nanoparticles in epoxy matrix were obtained as the morphology of the quaternary nanocomposite.

Ye *et al.* (2011) prepared a series of EP/HNT/CF composites with high performance using halloysite nanotubes as the reinforcing fillers and investigated the morphology, thermal and mechanical properties of the hybrid composites. The microstructure study was also done which uncovers that HNTs are inhomogeneously dispersed in the epoxy matrix, forming a unique microstructure with extensive HNT-rich composite particles distributed in a continuous epoxy-rich phase. By experienation it is seen that both the storage modulus and Tg of the composites have been improved with the addition of HNT, also a 25% enhancement in the Izod impact strength has been achieved with 2 wt% HNT. The synergistic effect between HNT and carbon fibres has been observed and investigated. The enhancements on the impact properties was explained mainly by two factors, firstly, the increased strength and toughness of the epoxy matrix caused by the nanoreinforcements, secondly a strengthened interface between the carbon fibers and the modified matrix.

Ayatollahi *et al.* (2011) studied the effects of multi-walled carbon nanotubes (MWCNTs) on the mechanical properties of epoxy/MWCNT nano-composites with emphasis on fracture toughness under bending and shear loading conditions. Several Finite Element (FE) analyses were performed to determine appropriate shear loading boundary conditions for a single-edge notch bend specimen (SENB) and an equation was derived for calculating the shear loading fracture toughness from the fracture load and seen that the increase in fracture toughness of nano-composite depends on the type of loading, also the presence of MWCNTs had a greater effect on fracture toughness of nano-composites under shear loading compared with normal loading. Scanning Electron Microscopy (SEM) pictures were taken from the fracture surfaces to study the fracture mechanisms and a correlation was found between the characteristics of fracture surface and the mechanical behaviors observed in the fracture tests.

He *et al.* (2011) performed TGA and mechanical tests and evaluated the effect of nano-$CaCO_3$ particles on thermal and mechanical properties of epoxy resin cast. The introduction of a silane coupling agent KH550 as an interfacial modifier into nanocomposites through preparing KH550/nano-

$CaCO_3$ master batch revealed that epoxy resin cast filled with nano-$CaCO_3$ particles represents higher thermal stability and mechanical strength. The improvement was attributed to the surface modification of nano-particles, which enhanced the interfacial properties between nano-$CaCO_3$ fillers and epoxy resin. It was shown that the mechanical properties of nano-$CaCO_3$/epoxy/carbon fibers composites based on the modified epoxy matrix were also enhanced.

Gu *et al.* (2011) prepared EPPZT/epoxy resin composites by obtaining novel epoxy-group modified phosphazene-containing nanotubes (EPPZTs) through two convenient steps and were used to reinforce the epoxy resin matrix. The mechanical tests were performed and the results showed the mechanical properties had a close relationship with the dispersion of EPPZTs in the matrix. The thermal stability analysis was also done and the results showed that the addition of EPPZTs effectively increased the residue and decreased the weight loss rate.

Chen *et al.* (2012) developed hybrid multi-scale composites from glass microfiber fabrics and nano-epoxy resins containing electrospun glass nanofibers (EGNFs) with the technique of vacuum assisted resin transfer molding and with the hypothesis that, through dispersing a small amount of EGNFs into epoxy resin, mechanical properties (particularly out-of-plane mechanical properties) of the resulting hybrid multi-scale composites significantly improved. The evaluation of the interlaminar shear strength, flexural properties, impact absorption energy, and tensile properties of the composites was done. The results were compared to those acquired from GFs/epoxy composite as well as GFs/epoxy composites containing chopped glass microfibers (GMFs). The substantial improvements on mechanical properties of composites with nanoepoxy resin with 0.25 wt % of EGNFs were seen.

Ionita (2012) conducted atomistic and mesoscale simulations and estimated the effect of the diameter and weight fraction of single walled carbon nanotubes (SWCNTs) on mechanical behaviour and glass transition temperature (Tg) of SWCNTs reinforced epoxy resin composites. The atomistic periodic systems of epoxy resin and epoxy resin/SWCNTs were built with different weight ratios. The molecular dynamics simulations were used and estimated glass transition temperature, Young modulus and solubility parameter of epoxy resin and epoxy resin/SWCNTs composites. The results showed that incorporation of SWCNTs with diameters ranging from 10 to 14 Å had beneficial effect on mechanical integrity and glass transition temperature (Tg).

Alamri and low (2012) studied the effect of water absorption on the mechanical properties of nano-filler reinforced epoxy nanocomposites and investigated the influence of the nano-filler such as nanoclay platelet, HNT and n- SiC on enhancing the mechanical and barrier properties of epoxy based nanocomposites in wet condition. The results indicated that the presence of nano-filler into epoxy matrix led to significant reduction in both water uptake and diffusion coefficients and the reduction was attributed to the tortuosity path created by the addition of the nano-fillers. The flexural strength and modulus of all types of nanocomposites decreased due to the plasticization effect of the water uptake compared to dry nanocomposites where as fracture toughness and impact strength were found to increase as a result to water absorption. The mechanical properties of the nanocomposites by addition of nanoclay, HNT and n-SiC particles was improved after exposing to water as compared to neat epoxy in same condition. The reinforcement with 1 wt% nano-filler showed better mechanical properties than other filler content and the enhancement in barrier and mechanical properties of nanocomposites were more pronounced for nanocomposites filled with n-SiC than those filled with nanoclay platelet and halloysite nanotubes.

Azeez *et al.* (2012) reviewed that the work carried out on epoxy clay nanocomposites. The reviewer stated that the final morphology, physical, chemical and barrier properties of the nanocomposites were influenced by processing method, clay modifier and curing agents. Epoxy clay nanocomposites showed remarkable improvement in tensile, flexural and fracture toughness properties. Thermal stability and barrier properties were significantly improved by the incorporation of clay particles to epoxy systems. Coefficient of Thermal Expansion (CTE) and water permeation of the nanocomposite were reduced considerably.

