POLYETHYLENE TEREPHTHALATE FIBER REINFORCED EPOXY NANO COMPOSITES

A
Thesis Report

Submitted in partial fulfillment of the requirement for the award of degree

MASTER OF ENGINEERING
In

PRODUCTION & INDUSTRIAL ENGINEERING

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CERTIFICATE

This is to certify that the work in this thesis report "**Polyethylene Terephthalate Fiber Reinforced Epoxy Nano Composites**" submitted in partial fulfillment of requirement for the award of **Master of Engineering Degree** in **Production & Industrial Engineering** in Mechanical Engineering Department of Thapar University, Patiala, is an authentic record of work carried out by me under the guidance of **Mr. Bikramjit Sharma**, Assistant Professor, Mechanical Engineering Department, Thapar University, Patiala and **Dr. Rajeev Mehta**, Head & Associate Professor, Chemical Engineering Department, Thapar University Patiala.

The matter embodied in this report has been submitted in part or full to any university or institute for the award of any degree.

Date: 07 Jan. 2013

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This is to certify that the above declaration made by the student concern is correct to the best of my knowledge and belief.

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ABSTRACT

An economical and viable option to conventional and high cost materials is the use of fiber glass/epoxy composites, but for impact applications their toughness still has to be enhanced. The toughness and other mechanical properties can be improved by using very small amount of PET into an epoxy system. In the present work epoxy modified with MMT Clay (3 wt % of Epoxy) & PET fiber is manufactured using hand layup method. The nano composites have been characterized using Impact, Tensile, Bending and Microhardness tests. The mechanical properties are compared with those found for PET introduced epoxy nano composites. The mechanical test shows that the presence of 1 wt% PET fiber largely increases impact strength and flexural strength. Micro hardness decreased at PET fiber loading.

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CHAPTER 1: INTRODUCTION

1.1 INTRODUCTION

Nanotechnology involves the control and manipulation of materials at the nanoscale (particle sizes from 1 to 100 nano meter (nm), where 1 nm equals 1 billionth of a meter) to create new materials and structures that have novel properties due to their small size (increased surface area) is a topic of great current research. Materials with feature on the scale nano meters (10^{-9}meter) often have properties dramatically different from their bulk-scale counterparts. At nano level, some compounds transform from inert to active, from electrical insulator to conductors, from fragile to tough. They can become stronger, lighter and more resistant. These transformed properties are what account for the infinite potential application of nano particles. One of the major factors, which alter these properties, is the increase in the ratio of surface area to volume. As the surface area of a particle increases exponentially, creating more sites for bonding, catalysis or reaction with surroundings material, resulting in improved properties such as increased strength or chemical or heat resistance. Hence, due to the high surface-to volume ratio associated with nano meter sized particles it is possible to control the fundamental properties of materials through the surface/size effect. There is a great variety of nano materials and their range of properties and possible applications appears to be enormous, from extra-ordinary tiny electronics devices, including miniature batteries, to biomedical uses and as components of parts of automobiles.

Nanotechnology is directed towards the formation of various nano materials such as:

- Nanocomposites
- Nano fibers
- Nano particulate fillers
- Nano porous

Nanocomposites are found in nature, for example in the structure of the abalone shell and bone. The use of nano particle-rich materials long predates the understanding of the physical and chemical nature of these materials**.** From the mid 1950s nanoscale organic-clays have been used to control flow of polymer solutions (e.g. as paint viscosifiers) or the constitution of gels (e.g. as a thickening substance in cosmetics, keeping the preparations in homogeneous form). By the 1970s

polymer/clay composites were the topic of textbooks, although the term "nano composites" was not in common use.

In mechanical terms, nano composites differ from conventional composite materials due to the exceptionally high surface to volume ratio of the reinforcing phase and/or its exceptionally high aspect. The reinforcing material can be made up of particles (e.g. minerals), sheets (e.g. exfoliated clay stacks) or fibers (e.g. carbon nano tubes or electro spun fibers). The area of the interface between the matrix and reinforcement phase(s) is typically an order of magnitude greater than for conventional composite materials. The matrix material properties are significantly affected in the vicinity of the reinforcement. Polymer nano composites, properties related to local chemistry, degree of thermosets cure, polymer chain mobility, polymer chain conformation, degree of polymer chain ordering or crystallinity can all vary significantly and continuously from the interface with the reinforcement into the bulk of the matrix.

This large amount of reinforcement surface area means that a relatively small amount of nanoscale reinforcement can have an observable effect on the macro scale properties of the composite. For example, adding carbon nano tubes improves the electrical and thermal conductivity. Other kinds of nano particulates may result in enhanced optical properties, dielectric properties, heat resistance or mechanical properties such as stiffness, strength and resistance to wear and damage. In general, the nano reinforcement is dispersed into the matrix during processing. The percentage by weight (called *mass fraction*) of the nano particulates introduced can remain very low (on the order of 0.5% to 5%) due to the low filler percolation threshold, especially for the most commonly used non-spherical, high aspect ratio fillers (e.g. nanometer-thin platelets, such as clays, or nanometer-diameter cylinders, such as PET fibers).

1.2 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. 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.

1.2.1 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.

1.2.2 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.

1.2.3 Properties of composites depend on

1. Properties of phases
2. Geometry of dispersed phase (particle size, distribution, orientation)
3. Amount of phase

1.2.4 Classification of Composite

Composites can be broadly classified in to two groups.

1. **Natural Composites:** Several natural materials can be grouped under natural composites, e.g. Bones, wood, shells, pearlite (steel which is a mixture of a phase and Fe3C) etc.
2. **Man-Made Composites:** Man-made composites are produced by combining two or more materials in definite proportions under controlled conditions. e.g. Mud mixed straw to produce stronger mud mortar and bricks, Plywood, Chipboards, Decorative laminates, Fiber Reinforced Plastic (FRP), Carbon Composites, Concrete and RCC, Reinforced Glass etc

1.2.5 Uses of Composite Materials

1. Extensively used in space technology and production of Aerospace Components (tails, wings etc.)
2. Used in the production of sport goods e.g. racing car bodies and bicycle frames etc.

3. Used for general industrial and engineering structures
4. Used in high speed and fuel efficient transport vehicles
5. Carbon composite is a key material in today's launch vehicles and spacecraft. It is widely used in solar panel substrates, antenna reflectors and yokes of spacecraft. It is also used in payload adapters, inter-stage structures and heat shields of launch vehicles.

1.2.6 Advantages of Composites

1. High resistance to fatigue and corrosion degradation.
2. High 'strength or stiffness to weight' ratio. As enumerated above, weight savings are significant ranging from 25-45% of the weight of conventional metallic designs.
3. Due to greater reliability, there are fewer inspections and structural repairs.
4. Directional tailoring capabilities to meet the design requirements. The fiber pattern can be laid in a manner that will tailor the structure to efficiently sustain the applied loads.
5. Fiber to fiber redundant load path.
6. High resistance to impact damage.
7. Thermoplastics have rapid process cycles, making them attractive for high volume commercial applications that traditionally have been the domain of sheet metals. Moreover, thermoplastics can also be reformed.
8. Like metals, thermoplastics have indefinite shelf life. Etc.

1.3 NANO COMPOSITES

The definition of nano-composite material has broadened significantly to encompass a large variety of systems such as one-dimensional, two-dimensional, three-dimensional and amorphous materials, made of distinctly dissimilar components and mixed at the nanometer scale.