Shadlou *et al.* (2012) studied mixed mode fracture resistance of epoxy-based nanocomposites reinforced with carbon nanoparticles of three different shapes. The nanocomposites were prepared by using the nanodiamond (ND) of spherical shape, the carbon nanofiber (CNF) of cylindrical shape and the graphene oxide (GO) nanoplatelets. The semi-circular bending specimen (SCB) was employed to perform a total number of 36 mixed mode fracture tests on the prepared nanocomposites and found that fracture toughness of nanocomposites having high aspect ratio fillers (i.e. CNF and GO) was higher than that of ND nanocomposites. In addition, the dispersion state of reinforcements and the fracture surface characteristics were investigated using the photographs taken by Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM).

Jumahat *et al.* (2012) studied the effect of montmorillonite clay on the compressive properties of Epikote 828 epoxy and prepared a series of epoxy-based nanocomposites with 1-5 wt% nanoclay content. Using transmission electron microscopy the degree of dispersion and exfoliation was investigated. Also the static uniaxial compression tests were conducted in order to study the effect of

Nanoclay on the compressive stress-strain behaviour and compressive properties of the Epikote 828 polymer. It was found that the compressive properties depend on the degree of exfoliation of the clay nanoplatelets in the epoxy and recorded reduction in compressive strength for 1 wt% and 3 wt% Nanoclay. This is because the intercalated structure of Nanoclay in the polymer created high localized stresses in the matrix during compression that leads to premature failure.

Jumahat *et al.* (2012) studied the effect of nanosilica on the tensile stress-strain response of Epikote 828 epoxy polymer and a 40 wt% nanosilica/epoxy masterbatch was used to prepare a series of nanocomposites with 5–25 wt% nanosilica content. The static uniaxial tensile tests were conducted and the tensile stress-strain response and tensile properties of unmodified and nanomodified epoxy polymers were investigated. Transmission electron microscopy was used and the degree of dispersion of the silica nanosphere particle in the epoxy matrix was investigated. It was found that the incorporation of a well-disperse nanosilica improved the tensile properties of the polymer. The addition of 25 wt% nanosilica enhanced the tensile modulus and strength to about 38% and 24%, respectively, compared to the neat polymer without sacrificing the failure strain.

Zhou *et al.* (2012) performed dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA), and flexural tests on unfilled, 1, 2, 3, and 4 wt% clay filled SC-15 epoxy to identify the effect of clay weight fraction on thermal and mechanical properties of the epoxy matrix. The flexural results indicate that 2 wt% clay filled epoxy showed the highest improvement in flexural strength and the DMA studies also revealed that 2 wt% system exhibit the highest storage modulus and Tg as compared to neat and other weight fraction. However, TGA results show that thermal stability of composite was insensitive to the clay content. Based on these results, the nanophased epoxy with 2 wt% clay was then utilized in a vacuum assisted resin transfer molding set up with carbon fabric to fabricate laminated composites. The effectiveness of clay addition on thermal and mechanical properties of composites was evaluated by TGA, DMA, tensile, flexural, and fatigue test. 5^{o}C increase in glass transition temperature was found in nanocomposite, and the tensile and flexural strengths improved by 5.7 and 13.5 %, respectively as compared to the neat composite. The fatigue strength was also improved significantly. Based on the experimental result, a linear damage model combined with the Weibull distribution function were established to describe static failure processing of neat and nanophased carbon/epoxy.

The summary of discussed research work is given in the Table 2.1.

Table 2.1 Summary of Literature Review

S.No.	AUTHOR	MATERIALS USED	PROPERTIES TESTED
1	Myskove *et al.* (2003)	Montmorillonite Clay, Epoxy resin	Tensile Mechanical properties.
2	Brunner *et al.*(2006)	Silicate-based Nano filler, Epoxy resin	Mechanical properties. (Fracture Toughness).
3	Chowdhury *et al.*(2006)	Plain weave carbon, Epoxy resin, Nanoclay	Thermal and Flexural properties.
4	Li *et al.*(2007)	Nano-SiO_2, standard SiO_2 particles, Epoxy resin	Toughness, Impact strength.
5	Kim *et al.*(2008)	Carbon black, Nanoclay, Epoxy resin	Fracture toughness.
6	Fu *et al.*(2008)	Layered Silicate, Carbon Nanotube	Young's Modulus, Strength, Fracture Toughness.
7	Uddin and Sun (2008)	Glass fiber, Epoxy resin, Silica Nanoparticle	Compressive and Tensile properties.
8	Xu and Hoa (2008)	Carbon fiber, Epoxy resin, Nano clay	Fracture Toughness, Flexural Strength, Fracture surfaces.
9	Sundaram *et al.*(2008)	Polyester resin, E-glass fiber, Nano-montmorillonite (Nanoclay)	Tensile properties.
10	Schilde *et al.*(2010)	Nano-particles, Epoxy matrix	Mechanical, Electrical and Thermal properties.
11	Kuilla *et al.*(2010)	Graphene-based Polymer Nanocomposites	Fabrication of Graphine based Polymer Nanocomposites.
12	Mirmohseni and Zavareh (2010)	Poly(Acrylonitrile-Co-Butadiene-Co-Styrene) (ABS), Clay (Layered Lano-filler) and Nano-TiO_2 (particulate	Impact and Tensile strengths.

		nano-filler), Epoxy resin	
13	Ye *et al.*(2011)	Halloysite Nanotubes (HNT) filled Epoxy resin, Woven Carbon fibres	Thermomechanical properties (Flexural Modulus and Strength).
14	Ayatollahi *et al.*(2011)	Epoxy resin, Carbon Nanotube	Tensile properties, Fracture Toughness, Fractography.
15	He *et al.* (2011).	Nano-Calcium Carbonate, Epoxy resin	Thermal and Mechanical properties.
16	Gu *et al.*(2011)	Epoxy resin, Phosphazene-containing Nanotubes (EPPZTs)	Impact Strength and Tensile Strength.
17	Chen *et al.*(2012)	Glass Microfiber fabrics (GFs), Nano-Epoxy resins, Electrospun Glass Nanofibers (EGNFs)	Interlaminar Shear Strength, Flexural properties, Impact Absorption energy, and Tensile properties.
18	Mariana Ionita (2012)	Single walled Carbon Nanotubes (SWCNTs), Epoxy resin	Glass transition temperature, Young modulus and Solubility parameter.
19	Alamri and Low. (2012)	Nano-clay platelets, Halloysite Nanotubes (HNTs), Nano-Silicon Carbide (n-SiC) particles, Epoxy resin	Flexural Strength, Modulus, Fracture Toughness, Impact Strength.
20	Azeez *et al.*(2012)	Epoxy resin, Clay	Mechanical, Thermal and Barrier Properties.
21	Shadlou *et al.*(2012)	Epoxy resin, Nanodiamond (ND),Carbon Nanofiber (CNF), Graphene Oxide (GO)	Fracture behavior (Effective Fracture Resistance).
22	Jumahat *et al.*(2012)	Epoxy resin, Nano clay.	Compressive Stress-Strain behavior, Compressive properties.
23	Jumahat *et al.*(2012)	Nanosilica, Epoxy resin.	Tensile properties.
24	Zhou *et al.*(2012)	Carbon fiber, Nanoclay, Epoxy resin.	Thermal and Mechanical properties.