The general class of nano composite organic/inorganic materials is a fast growing area of research. Significant effort is focused on the ability to obtain control of the nanoscale structures via innovative synthetic approaches. The properties of nano-composite materials depend not only on the properties of their individual parents but also on their morphology and interfacial characteristics.

A nano-composite is as a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nanometer (nm), or structures having nano-scale repeat distances between the different phases that make up the material. In the broadest sense this definition can include porous media, colloids, gels and copolymer, but is more usually taken to mean the solid combination of a bulk matrix and nano-dimensional phase(s) differing in properties due to dissimilarities in structure and chemistry. The mechanical, electrical, thermal, optical, electrochemical, catalytic properties of the nano-composite will differ markedly from that of the component materials.

1.4 POLYMER FIBRE EPOXY NANOCOMPOSITE

In 1946, the first industrially-produced epoxy resin was introduced to market. Since then, the use of thermosetting polymers has steadily increased. The wide range of epoxy resin applications includes: coating, electrical, automotive, marine, aerospace and civil infrastructure as well as tool fabrication and pipes and vessels in the chemical industry. Due to their low density of around 1.3g/cm and good adhesive and mechanical properties, epoxy resin became a promising material for high performance applications in the transport industry, usually in the form of composite materials such as fiber composite or in honeycomb structures. In the aerospace industry, epoxy composites material can be found in various part of the body and structure of military and civil aircrafts, with the number of applications on the rise. A recent approach to improve and diversify polymer properties in the aerospace industries is through the dispersion of nanometer-scaled fillers in the polymer matrix. A significant number of academic and industrial projects have investigated the possibilities to further improve epoxy resin (and in some cases composites or other binary systems) through the strategy of producing nano composites.

The term epoxy resin refers to both the polymer and its cured resin/hardener system. The former is a low molecular weight oligomer that contains one or more epoxy groups per molecule (more than one unit per molecule is required if the resultant material is to be cross-linked). The characteristic group, a three-member ring known as epoxy, epoxide, oxirane, glycidyl or ethoxyline group is highly strained and therefore very reactive. Epoxy resins can be cross-linked through a polymerization reaction with a hardener at room temperature or at elevated temperature (latent reaction). Curing agents are used for room temperature cure are usually aliphatic

amines, whilst commonly used higher temperature, higher performance hardener are aromatic amines and acid anhydrides. However, an increasing number of specialized curing agents, such as poly-functional amines, polybasic carboxylic acids, mercaptans and inorganic hardener are also used. All of these results in different, tailored properties of the final polymer matrix. In general, the higher temperature Cured resin systems have improved properties, such as higher glass transition temperatures, strength and stiffness, compared to those cured at room temperature.

Materials used in our study for prepare the polymer epoxy nano composite are following: -

- Epoxy & Hardener
- Montmorillonite clay
- Polymer Fibers (PET)

1.4.1 MONTMORILLONITE CLAY

Clay as nano particles such as Semitic clays (e.g. Montmorillonite) are incorporated into polymers to form resulting polymer nano composite, which may possess unique electrical, mechanical and optical properties. The presence of clay as filler is expected to strengthen the mechanical properties.

Montmorillonite is a very soft phyllosilicate group of minerals that typically form in microscopic crystals, forming clay. It is named after Montmorillon in France. Montmorillonite, a member of the smectite family, is 2:1 clay, meaning that it has 2 tetrahedral sheets sandwiching a central octahedral sheet. The particles are plate-shaped with an average diameter of approximately one micrometer.

Montmorillonite clay nano particle possess electrical properties, heat, chemical resistance and has the ability of blocking UV light. By reinforcing this clay nano particles to composite fibers will give rise to specific properties such as UV blocking, flame retardant and anti-corrosive behaviors.

The mechanical properties with a clay mass fraction of only 5% exhibit a 40% higher tensile strength, 68% greater tensile modulus, 60% high flexural modulus. In addition, the heat distortion temperature (HDT) increased from 650C to 1520C.

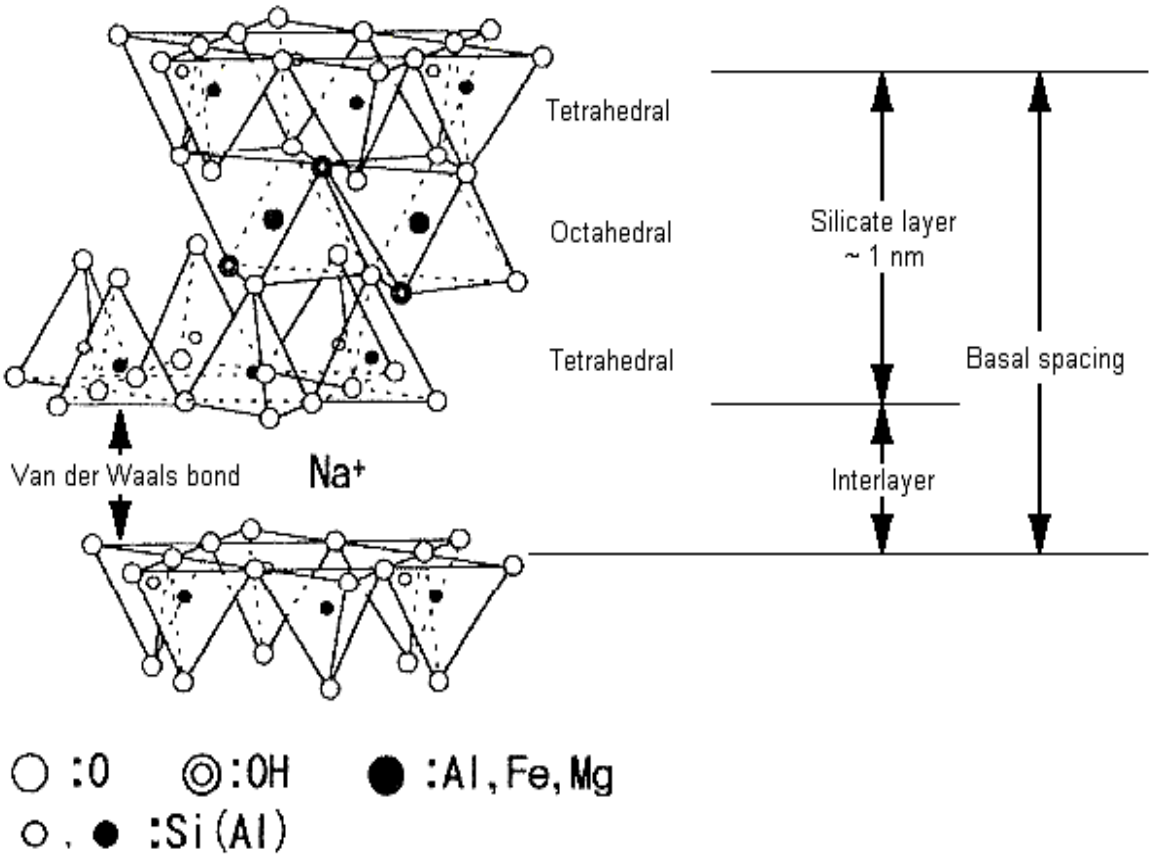

Fig 1.4.1: Chemical Structure of Montmorillonite Clay

1.4.1.1 Effect of Addition Clay

The tensile and compressive modulus showed improvements with increased nanoclay content. However, the tensile and compressive strengths decreased as nanoclay content increased. The impact strength and energy absorption for nano composites were higher for mechanically mixed specimens, but lower than the neat epoxy resin. Various mechanical properties exhibited mixed trends with increased nanoclay content in the composite. In most cases, exfoliated specimens showed better properties than intercalated specimens. Hence, applications of these materials should be selected in such a way that enhanced performance can be obtained by using the improved properties. Also it was found that the flexural modulus values were not affected by the clay addition.