2.2 PROBLEM DEFINATION

Composite materials have been extensively applied to the areas of aerospace, aircraft, sports and military industries. Advanced composite materials have progressed from a laboratory curiosity to a production reality. However, the limits of improving composite properties made of traditional micrometer-scale fillers have been reached, since the composite properties achieved generally involved compromises, for example stiffness is obtained at the cost of toughness. So, there is a need to develop a hybrid composites in which, the addition of nano particles is there in order to get the desired properties without any compromises. Addition of Nanoparticles can significantly improve the properties of the nanocomposites.

Significant amount of work can be found in the literature on the addition of different fillers in composites and their effect on mechanical properties. However, there has not been much work done on the effect of adding nano particles such as TiO_2 combined with Nanoclay into the epoxy on the mechanical properties of polymer nanocomposites. Hence, the present work developed a Polymer Nanocomposite material with addition of Nanoclay and TiO_2 and the testing of the developed material was done to find the different mechanical properties.

CHAPTER 3
EXPERIMENTATION

The following sections give the details of the different materials used, methodology followed and different apparatus used for the experimentation of the present work.

3.1 MATERIALS

The present work is based on the Epoxy Nanocomposites. The materials used are DGBA based Epoxy Resin L12, Amine based Hardner K12, and Accelerator K13 supplied by Atul Ltd., Gujrat, India. TiO_2 (Degussa P-25), which was 99% pure and size less than 20 nm, was supplied by Degussa company, Frankfurt, Germany. It has BET surface area of 50 ± 15 m^2/g and is 80% in antase crystal form and 20% rutile with average particle size of 30 nm. Organically modified Nanoclay Cloisite 30B was supplied by Connell Bros., Mumbai, India.

3.2 MATERIAL PREPARATION

The Nanocomposites were prepared by following a standard procedure after an intense study of the literature. There are many methods for the preparation of nanocomposites, the one used in the present work is Hand Layup Method. For the preparation of the specimens various types of apparatus and equipments were used i.e., Borosilicate beakers, Electronic weight Machine, Mechanical stirrer, Water Bath Sonicator etc.

Different steps used for material preparation are given below:

(i) Mechanical Stirring

Epoxy base is a transparent in colour thick fluid. It is quite difficult to mix nano particles into it manually. So a mechanical stirrer is used for proper mixing of Nanoclay as shown in Fig. 3.1. Mechanical stirring was done for two hours at 2000 rpm. Different weight percentages of clay - 0, 1, 2, 3 and 4 % by weight of epoxy, were added and stirred for 2 hours.

(ii) Ultrasonication

Mechanical stirring was followed by Ultrasonication. Sonication is the process in which the sound energy is applied to agitate particles in a sample. In the laboratory, it is usually carried out using an ultrasonic bath (shown in Fig. 3.2) known as a sonicator. Sonication can be used to speed dissolution, by breaking intermolecular interactions. Sonication was done for evenly dispersing nanoparticles in liquids. After mechanical stirring of the epoxy solution container was placed into the ultrasonication bath for 2 hours.

Fig. 3.1 Mechanical Stirrer

Fig. 3.2 Ultrasonication Bath

(iii) Mixing of Hardner

After Ultrasonication, the solution is mixed with the hardener in the ratio 1:1 by weight and 1% accelerator is also added as per the instructions of the epoxy system resin. After mixing, mechanical stirring was done for 15 minutes, followed by ultrasonication for 15 min which results in proper dispersion of nanoparticles.

(iv) Degassing and Fabrication of Nanocomposite

After the sonication process, a large amount of bubbles were present, which can cause defects in the samples and can lead to negative results. To remove the bubbles degassing was done in a vacuum oven for 1 hour. The bubble free mixture was then poured into the Teflon coated mould and dispersed with the help of steel scrapper. Commercially available aluminum plate was used to make the mould for the samples. The aluminum plate was coated with the Teflon sheet (1 mm thick), so the cured samples are easily removed from the mould. The full curing of sheet was done by leaving it for one day at the room temperature and then curing at 120^0 C for 2 hours.

The samples of different proportions of Nanoclay and TiO_2 were prepared using the procedure discussed above.

(v) Specimen Preparation

Once the Epoxy was fully cured, the prepared sheet was manually cut (shown in Fig. 3.3) into specimen as per dimensions given in the Table 3.1. The size of the specimens was as per ASTM D638 and ASTM D790 for tensile and bending tests respectively.

Table 3.1 Specimen Specifications for Testing

Parameters	**Tensile Testing**	**Flexural Testing**
Length (mm)	150	56
Width (mm)	25	25
Thickness (mm)	2	2

Fig. 3.3 Cutting with Hacksaw Blade

3.3 MECHANICAL PROPERTIES

The following mechanical properties were tested from the prepared samples.

3.3.1 Tensile Testing

A Universal Testing Machine (UTM), shown in Fig. 3.4, was used to find the strength of the prepared samples. The test specimens were prepared as per dimensions in the Table 3.1. The tensile test was performed with a test speed of 5mm/min and a preload of 0.1 MPa.

Fig. 3.4 Specimen in UTM

3.3.2 Three Point Flexural Test

Three point Flexural test of specimen was carried out using UTM. The jaw setting on the UTM for three point flexural test is shown in the Fig. 3.5. The test specimens were prepared as per dimensions in the Table 3.1. The flexural test was performed with the the test speed of 1%/min and a preload of 0.1 MPa.

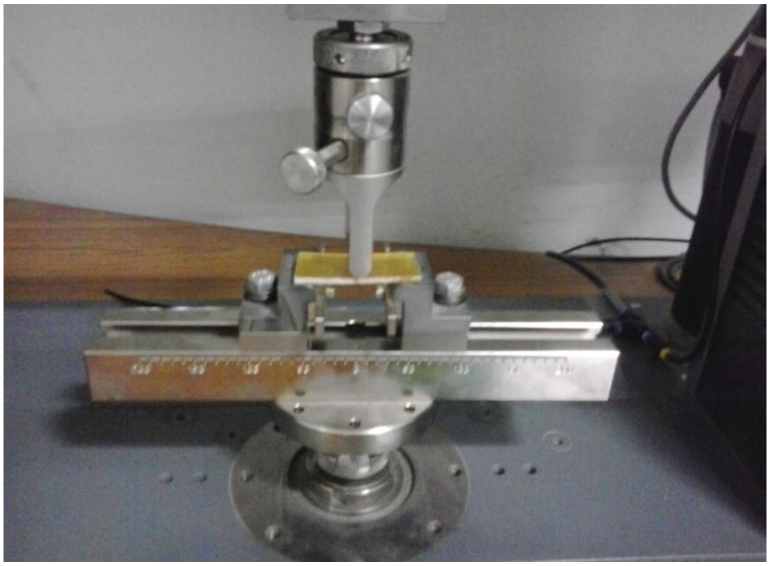
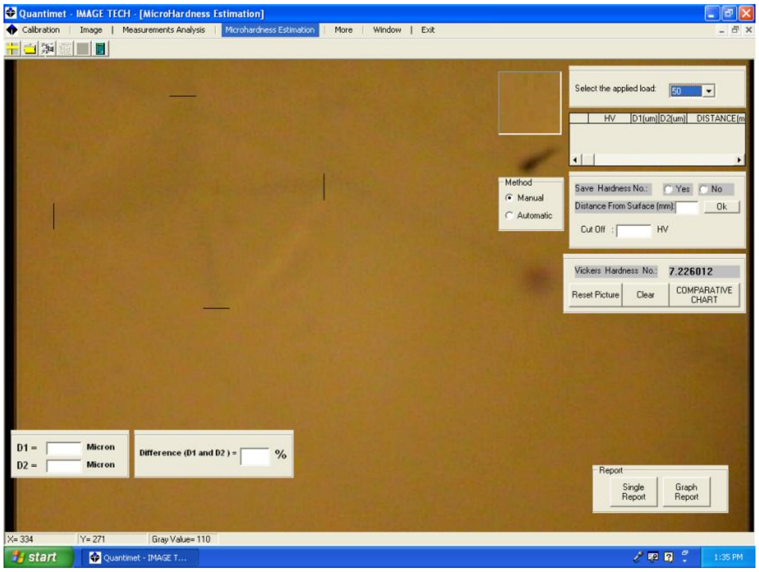


Fig. 3.5 Specimen positioning in three point bend test on UTM

3.3.3 Micro Hardness Test

Micro hardness tests were conducted on the prepared samples using Micro Hardness Tester, shown in Fig. 3.6. Vickers' Hardness value was determined by applying a preload of 50gm. The Dwell time used during the load application was 20 seconds. With the application of load, an indent was formed on the surface of the prepared specimen. A view of one such indent is shown in Fig. 3.7. The indent was marked on the different random points on the specimen to take the average hardness value. The Hardness value was calculated from the marked indent.

Fig. 3.6 Micro Hardness Equipment



Quantimet - IMAGE TECH - [MicroHardness Estimation]

Select the applied load: 50

Method: ● Manual ○ Automatic

Save Hardness No.: ○ Yes ○ No

Distance From Surface (mm):

Cut Off : HV

Vickers Hardness No.: 7.226012

D1 = Micron

D2 = Micron

Difference (D1 and D2) = %

X= 334 Y= 271 Gray Value= 110

Fig. 3.7 Indent of Specimen

CHAPTER 4

RESULTS AND DISCUSSIONS

The different mechanical properties were tested on the prepared samples of Epoxy with variation of Nanoclay content. The samples were prepared using the procedure discussed in chapter 3. Table 4.1 shows the number of samples prepared.

Table 4.1 Initial Testing Specimens

Specimen with wt% of Nanoclay	**No. of Specimens**		**Total Specimens**
	Tensile Test	**Bending Test**	
0 wt% *i.e* Neat Epoxy	3	3	6
1 wt%	3	3	6
2 wt%	3	3	6
3 wt%	3	3	6
4 wt%	3	3	6
Total Specimens			30

4.1 TENSILE TEST

The results obtained by conducting tensile tests on prepared Nanocomposites using Universal Testing Machine are shown in Table 4.2.

Table 4.2 Results of Specimens from Tensile Test

Specimen	**Specimen No.**	**Tensile Modulus (MPa)**	**Tensile Strength (MPa)**
0 wt%	Specimen No. 1	123.61	9.24
	Specimen No. 2	120.00	8.97
	Specimen No. 3	116.38	8.70
1 wt%	Specimen No. 1	96.41	11.80
	Specimen No. 2	90.80	12.40
	Specimen No. 3	89.33	12.20

2 wt%	Specimen No. 1	84.12	13.40
	Specimen No. 2	79.10	12.60
	Specimen No. 3	80.35	12.80
3 wt%	Specimen No. 1	53.74	11.90
	Specimen No. 2	56.90	12.60
	Specimen No. 3	54.64	12.10
4 wt%	Specimen no. 1	98.52	8.20
	Specimen no. 2	96.00	7.99
	Specimen No. 3	88.90	7.40