Fig 1.4.2: Montmorillonite Clay

1.4.2 POLYETHYLENE TEREPHTHALATE (PET)

Polyethylene Terephthalate, commonly abbreviated as **PET**, **PETE**, or the obsolete PETP or PET-P, is a thermoplastic polymer resin of the polyester family and is used in synthetic fibers; beverage, food and other liquid containers; thermoforming applications; and engineering resins often in combination with glass fiber. The term polyethylene terephthalate is a source of confusion because this substance, PET, does not contain polyethylene. Thus, the alternate form, poly *(*ethylene terephthalate*)*, is often used in scholarly journals for the sake of accuracy and clarity.

Depending on its processing and thermal history, polyethylene terephthalate may exist both as an amorphous (transparent) and as a semi-crystalline polymer. The semi crystalline material might appear transparent (particle size < 500 nm) or opaque and white (particle size up to a few microns) depending on its crystal structure and particle size. Its monomer (bis-β- hydroxyls terephthalate) can be synthesized by the etherification reaction between terephthalic acid and ethylene glycol with water as a byproduct, or by transesterification reaction between ethylene glycol and dimethyl terephthalate with methanol as a byproduct. Polymerization is through a poly condensation reaction of the monomers (done immediately after esterification/ transesterification) with water as the byproduct.

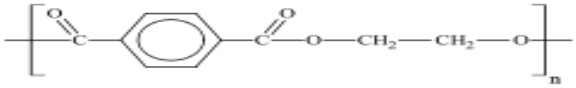

Fig 1.4.3: Chemical formula for Polyethylene terephthalate fiber

Polyethylene terephthalate is produced from ethylene glycol and dimethyle terpthalate ($C_6H_4(CO_2CH_3)_2$) or terepthalic acid.

Fig 1.4.4: Polyethylene terephthalate fiber

1.4.3 EPOXY RESINS & HARDENER

Epoxy resins, also known as epoxide resins, are a class of polymers, containing reactive groups which are converted to thermosets resins by reaction with compounds known as curing agents. It is the choice of curing agent which generally exerts the most influence on the final properties of the cured product. The term “epoxy resin” is used throughout this bulletin to represent the full epoxy system. The first epoxide resins were synthesized in 1930 from work in Switzerland/U.S.A. Commercial production commenced in the late 1940’s and by the 70’s over twenty five types of resins were available, all carrying the generic term of “epoxy resin” and current production internationally exceeds hundred of thousands of tones.

The term epoxy resin refers to both the polymer and its cured resin/hardener system. The former is a low molecular weight oligomer that contains one or more epoxy groups per molecule (more than one unit per molecule is required if the resultant material is to be cross-linked). The characteristic group, a three-member ring known as epoxy, epoxide, oxirane, glycidyl or ethoxyline group is highly strained and therefore very reactive. Epoxy resins can be cross-linked through a polymerization reaction with a hardener at room temperature or at elevated temperature (latent reaction).

Properly cured epoxy resins exhibit a number of highly desirable properties, probably unequalled in any other single class of polymer and these properties are responsible for the versatility of epoxies and for the diverse applications in which they have been successfully used. These properties can be summarized as follows:-

- Outstanding chemical resistance
- Low shrinkage or curing
- Excellent adhesion to a many substrates
- High mechanical strength
- Good electrical insulating properties

A simple, standard, unfilled, epoxy/curing agent system would possess the following typical properties, after seven days curing.

- Flexural Strength (KPa)- 87,560
- Compressive Strength (KPa)- 85,500
- Tensile Strength (KPa)- 38,610
- Elongation at Break (%)- 2.0

Mbrace Saturant (Epoxy)

Physical And Chemical Properties

Appearance	**:**	Blue translucent liquid
Odour	**:**	Mild characteristic odour.
Solubility in water	**:**	Insoluble
Specific gravity	**:**	0.950 - 1.150 g/cm3 at 23ºC
Boiling point	**:**	> 200ºC

Hazardous reactions: Reacts with amines to polymerize releasing heat.

Mbrace Saturant (Hardener)

Composition / Information on Ingredients

Chemical Characterization: Hardener for concrete adhesive resins based on amines

Physical and Chemical Properties

Appearance	**:**	Clear, colourless to slight amber low viscosity liquid
Solubility in water	**:**	Insoluble Hydrophobic.
Specific gravity	**:**	0.96 - 1.00 kg/L at 23ºC
Flash point	**:**	> 100ºC

1.4.3.1 Importance of Epoxy Resins

- Epoxy represents the most common type of structural adhesive. When polymerized, epoxy adhesives are amorphous and highly-cross linked materials.
- Due to highly cross linked structure results in many useful properties for structural engineering applications, such as a high modulus and failure strength, low creep.
- It provides good performance at elevated temperatures.
- Epoxy structure leads to one highly undesirable property in that they are relatively brittle materials, with a poor resistance to crack initiation and growth.
- Epoxy polymer can greatly increase their toughness without significantly impairing the other desirable engineering properties.
- Epoxy leads to increase in the dielectric strength of the material.

CHAPTER 2: LITERATURE REVIEW

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 nano polymer fillers to matrix system. PET fibers with nanoclay and their environmental degradation under different conditions have not been addressed so far.

Lepoittevin et al.(2001) studied the mechanical, thermal and rheological properties of poly(ε-caprolactone) nano composites (PCLN) prepared by melt blending the polymer with natural Na^+ MMT and MMT modified by hydrogenated tallow alkyl (HTA)-based quaternary ammonium cations dimethyl 2-ethylhexyl(HTA) ammonium and methyl bis(2-hydroxyethyl) HTA ammonium. An intercalated/exfoliated structure was observed by both XRD and TEM analyses. Stiffness and thermal stability improved with the filler loading until a content of 5 wt%. Further loading resulted in the leveling off. A significant improvement in thermal stability of PCL was noted at very low clay content (1 wt %).

Ke et al. (2002) prepared PET/clay nano composites by controlling different parameters such as the pretreatment of the MMT, the content of the MMT, the kinds of reagents used, and the manner by which they added MMT. According to TEM results, they did not observe any agglomeration until 3% weight of clay was added, but as the clay weight % increased above 3, agglomeration become unavoidable. They concluded that 3% weight of clay is a critical weight percentage for preparing PET nano composites. DSC results proved that MMT affect the nucleation process and increase the rate of crystallization. They also found that exfoliated lamellae's interaction with the molecular chain result into more regular chain patterns and this affects the PET‟s crystallization behavior and morphology.

Jong *et al.* (2002) investigated the mechanism of nanoclay exfoliation was investigated in epoxy clay nano composites system. The elastic force exerted by cross-linked epoxy molecules inside the clay galleries was found responsible for exfoliation of clay layers from the intercalated tactoids. Complete exfoliation of clay galleries was observed under the conditions of slow increase of complex viscosity and fast rise of storage modulus. It was observed that faster intra gallery polymerization, though expedited the exfoliation process, was not necessary for exfoliation. It was

also observed that clays containing hydroxylated quaternary ammonium ions and quaternary ammonium ions with no polar functional groups produced exfoliated structures equally easily, provided the ratio of storage modulus to complex viscosity was maintained above 2-4 1/s. Both higher curing temperature and the presence of organically modified clay particles accelerated the formation of gels, and the gel time presented an upper bound of time available for exfoliation

Salahuddin et al. (2002) prepared a highly filled epoxy-montmorillonite (MMT) nano composite using an organically modified MMT. Composites with clay content up to 70 wt. % exhibit unusual transparencies, which is related to the spatial distribution of the mineral nano domains. Dispersion of the layered silicate within the cross linked epoxy matrix was verified using X-ray diffraction pattern, revealing layer spacing of 30 and 70 d-spacing. Examination of these materials by scanning electron microscopy and transmission electron microscopy showed that intercalates have wholly layered morphology at all scales, oriented parallel to the surface of the specimen and have good wetting to the silicate surface by the epoxy matrix. Silicate lamellae intercalated with epoxy resin assembled into a cluster of about 50–120 nm thickness. These clusters assembled into super clusters with an average thickness of 300 nm. Studies by the Vickers hardness test of an epoxy-MMT nano composite containing 60 wt. % MMT indicated that the diamond pyramid hardness was 10–29 kg/mm^2.

Z.-M. Liang et al. (2002) stated that the preparation and processing of most of polymer/clay nano composites need high temperature. This limits the application of commonly used organic modifiers of long carbon-chain alkyl ammonium salts because of their low thermal stability. In this study, they synthesized two novel thermally stable, rigid-rod aromatic amines. Montmorillonite (MMT) treated by these amines exhibited larger layer-to-layer spacing, higher thermal stability than that treated by commonly used 1-hexadecylamine and also high ion-exchange ratio. They were applied to prepare nano composites with polyimide (PI) by in situ polymerization. XRD, TEM were used to obtain the information on morphological structure of PI/MMT nano composites. DMA, TGA, DSC, universal tester were applied to characterize the mechanical and thermal properties of the nano composites. When the MMT content was below 3 wt%, the PI/MMT nano composites were strengthened and toughened at the same time. The introduction of a small amount of MMT also led to improvement in thermal stability, slight increase in glass transition

temperature, marked decrease in coefficient of thermal expansion and decrease in solvent uptake. MMT treated by these aromatic amines exhibited better dispersibility and (probably) interfacial interaction with PI matrix than that treated by 1-hexadecylamine. The nano composites based on these MMT resultantly exhibited better mechanical, thermal and solvent resistance properties than those based on 1-hexadecylamine treated MMT.

Isik *et al.* (2003) synthesized diglycidyl ether of bisphenol A type epoxy resin-polyether polyol-organically treated montmorillonite ternary nano composites. The effects of addition of polyether polyol as an impact modifier on morphological, thermal and mechanical properties of nano composites were investigated by X-ray diffraction, scanning electron microscopy (SEM), differential scanning calorimetry, impact and tensile testing. The results showed that organically treated montmorillonite is intercalated by epoxy, since the interlayer spacing expanded from 1.83 to 3.82 nm upon nano composite synthesis. The addition of polyether polyol impact modifier had no effect on the interlayer spacing. SEM examination showed that polyol forms an immiscible phase in the epoxy matrix. In polyether polyol modified nano composites, the impact and tensile strengths decreased with respect to increasing amount of montmorillonite and showed a maximum with respect to the polyether polyol content at constant clay loading.

Ray *et al.* (2003), studied the academic and industrial aspects of the preparation, characterization, materials properties, and crystallization behavior, melt treology and processing of polymer/layered silicate nano composites. Smectite are a valuable mineral class for industrial applications because of their high cat ion exchange capacities, surface area, surface reactivity, adsorptive properties. Hectorite and Montmorillonite are among the most commonly used smectite-type layered silicates for the preparation of nano composites. They suggested that these composites are generally exhibit improved mechanical properties compared to conventional composites. They exhibit a remarkable increase in thermal stability, as well as self-extinguishing characteristics for flammability, such that the flammability of pristine polymers is significantly reduced after nano composite formation with layered silicate.

Chang et al. (2004) studied, PET nano composites made from monomers and organoclay via an in-situ interlayer polymerization method. Nanohybrid fibers were examined to compare the influences of the clay content, the different draw ratios

(DR), the dispersion, and the intercalation states. It was concluded that the addition of small amounts of modified clay were found to be enough to improve the thermal stability and the tensile properties of PET hybrid fibers at DR =1. When the DR was increased from 1 to 16, the organoclay in the PET caused significant decreases in the values of the ultimate tensile strength and the initial modulus due to debonding around the polymer-clay interfaces and void formation.

Lam *et al.* (2004) experimentally studied the hardness and inter-laminar shear properties of nanoclay/epoxy composites with different amount of nanoclay content, which formed different sizes of nanoclay/epoxy clusters after mixing in an extruder. The results showed that the micro-hardness of the composites could be enhanced when a small amount of nanoclay was added into the epoxy. However, there was an optimal limit in which the hardness was dropped by continuously increasing the nanoclay content. Microscopic observation on the fracture surfaces showed that the size of the clusters varied with the amount of nano clays used in the composites.

Guan et al. (2005) prepared PET/clay nano composites by in-situ poly condensation polymerization to study in depth crystallization behavior of the nano composites. It was reported that different surface modification strategies of MMT resulted in odd crystallization behavior. The reason for this behavior was attributed to (1) dispersion morphology of clay in the matrix; (2) surface shielding effect of small organic surfactant molecules; (3) nucleating effects of metallic derivatives released from MMT during in situ poly condensation. From crystallization behavior study and secondary nucleation analysis, it was concluded that nucleating abilities of MMT depends on the dispersion state of clay in polymer matrix, the surface modification and the metallic derivatives released from MMT during in situ synthesis.

Kornmann *et al.* (2005) synthesized and successfully used epoxy-layered silicate nano composites based on anhydride cured epoxy and octadecylamine modified fluorohectorite as matrix in glass-fiber-reinforced laminates by hand lay-up technique. The material used was the synthetic layered silicate Somasif ME-100. One hundred and twenty mille equivalents per 100 g of Somasif ME-100 of octadecylamine were dispersed in deionised water at 80^0C. They had done the flexural tests on the laminates and indicated that the presence of silicate layers in the epoxy matrix leads to a flexural strength improvement of 27%. According to dynamic mechanical measurements, the presence of organ silicate causes a decrease of the glass transition

temperature. The glass transition temperature decrease is apparently responsible for the larger water uptake observed in the nano composite.

Teh et al (2005), Thermoplastic polyethylene terephthalate (PET) fibers have been used to toughen an intrinsically brittle epoxy resin with high glass transition temperature. The morphologies and chemical properties of the as-received and the surface-modified PET fibers are comparatively investigated by scanning electron microscopy (SEM) and time-of-flight static secondary ion mass spectrometry (ToF-SIMS). Strong fiber– matrix adhesion is successfully achieved by optimizing surface modification of PET fibers with NaOH. Compared with neat epoxy resin, the fracture toughness of PET fibers filled epoxy composites is almost doubled when loading only 1 wt% chemically treated fiber. The fracture behavior and toughening mechanisms are studied by SEM observations on the fracture surfaces. Good correlation is found between the surface morphologies of the treated fibers, the fracture surfaces and the observed fracture toughness. SEM shows that fiber pullout, fiber breakage and formation of step structures due to fiber addition are among the operative toughening mechanisms observed.