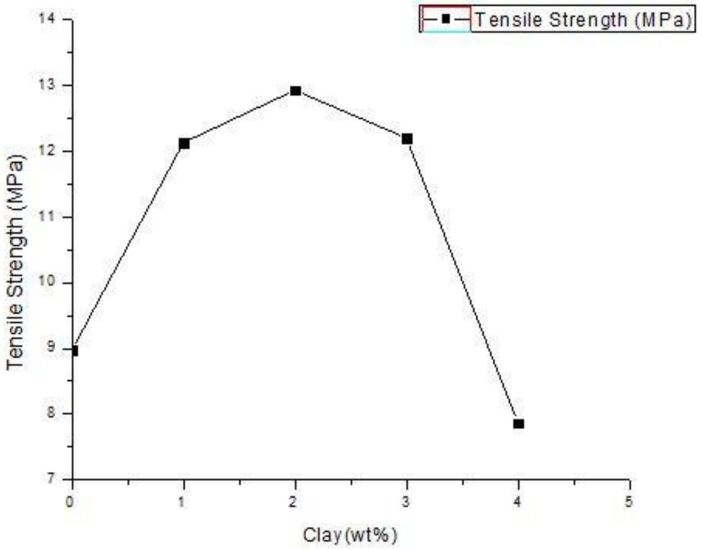


Fig. 4.1 Tensile strength of Specimen as a function of weight percentage of Nanoclay in Epoxy

The variation of ultimate tensile strength as a function of weight percentage of Nanoclay in Epoxy is shown in Fig. 4.1. The Tensile Strength of Nanoclay Epoxy Nanocomposites specimen was increased with the increasing wt% of Nanoclay with maximum Tensile Strength at 2 wt% of Nanoclay. The strength is around 44% higher than neat Epoxy Nanocomposites. The increase in the strength of the Epoxy samples is due to the addition of Nanoclay, which hindered the molecular movement of polymer chains. However, the strength decreases with further increase in the Nanoclay content.

4.2 THREE POINT FLEXURAL TEST

The results obtained by conducting Three Point Flexural tests on prepared Nanocomposites are shown in Table 4.3.

Table 4.3 Results of Specimens from Three-Point Bending Test

Specimen	Specimen No.	Elastic Modulus (MPa)	Flexural Strength (MPa)
0 wt%	Specimen No. 1	4450	73.6
	Specimen No. 2	4680	77.4
	Specimen No. 3	4909	81.2
1 wt%	Specimen No. 1	3930	60.1
	Specimen No. 2	5040	124
	Specimen No. 3	4145	102
2 wt%	Specimen No. 1	3180	129
	Specimen No. 2	3220	146
	Specimen No. 3	3043	138
3 wt%	Specimen No. 1	6820	110
	Specimen No. 2	6510	105
	Specimen No. 3	7750	125
4 wt%	Specimen No. 1	1982	90.2
	Specimen No. 2	2040	92.8
	Specimen No. 3	2163	98.4

The Flexural Strength of samples against the weight percentage of Nanoclay in epoxy is shown in Fig. 4.2. As seen from the figure, the addition of Nanoclay increases the Flexural Strength. A significant rise in the Flexural Strength was seen with maximum value at 2 wt% of Nanoclay. A 77% improvement in Strength of specimen with 2 wt% Nanoclay loading is observed when compared with neat Epoxy Nanocomposites. The enhancement in the flexural properties is attributed to the improved interfacial properties responsible for transfer of stresses and elastic deformation in the presence of Nanoclay particles. The presence of Nanoclay in the epoxy matrix strengthens and stiffens the surrounding matrix, effectively increasing the compressive strength of the composite. However, with further increase in the Nanoclay content the flexural strength decreases. The results are in accordance with the work carried out by Zhou *et al.* (2012).

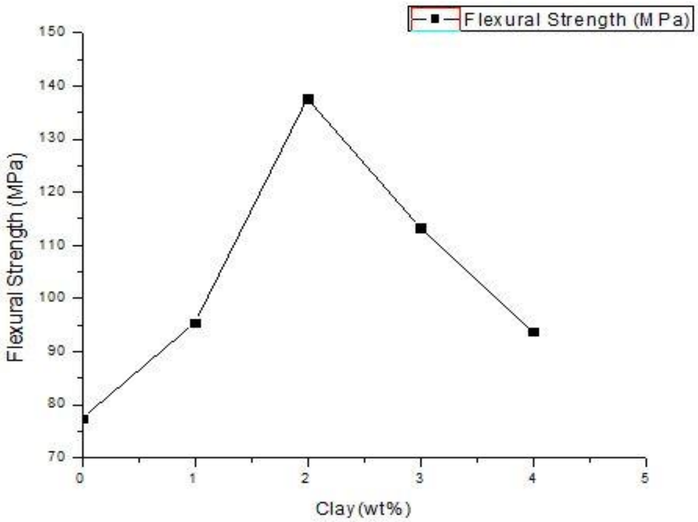


Fig. 4.2 Flexural Strength of samples as a function of weight percentage of Nanoclay in Epoxy

4.3 MICRO HARDNESS TEST

The micro hardness was tested at different loading points on the prepared specimen. The Table 4.4 shows the hardness value for different specimen.

Table 4.4 Micro Hardness Values for Different Clay Loading Specimens

Clay Loading → **Loading Points**	**Micro Hardness values**				
↓	0 wt%	1 wt%	2 wt%	3 wt%	4 wt%
Point 1	6.475	6.523	6.893	6.508	6.391
Point 2	6.316	6.704	6.594	6.482	6.254

Point 3	6.684	6.541	6.626	6.475	6.006
Average	**6.492**	**6.589**	**6.704**	**6.488**	**6.217**

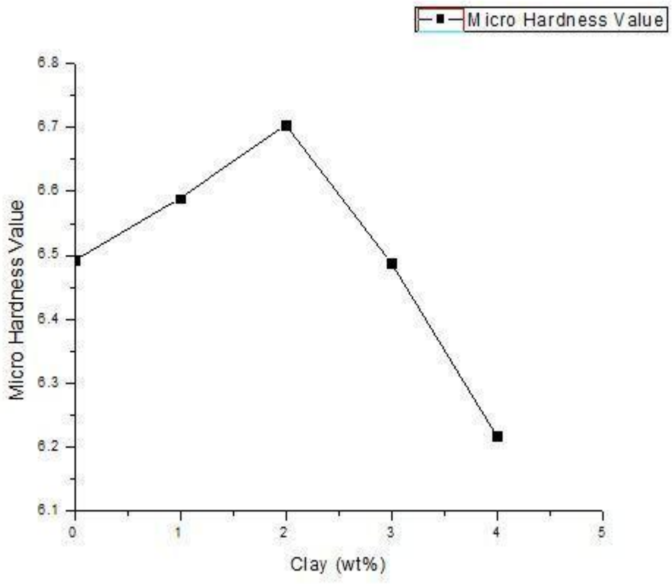


Fig. 4.3 Vickers' Hardness value of specimen as a function of weight percentage of Nanoclay in Epoxy