Uhl et al (2005) prepared Polyamide-6 (PA-6)/graphite nano composites by melt blending, using a variety of graphite, including virgin graphite, expandable graphite and expanded graphite. The resulting nano composites were characterized by X-ray diffraction, thermo gravimetric analysis, calorimetric, and tensile mechanical analysis. Nano composite formation does occur, as denoted by the nano meter dispersion of graphite layers in the polymer matrix, and the dispersion depends on the graphite treatment. The material properties of the resulting composites are improved relative to the virgin/unfilled polymer; in particular, there is an enhancement of the thermal stability without any significant deterioration of the mechanical properties.

Avila *et al.* (2006) investigated the influence of montmorillonite (MMT) silicate layers on glass fiber- epoxy laminated composites behavior by low-velocity impact and X-ray diffraction tests. The nanostructure laminate prepared for this investigation is a S2-glass/epoxy-nanoclay. The nanoclay used in this was nanomer I30E. The amount of nanoclay dispersed into the epoxy system, in weight, was 1%, 2%, 5%, 10%, respectively. As the amount of nanoclay dispersed gets bigger, there is an increase in stiffness. As the stiffness reaches its peak value, the fracture toughness and damping were reduced. Specimens with 5% nanoclay content showed the best performance with respect to damping. As the energy increases, the nanostructure

laminate response gets weaker. When the low-velocity impact results were analyzed they showed an increase on energy absorption close to 48% for low energies, 20 J, 15% increase for medium– high energies, 60 J, and 4% for high energy, 80 J. As the amount of intercalated nanoclay content varied from 0% to 10%, the optimum condition for low-velocity impact seems to be around 5%.

Choi et al. (2006) prepared PET nano composites by direct polymerization in the presence of clay supported catalyst. Clay supported catalyst was prepared by suspending clay into anhydrous tetra hydro furon and adding chlorotitanium triisopropoxide to this suspension. This mixture was then stirred for 24 hr and clay supported catalyst was separated by filtration. Wide angle X-ray diffraction (WAXD) results showed intercalation of PET chains into the galleries of silicate layers but exfoliation was not observed. An improvement of oxygen permeability by 11.3-15.6 factors for PET/Clay supported catalyst over that of the neat PET was observed.

Yasmin *et al.* (2006) prepared the clay/epoxy nano composites by shear mixing. They used the 1-10 wt. % of clay concentration to prepare the samples. The epoxy matrix was reinforced with MMT clay particles to fabricate clay/epoxy nano composites. They used bisphenol A as epoxy resin and methyl tetra hydro phthalic anhydride as the hardener. Two types of clay nano particles were used as the reinforcement, one is Nanomer I.28E and other is Closite 30B. In this study Closite 30B shows a homogeneous dispersion of nano particles throughout the cross section compared to Nanomer I.28E/epoxy. As the clay content increases, the strain to failure decreases. It was also found that the modulus of the nano-composites increases monotonically with increasing clay content. For 10 wt% of clay, the Cloisite30B/epoxy shows an increase of 53% over the neat resin, where as the other shows and increase of about 22% at room temperature. This observation further confirms the direct relation between the degree of exfoliation and the mechanical properties of these nano composites. The addition of clay also found to reduce the CTE (coefficient of thermal expansion) of pure epoxy.

Wetzel *et al.* (2006) studied the manufacturing and the characterization of epoxy nano composites. Special attention was directed towards reinforcing effects of nano particles on the polymer toughness. The incorporation of both Al_2O_3 and TiO_2 nano particles into the epoxy resin improved flexural stiffness, flexural strength, and fracture toughness of the polymer at the same time. Cracks in dynamically loaded nano composites propagated at lower rates than in neat epoxy. The fillers were well

bonded to the matrix, which was indicated by both the shift of the glass transition temperature to higher temperatures and the increase in the rubbery plateau modulus. Moreover, the presence of Al2O3 in epoxy increased the apparent yield stress, the yield strain, and the size of the plastic zone. Debonding effects in the process zone, as often observed in glass bead filled epoxies, are rather unlikely to participate in the toughening of EP/Al2O3 nano composites, due to the small dimensions of fillers. Further investigations will help to find relationships especially between the morphology, the relevant toughening mechanisms, and the toughness of EP/Al2O3 nano composites. It is believed that the observed property characteristics are related to the influence of nano particles on the molecular structure of the matrix itself.

Chow *et al.* (2007) has prepared the epoxy/glass fiber/ organo- montmorillonite (OMMT) nano composites by hand lay-up method. In this work, the epoxy nano composites were characterized by X-ray diffraction (XRD), differential scanning calorimetry (DSC) and water absorption tests. Epoxy/glass fiber/OMMT hybrid nano composites prepared by hand-layup technique showed exfoliation characteristics and slight enhancement in glass transition temperature. The water resistance properties of epoxy were improved by an addition of both glass fiber and OMMT, which is maybe attributed to the increasing of the tortuosity path for water penetration.

Lin *et al.* (2007) performed experimental investigation of nano composite coatings for healing surface flaws of glass fibers and improving alkali-resistance. He found that, with low fraction of nano-reinforcements, the nanostructures and functionalized traditional glass fibers show significantly improved both mechanical properties and environmental corrosion resistance. The most remarkable mechanical strength improvement is found for glass fibers with nano tubes coatings, corresponding to the highest healing efficiency factor. No apparent strength variation appears for nanoclay coated fiber subjected to alkaline attack, which indicates that, the influence of moisture solvent uptake and concentration on mechanical properties decreases when the organoclay is dispersed in coating polymer. Overall, the hybrid nano coatings cause improved fiber strength, corrosion resistance, and interfacial properties.

Aht-Ong et al. (2008) prepared PET/MMT nano composites by a solution technique using 50/50 phenol/tetrachloroethane. To increase dispersion and compatibility of MMT in PET solution, he used ultrasonic power and different types of MMT, pristine MMT and MMT modified with dimethyl dioctadecyl ammoniaum. In the XRD study, it is observed that with pristine MMT, clay diffraction peak appeared at $2\Theta = 5.5°$

(15.9 A) and with modified MMT, there was no significant clay diffraction peak observed which may be result of almost complete exfoliation of clay platelets into the polymer matrix. It is found that for nano composites the maximum tensile strength and Young‟s modulus were obtained at low percentage of clay and they decreased with further increase in clay contents. This was attributed to the high interfacial properties and clay agglomeration respectively. Also the % elongation at break decreased with increase in clay content of both clay types, because of natural rigidity of silicate-sheet nano fillers.

Hwang et al. (2008) prepared PET nano composites by using pristine as well as modified clay (A-10 MMT). They found that modified MMT is more uniformly dispersed than pristine MMT. They also concluded that enhancement of properties is related to the good dispersion of the clay and not the total clay content in the polymer nano composite. Modified clay improved compatibility between the PET and clay was observed because of the alkyl modifier. They used Avrami and Ozawa equation to describe the non-isothermal crystallization kinetics, which showed that Na+MMT were more effective as a nucleation agent than A10-MMT. Finally they concluded that PET/A-10 MMT nano composite showed superior mechanical and thermal properties in comparison to neat PET.

Paul *et al.* (2008) states that exfoliated clay-based nano composites have dominated the polymer literature but there are a large number of other significant areas of current and emerging interest. This review will detail the technology involved with exfoliated clay-based nano composites and also include other important areas including barrier properties, flammability resistance, biomedical applications, electrical or electronic or optoelectronic applications and fuel cell interests. The important question of the "nano-effect" of nano particle or fiber inclusion relative to their larger scale counterparts is addressed relative to crystallization and glass transition behavior. Of course, other polymer (and composite)-based properties derive benefits from nanoscale filler or fiber addition and these are addressed.

Karunanayaka & Sarasanantham (2010) studied that montmorillonite clay nano particle possess electrical properties, heat, and chemical resistance and has the ability of blocking UV light. By reinforcing this clay nano particles to composite fibers gave rise to specific properties such as UV blocking, flame retardant and anti-corrosive behaviors. Electro spinning technology has the ability to produce nano fiber composites containing montmorillonite nano particles which can be used to produce

non woven fabrics or yarns with properties of UV blocking and flame retardant. This nano scale modification to the composite will give rise the ability to extract the improved performance on the end product. Fabrics or nonwovens developed from nano fibers which contain the anti UV and flame retardant properties are more durable and efficient than fabrics coated with anti UV or flame retardant agents. This research was focused on analyzing the UV blocking property of sodium- montmorillonite from Southern Clay, USA and purified clay from Sri Lanka. Testing was carried out to compare and contrast the UV blocking property of Na-MMT and Sri Lankan clay (SL Clay) in powder and liquid form. This research study will also focus in future on extruding Nano fiber composite by mixing the Montmorillonite clay nano particle with polyacrylonitrile (PAN), polymer via electro spinning technology.

Parvinzadeh et al (2010), prepared Poly ethylene terephthalate (PET)-based nano composites containing three differently modified clays, prepared by melt compounding. The influence of type of modified clay on surface properties of the resultant nano composite was investigated by various analytic techniques, namely, Fourier transform infrared spectroscopy (FTIR), atomic force microscopy (AFM), contact angle measurement (CAM), scanning electron microscopy (SEM) and reflectance spectroscopy (RS). Any possible interaction between each nanoclay and PET at the surface was elucidated by Fourier transform infrared spectroscopy. Atomic force microscopy studies of the resultant nano composites showed increased in surface roughness compared to pure PET. Contact angle measurements on the resultant PET composites demonstrated that the wettability of such composites depends on hydrophilicity of the nanoclay particles. Scanning electron microscopy images illustrated poor interfacial interaction between PET and Naþ clay particles causing fracture type non-uniformity of PET/Naþ clay nano composite.

Singh *et al.* (2010) reports on the durability of epoxy-clay nano composites upon exposure to multiple environments. Nanocomposites are fabricated by mixing the clay particles using various combinations of mechanical mixing, high-shear dispersion, and ultrasonication. Clay morphology is characterized using X-ray diffraction and transmission electron microscopy. Specimens of both neat epoxy and the epoxy-clay nano composite are subjected to two environmental conditions: combined UV radiation and condensation on 3-hour repeat cycle and constant temperature-humidity, for total exposure duration of 4770 hours. Both materials lose mass under exposure to combined UV radiation and condensation due to the erosion of epoxy by a synergistic

process. Surprisingly, the epoxy-clay specimens exhibit greater mass loss, as compared to neat epoxy. Mechanical testing shows that either environment does not significant affect the flexure modulus of either material. On the other hand, both materials undergo degradation in flexural strength when exposed to either environment.

Tomer et al. (2010) works on polymer nano composites prepared by epoxy reinforced with high permittivity barium titanate BT fillers or high aspect ratio montmorillonite (MMT) fillers exhibited marked changes in their high electric field properties and their relaxation dynamics, depending on the nano particle type and concentration, the nano particle size, and the epoxy matrix conversion. We investigated epoxy resin composites based on organically modified Montmorillonite oMMT or BT BaTiO3 nano particle in order to delineate the effects of the high aspect ratio of the MMT and the high permittivity of the BT particles. They also explored the potential benefits of the synergy between the two fillers in systems consisting of epoxy and both oMMT and BT particles. It was observed that the nature of the organic–inorganic interfaces dominate the glass transition temperature and the dielectric properties of these composites. Specifically, using dielectric relaxation spectroscopy, we probed the local dynamics of the polymer at the interfaces. The MMT systems had approximately three orders of magnitude slower interfacial dynamics than those at the BT interfaces, indicating more robust interfaces in the MMT composites than in the BT-based composites; the corresponding energy barriers activation energies associated with these motions were also doubled for the MMT systems. Furthermore, we investigated the effect of the decreased glass transition, interfacial area, polymer-phase at the organic–inorganic interface, and of the dielectric breakdown on the electrical energy storage capabilities of these composites.

Chakradhar (2011), developed and characterized inter-cross-linked networks of unsaturated polyester (UP) toughened epoxy blends Mechanical properties like tensile strength (TS), impact strength (IS), inter laminar shear strength (ILSS), scanning electron microscope (SEM) analysis and transmission electron microscope (TEM) analysis were characterized for the above nano composites. Montmorillonite (MMT) clay was dispersed into the same system to prepare blended epoxy/UP/clay nano composites in different weight ratios viz. 0%, 1%, 2%, 3% and 5%. Blended nano composites were fabricated by high shear mechanical mixing followed by ultra-sonication process to get homogeneous mixing under the aid of *in situ* polymerization.

Mechanical properties were studied as per ASTM standards. Data obtained from mechanical studies indicated that the epoxy/UP/clay combination improved the mechanical properties to an appreciable extent. The ILSS,TS and IS of the 3 wt % clay-filled blend nano composite system was increased by 52%, 30% and 16% respectively compared to that of the neat blend (0wt. % clay) resin system. The homogeneous morphologies of the UP toughened epoxy and epoxy/UP/clay nano composite systems were ascertained using scanning electron microscope (SEM) and transmission electron microscope (TEM) studies. The objective of this study is to identify a suitable nano composite which offers low-cost, high strength material, which can be applied in making light weight components for automobile parts, transportation systems and consumer products.

Teli et al (2011) studied Polyester Nano composite fibers with Antibacterial Properties. Antibacterial nano composite polyester (PET) fibers were melt spun by adding nano ZnO loaded Linear Low Density Polyethylene (LLDPE) master batch (MB) to the PET chips. The influence of content of nano ZnO on the antibacterial properties, crystallization behaviour and mechanical properties was studied. It was found that PET composite fibers having 1 % nano ZnO showed the optimum antibacterial activity. The presence of nano particles advanced the onset of crystallization temperature and also adversely affected the mechanical properties but well within acceptable limit.

Amendola et al. (2012) evaluated the effect of MMT silylated by 3-aminopropyltriethoxysilane and N-(2-aminoethyl)-3-amino propyl trimethoxysilane on the mechanical behavior of MMT/epoxy nano composites by evaluation of dynamical mechanical analysis and nano indentation technique. The silicate clay layers were dispersed in the epoxy matrix by Sonication process obtaining the intercalation of the epoxy resin inside the inorganic galleries of MMT. The results showed that the MMT modified with N-(2-aminoethyl)-3- amino propyl trimethoxysilane, which is characterized by the longer alkyl functional group, exhibits a higher compatibility with polymer matrix and improved mechanical properties.

CHAPTER 3: GAPS IN LITERATURE

From the literature review it is found that work so far reported in literature has been mainly focused on the synthesis of polymer nano composites and the characterization of the mechanical properties. There are no detailed studies on PET (Polyethylene terephthalate) addition to the epoxy. Some of the following gaps in the reposted research are:

1. There are very few studies that have been carried out on the combination of PET fiber, epoxy and MMT clay.
2. There are still difficulties in distributing PET fiber homogeneously in the matrix.
3. NaOH has not been used yet for washing of PET fibers before inserting into Epoxy matrix which increase the adhesion of PET fiber.