The variation of Micro Hardness as a function of weight percentage of Nanoclay in Epoxy is shown in Fig. 4.3. As seen from figure, the hardness increases with increase in the Nanoclay content. The specimen with 2 wt% of Nanoclay had the maximum hardness. However, with further increase in the Nanoclay content the hardness decreases drastically. Hence, adding a small amount of Nanoclay into polymer-based materials could potentially enhance hardness of the material. However, it is also reasonable that it should have an optimal limit depending on choice of constituent material and processing conditions.

4.4 OPTIMIZATION

As per the results of the Tensile Test, Three-Point Bending Test and Vicker's Hardness Test, the specimen with 2 wt% of Nanoclay gave the best results. Thereafter, the hybrid Nanocomposites were prepared with fixing 2 wt% of Nanoclay and adding TiO_2 in different compositions. The procedure discussed in chapter 3 was followed for the preparation and testing of the samples. The compositions of TiO_2 were 2 wt%, 4 wt% and 6 wt%. Table 4.5 shows the number of samples prepared after optimization.

Table 4.5 Testing specimens after the Optimization

Specimen		**No. of specimens**		**Total specimens**
Clay	TiO_2	**Tensile Test**	**Bending Test**	
2 wt%	2 wt%	3	3	6
2 wt%	4 wt%	3	3	6
2 wt%	6 wt%	3	3	6
Total specimens				18

4.5 TENSILE TEST

The results obtained by re-conducting tensile tests on prepared Hybrid Nanocomposites on UTM are shown in Table 4.6.

Table 4.6 Results of Specimens from Tensile Test

Specimen		**Specimen No.**	**Tensile Modulus (MPa)**	**Tensile Strength(MPa)**
Clay	TiO_2			
2 wt%	0 wt%	Specimen No. 1	84.12	13.40
		Specimen No. 2	79.10	12.60
		Specimen No. 3	80.35	12.80
2 wt%	2 wt%	Specimen No. 1	121	14.8
		Specimen No. 2	221	11.8
		Specimen No. 3	104	12.7
2 wt%	4 wt%	Specimen No. 1	117	4.14
		Specimen No. 2	116	5.19
		Specimen No. 3	140	4.68
2 wt%	6 wt%	Specimen no. 1	70.1	2.45
		Specimen no. 2	69.00	1.78
		Specimen No. 3	86.06	2.22

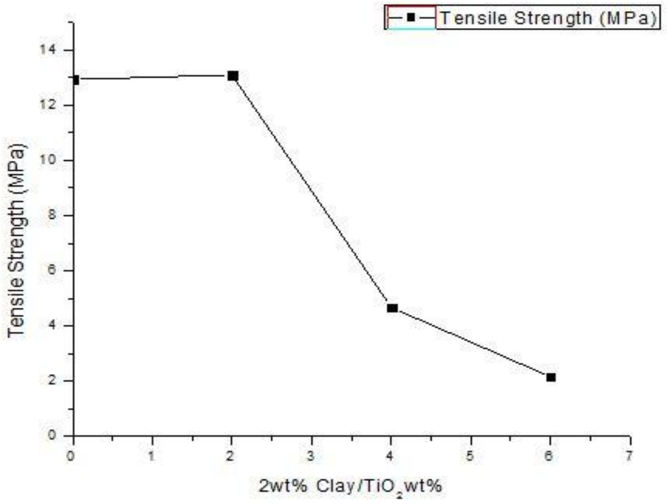


Fig. 4.4 Tensile strength of Specimen as a function of weight percentage of TiO_2 in 2 wt% Nanoclay Epoxy

Fig. 4.4 shows the variation of ultimate tensile strength as a function of weight percentage of TiO_2 in 2 wt% Nanoclay modified Epoxy. As seen from the figure, the Tensile Strength of Nanoclay/TiO_2 Epoxy Nanocomposites specimen increased with the increasing wt% of TiO_2. The maximum Tensile Strength was at 2 wt% of TiO_2. This maximum strength is slightly higher than Nanoclay Epoxy Composites. The increase in the strength of the Epoxy samples must be due to increased surface area of the nanofillers, which results in more bonds and more strength. However, further increasing the TiO_2 content does not have any significant effect on the tensile strength.

4.6 THREE POINT FLEXURAL TEST

The results obtained by re-conducting Three Point Flexural tests on prepared Hybrid Nanocomposites are shown in Table 4.7.

Table 4.7 Results of Specimens from Three Point Bending Test

Specimen		**Specimen No.**	**Elastic Modulus (MPa)**	**Flexural Strength (MPa)**
Clay	TiO_2			
2 wt%	0 wt%	Specimen No. 1	3180	129
		Specimen No. 2	3220	146

		Specimen No. 3	3043	138
2 wt%	2 wt%	Specimen No. 1	43.2	30.96
		Specimen No. 2	126	24.9
		Specimen No. 3	8.46	32.8
2 wt%	4 wt%	Specimen No. 1	37.1	20.8
		Specimen No. 2	35.4	24.2
		Specimen No. 3	24.4	23.4
2 wt%	6 wt%	Specimen No. 1	9.17	16.6
		Specimen No. 2	21.5	11.1
		Specimen No. 3	207	21.3

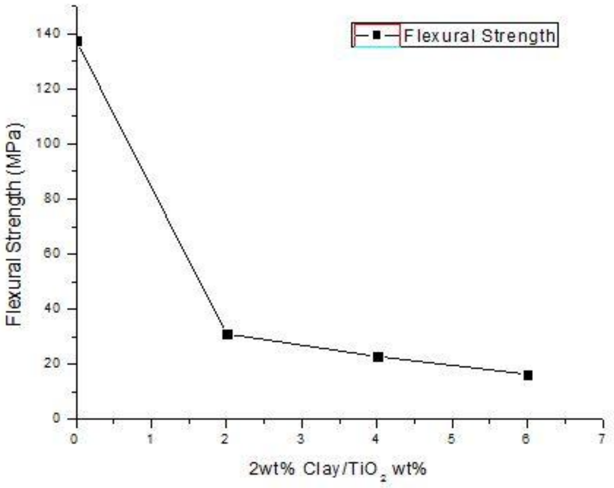


Fig. 4.5 Flexural Strength of samples as a function of weight percentage of TiO_2 in 2 wt% Nanoclay Epoxy

The variation of Flexural Strength as a function of weight percentage of TIO_2 in 2 wt% Nanoclay modified Epoxy. As can be seen from the figure, with the increase in the TiO_2 content the Flexural Strength decreases continuously. Hence, the addition of TiO_2 does not have the positive effect on the Flexural Strength of the Nanocomposites.

4.7 MICRO HARDNESS TEST

The micro hardness was again tested at different points on the prepared Hybrid Nanocomposites. Table 4.8 shows the hardness value for different specimen.

Table 4.8 Micro Hardness Values for Different TiO$_2$ Loading Specimens

Clay/TiO$_2$ Contents ⇒ **Loading Points** ⇓	**Micro Hardness Values**			
Clay	2 wt%	2 wt%	2 wt%	2 wt%
TiO$_2$	0 wt%	2 wt%	4 wt%	6 wt%
Point 1	6.893	7.226	7.858	5.931
Point 2	6.594	8.088	7.467	6.248
Point 3	6.626	7.474	6.824	5.843
Average	**6.704**	**7.596**	**7.383**	**6.007**

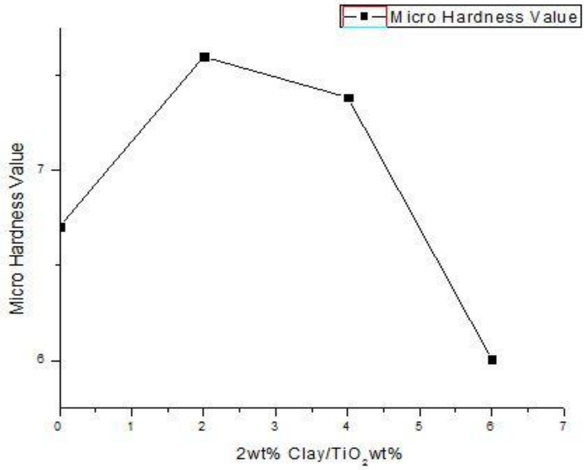


Fig. 4.6 Vickers' Hardness value of specimen as a function of weight percentage of TiO$_2$ in 2 wt% Nanoclay Epoxy

The variation of Vickers' Hardness value as a function of weight percentage of TiO$_2$ in 2 wt% Nanoclay modified Epoxy is shown in Fig. 4.6. Addition of TiO$_2$ increases the hardness value with maximum at 2 wt% of TiO_2. However with further increase in the TiO_2, the hardness value decreases. Thus, adding a small amount of TiO_2 can result in increases in hardness.

CHAPTER 5

CONCLUSIONS

5.1 CONCLUSIONS

From present work the following conclusions are drawn:

(i) The Tensile Strength of Nanoclay Epoxy Nanocomposites specimen was increased with the increasing wt% of Nanoclay with maximum Tensile Strength at 2 wt% of Nanoclay. This strength is around 44% higher than neat Epoxy Nanocomposites. However, the strength decreases with further increase in the Nanoclay content. After the optimization, TiO_2 in different concentrations is added into the 2 wt% Nanoclay modified Epoxy. With the addition of TiO_2 the Tensile Strength of Nanoclay/TiO_2 Epoxy Nanocomposites specimen increases with maximum at 2 wt% of TiO_2. This maximum strength is slightly higher than Nanoclay Epoxy Nanocomposites. The increase in the strength of the Epoxy samples must be due to increased surface area of the nanofillers. However, further increasing the TiO_2 content does not have any significant effect on the tensile strength.

(ii) The Flexural Strength increases with the increasing Nanoclay content with maximum strength at 2 wt% of Nanoclay. A 77% improvement in Strength of specimen with 2 wt% Nanoclay content is observed when compared with neat Epoxy Nanocomposites. The enhancement in the flexural properties is attributed to the improved interfacial properties responsible for transfer of stresses and elastic deformation in the presence of Clay nano particles. However, with further increase in the Nanoclay content the flexural strength decreases. Further with the addition of TiO_2, the Flexural Strength decreases. Hence, the addition of TiO_2 does not have the positive effect on the Flexural Strength of the Nanocomposites.

(iii) The Vickers' hardness value increases with increase in the Nanoclay content. The specimen with 2 wt% of Nanoclay had the maximum hardness. However, with further increase in the Nanoclay content the hardness decreases drastically. Hence, adding a small amount of Nanoclay into polymer-based materials could potentially enhance hardness of the material. Addition of TiO_2 increases the hardness value with maximum at 2 wt% of TiO_2. However with further increase in the TiO_2 the hardness value decreases. Thus, adding a small amount of TiO_2 can result in increases in hardness.

5.2 SCOPE FOR FUTURE WORK

The present work can be extended in the following dimensions:

(i) Effect of different Nanofillers in varying compositions can be studied.
(ii) Different preparation methods can be used to develop composites.
(iii) Different matrix and reinforcement materials can be studied.

REFERENCES

[1] S. T. Peters**,** Handbook of Composites, Chapman & Hall, London, 1998.

[2] Jinsong Leng and Alan kin-tak Lau, Multifunctional Polymer Nanocomposites, CRC press, USA, 2011.

[3] M. Zelenkova Myskova, J. Zelenka, V. Spacek, and F. Socha, Properties of Epoxy systems with Clay Nanocomposites, Mechanics of Composite Materials, Vol. 39, No. 2, pp.119-122, 2003.