Research Problem

The present study is mainly focused upon quantifying the effect of addition of PET fiber to the epoxy layered silicate nano composites. Also the degradation in mechanical properties under hygrothermal loading is to found.

Objectives

From the gaps in literature we select the following objectives of our study: -

1. To study effect of addition of PET fiber to an epoxy nanoclay composites.
2. To carry out the mechanical testing of the prepared material.
3. To study the effect of hygrothermal loading on the material.

CHAPTER 4: FABRICATION & EXPERIMENTATION

4.1 METHODOLOGY

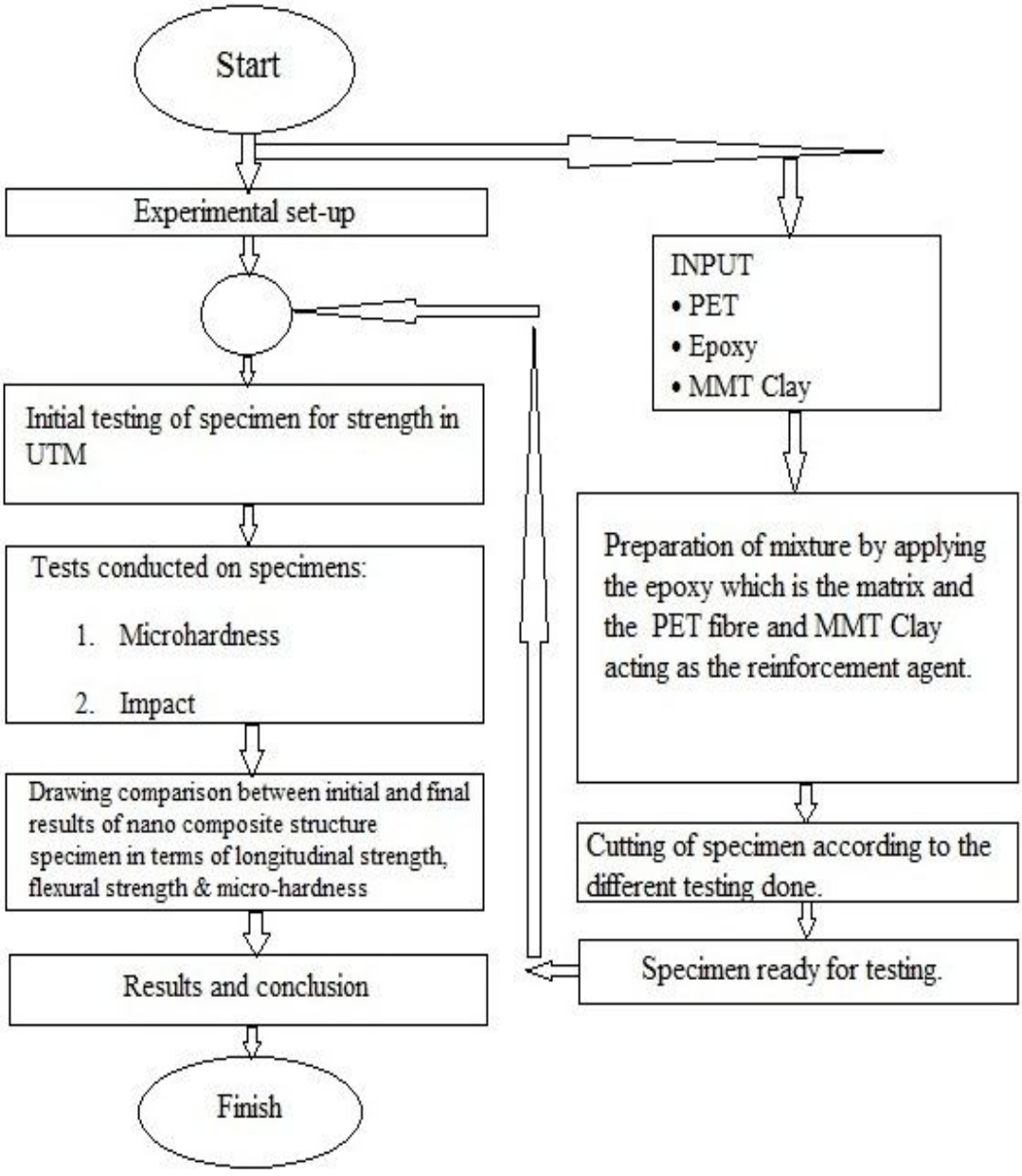

Fig 4.1.1: Methodology flow chart

4.2. FABRICATION OF SPECIMEN

4.2.1. MATERIAL

M Brace a two part **epoxy resin** (Density - 983 kg/m^3) was purchased from BASF Construction Chemicals (India) Private Limited.

Organically modified **nanoclay Closite 30B was** purchased from Connell Bros. Mumbai.

Recron fibers **PET (Poly ethylene Terephthalate)**, Diameter - 15µm, Length – 3mm are sold by Reliance India Ltd.

4.2.2. PROCESSING

4.2.2.1. Mixing of Nanoclay into Epoxy (base):

- **Preparation of Nanoclay:** Before mixing the nanoclay into the epoxy base, Nanoclay was dried at 120^{0}C for 2 hours in a vacuum oven.
- **Mechanical stirring**: Epoxy base is a blue colour thick fluid. It is quite difficult to mix nano silicates into it manually. So we used a mechanical stirrer and an oil bath for proper mixing of nanoclay (Fig. 4.2.1.). Oil bath was used to heat up the epoxy to desired (80^0 C) temperature, so that the viscosity of epoxy base is reduced. Proper mechanical stirring of epoxy at this stage resulted in a better dispersion of clay. Weight percentages of clay 3 % by weight of epoxy, were added and stirred at a temperature of 80^0 C for 1 hour.

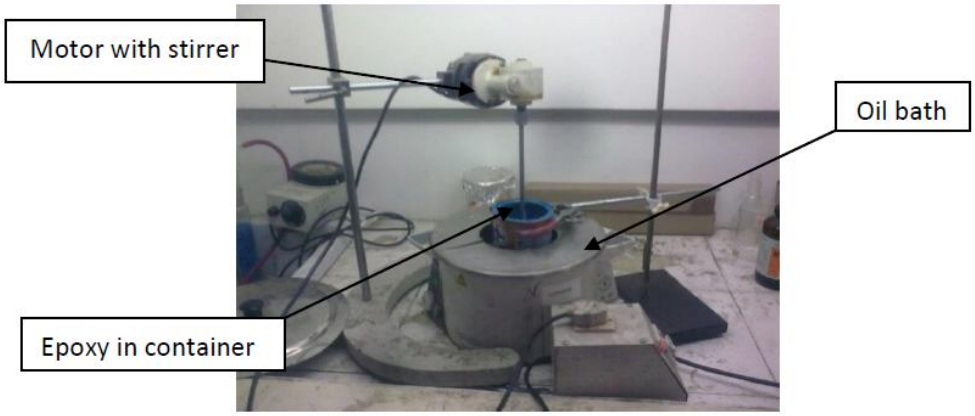

Fig. 4.2.1: Oil bath set-up with mechanical stirrer

- **Ultrasonication after Mechanical Stirring:** Sonication is an act of applying sound energy to agitate particles in a sample, for various purposes. In the

laboratory, it is usually carried out using an ultrasonic bath or an ultrasonic probe, colloquially known as a sonicator. Sonication can be used to speed dissolution, by breaking intermolecular interactions. Sonication was done for evenly dispersing nano particles in liquids. After mechanical stirring of the epoxy solution container was placed into the ultrasonication bath for up to 3 hours at 30^0 temperature (fig. 4.2.2).