[4] A.J. Brunner, A. Necola, M. Rees, Ph. Gasser, X. Kornmann, R. Thomann, M. Barbezat, The influence of silicate-based nano-filler on the fracture toughness of epoxy resin, Engineering Fracture Mechanics, vol.73, pp.2336-2345, 2006.

[5] F. H. Chowdhury, M. V. Hosur, S. Jeelani, Investigations on the thermal and flexural properties of plain weave carbon/epoxy-nanoclay composites by hand-layup technique, J Mater Sci, vol.42, pp.2690-2700, 2007.

[6] Haiyan Li, Zhisheng Zhang, Xiaofei Ma, Ming Hu, Xiuyu Wang and Panfeng Fan, Synthesis and characterization of epoxy resin modified with nano-SiO2 and γ-glycidoxypropyltrimethoxy silane, Surface & Coatings Technology, vol.201, pp.5269-5272, 2007.

[7] Byung Chul Kim, Sang Wook Park and Dai Gil Lee, Fracture toughness of the nano-particle reinforced epoxy composite, Composite Structures, vol.86, pp.69-77, 2008.

[8] Shao-Yun Fu, Xi-Qiao Feng, Bernd Lauke and Yiu-Wing Mai, Effects of particle size, particle/matrix interface adhesion and particle loading on mechanical properties of particulate–polymer composites, Composites: Part B, vol.39, pp.933-961, 2008.

[9] Mohammed F. Uddin and C.T. Sun, Strength of unidirectional glass/epoxy composite with silica nano particle-enhanced matrix, Composites Science and Technology, vol.68, pp.1637-1643, 2008.

[10] Yuan Xu, Suong Van Hoa, Mechanical properties of carbon fiber reinforced epoxy/clay nanocomposites, Composites Science and Technology, vol.68, pp.854-861, 2008.

[11] S. Sundaram, R. Nagalingam, R. Satheesh Raja, Experimental analysis on tensile properties of FRP with nano clay, Int J Adv Manuf Technol, vol.170, pp.1868-1876, 2008.

[12] Carsten Schilde, Hendrik Nolte, Christine Arlt and Arno Kwade, Effect of fluid–particle-interactions on dispersing nano-particles in epoxy resins using stirred-media-mills and three-roll-mills, Composites Science and Technology, vol.70, pp.657-663, 2010.

[13] Tapas Kuilla, Sambhu Bhadra, Dahu Yao, Nam Hoon Kim, Saswata Bose and Joong Hee Lee, Recent advances in graphene based polymer composites, Progress in Polymer Science, vol.35, pp.1350-1375, 2010.

[14] A. Mirmohseni and S. Zavareh, Preparation and characterization of an epoxy nanocomposite toughened by a combination of thermoplastic, layered and particulate nano-fillers, Materials and Design, vol.31, pp.2699-2706, 2010.

[15] Yueping Ye, Haibin Chen, Jingshen Wu, Chi Ming Chan, Evaluation on the thermal and mechanical properties of HNT-toughened epoxy/carbon fibre composites, Composites: Part B, vol.42, pp.2145-2150, 2011.

[16] M.R. Ayatollahi, S. Shadlou and M.M. Shokrieh, Fracture toughness of epoxy/multi-walled carbon nanotube nano-composites under bending and shear loading conditions, Materials and Design, vol.32, pp.2115-2124, 2011.

[17] Hongwei He, Kaixi Li, Jian Wang, Guohua Sun, Yanqiu Li and Jianlong Wang, Study on thermal and mechanical properties of nano-calcium carbonate/epoxy composites, Materials and Design, vol.32, pp.4521-4527, 2011.

[18] Xiaojun Gu, Xiaobin Huang, Hao Wei and Xiaozhen Tang, Synthesis of novel epoxy-group modified phosphazene-containing nanotube and its reinforcing effect in epoxy resin, European Polymer Journal, vol.47, pp.903-910, 2011.

[19] Qi Chen, Lifeng Zhang, Yong Zhao, Xiang-Fa Wu and Hao Fong, Hybrid multi-scale composites developed from glass microfiber fabrics and nano-epoxy resins containing electrospun glass nanofibers, Composites: Part B, vol.43, pp.309-316, 2012.

[20] Mariana Ionita, Multiscale molecular modeling of SWCNTs/epoxy resin composites mechanical behavior, Composites: Part B, vol.43, pp.3491-3496, 2012.

[21] H. Alamri and I.M. Low, Effect of water absorption on the mechanical properties of nano-filler reinforced epoxy nanocomposites, Materials and Design, vol.42, pp.214-222, 2012.

[22] Asif Abdul Azeez, Kyong Yop Rhee, Soo Jin Park,David Hui, Epoxy clay nanocomposites – processing, properties and applications: A review, Composites: Part B , vol.45, pp.308-320, 2012.

[23] S. Shadlou, E. Alishahi, M.R. Ayatollahi, Fracture behavior of epoxy nanocomposites reinforced with different carbon nano-reinforcements, Composite Structures, vol.95, pp.577-581, 2012.

[24] Aidah Jumahat, Costas Soutis, Jamaluddin Mahmud, Nurulnatisya Ahmad, Compressive properties of nanoclay/epoxy nanocomposites, Procedia Engineering, vol.41, pp.1607-1613, 2012.

[25] Aidah Jumahat, Costas Soutis, Shahrul Azam Abdullah, Salmiah Kasolang, Tensile properties of nanosilica/epoxy nanocomposites, Procedia Engineering, vol.41, pp.1634-1640, 2012.

[26] Yuanxin Zhou, Mahesh Hosur, Shaik Jeelani, P. K. Mallick, Fabrication and characterization of carbon fiber reinforced clay/epoxy composite, J Mater Sci, vol.47pp.5002-5012, 2012.

PUBLICATIONS

1. **Jatinder Singh, Toyesh Upreti, Jaswinder Singh Saini, Haripada Bhunia,** Mechanical properties of Nano-Clay/Nano-TiO$_2$ epoxy hybrid nanocomposites, International Conference on Nanotechnology (ICNT 2013), to be held on 25-26th October, 2013 at Haldia Institute of Technology, Haldia, Purba Medinipur, West Bengal, India (Accepted).