Fig.4.2.2: Ultrasonication bath

4.2.2.2 Mixing of Epoxy Base Solution with PET fibers:

- **Preparation of PET Fibers:** In order to improve the adhesion between the fiber and the matrix, the PET fibers were subjected to alkaline hydrolysis. The fibers were treated with a NaOH aqueous solution (50% w/v) at 80^0C for 2.5 min., then fibers were washed with distilled water until all the sodium hydroxide was eliminated and the water used for washing the fibers no longer gave any alkalinity reaction. Subsequently, the surface-treated fibers were dried at 60^0C for 24 h in a vacuum oven.
- **Mixing of Epoxy Base solution with modified PET fibers** After ultrasonication, PET fibers mixed into the solution in different ratios (0, 0.25, 0.5, 0.75 & 1% by volume). After mixing, manual stirring up to 5 to 10 minutes was done (fig. 4.2.3).

4.2.2.3. Mixing of Epoxy Base & PET Solution with Hardener:

After ultrasonication, the solution is mixed with the hardener in the ratio 10:4 by volume. After mixing, manual stirring for 5 to 10 minutes was done. The whole procedure is shown in Fig. 4.2.4.

Fig. 4.2.3: Mixing of PET fiber Epoxy solution

Fig. 4.2.4: Mixing of hardener to the solution

4.2.2.4. Making the PET/Epoxy Composite Sheets:

The mixture was then poured into the mould and applied uniformly using the hand layup method. Due to low viscosity, the solution maintained uniformity by self. It was made sure that there is no air bubbles entrapped inside the epoxy applied on sheet otherwise it would create a flaw there. After applying epoxy, the sheet was left overnight to dry. The full curing of sheet (Fig. 4.2.5) was done by leaving it under ambient temperature for at least seven days before processing further.

Fig. 4.2.5: Sheets placed for curing

4.2.2.5 Cutting the specimens according to ASTM slandered

Once the epoxy was fully cured, the sheet was cut to actual sample size using the Treadle shearing machine (Fig. 4.2.6).

Fig4.2.6: Treadle Shearing Machine

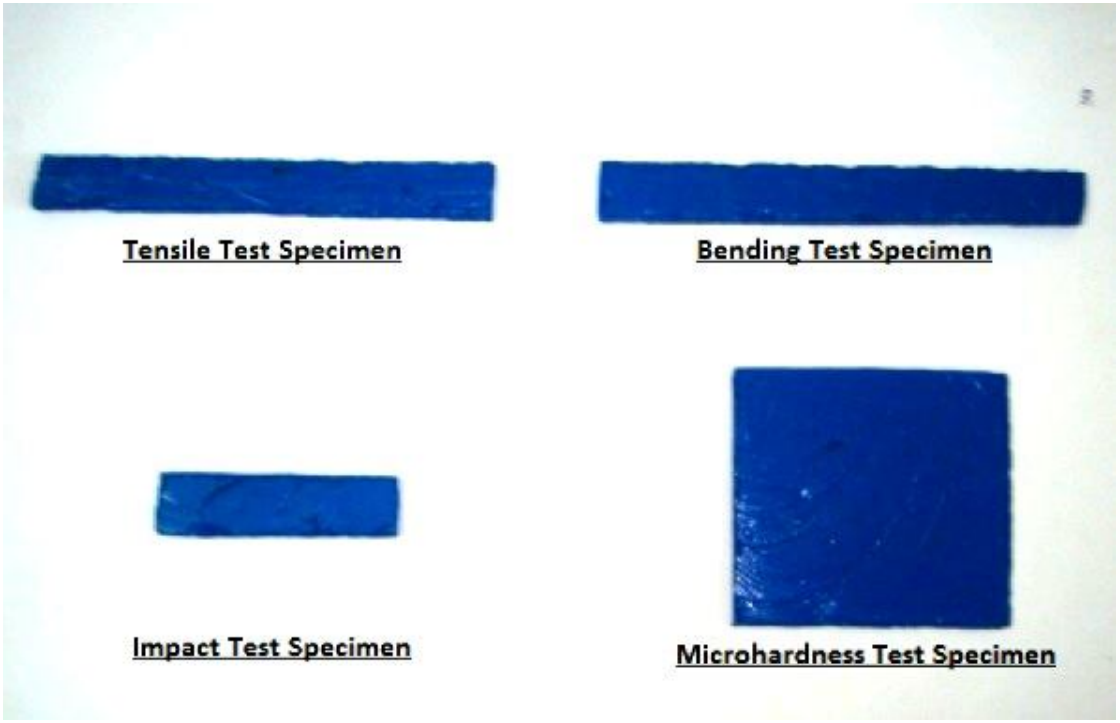

Fig 4.2.7: Prepared specimen

Specimen Specifications

The specimen had been cut and prepared as per the ASTM standards D638, D695 and D790 for tensile, Impact and bending tests respectively. The dimensions of specimens are shown below.

Table 4.2.1 Specimen Specifications for Testing

Parameter for Specimen	Specimens for Tensile Testing	Specimens for Impact Testing	Specimens for Bending Testing
Length	125 mm	62 mm	125mm
Width	15mm	10 mm	12.7mm
Thickness	4mm	4mm	4mm

Table 4.2.2: Record of specimen

PET Loading	No. of Specimen				Specimen
	Tensile	Micro Hardness	Flexural	Impact	
0 wt%	5	1	5	5	16
0.25 wt%	5	1	5	5	16
0.5 wt%	5	1	5	5	16
0.75 wt%	5	1	5	5	16
1.0 wt %	5	1	5	5	16
Total Specimen					**80**

4.3 TESTING METHODS USED IN EXPERIMENTATION

4.3.1Tensile Testing

A Universal Tensile Testing machine shown in Fig.4.3.1 and Fig.4.3.2 was used for the testing of the PET/Epoxy composite specimen for its tensile strength. The test specimen had been prepared according to ASTM-D-638 standard. The specimen were

tested until they broke indicating the peak load and ultimate stress value they can bear at required time period to estimate the degradation in the same machine.

Fig. 4.3.1: UTM testing machine

Fig. 4.3.2: Specimen in jaws

4.3.2. Three Point Flexural Test

Three point bending tests of specimen were carried out in Zwick / Roell using the arrangement as shown in fig. 4.3.3 & 4.3.4. The test specimen had been prepared according to ASTM-D-790 standard.

Fig. 4.3.3: Three point bend test machine

Fig. 4.3.4: Specimen positioning

4.3.3. Micro Hardness Test

Micro hardness test (shown in Fig.4.3.5) was conducted on specimen with different PET fiber contents.

Fig. 4.3.5: Micro hardness equipment

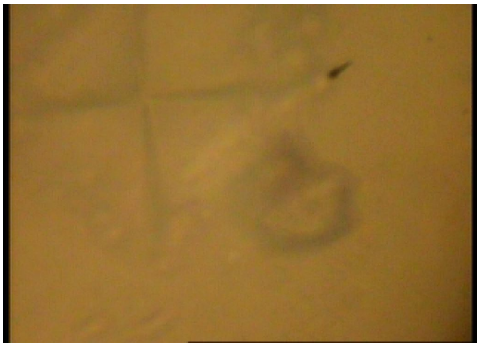

Fig4.3.6: Indent of specimen

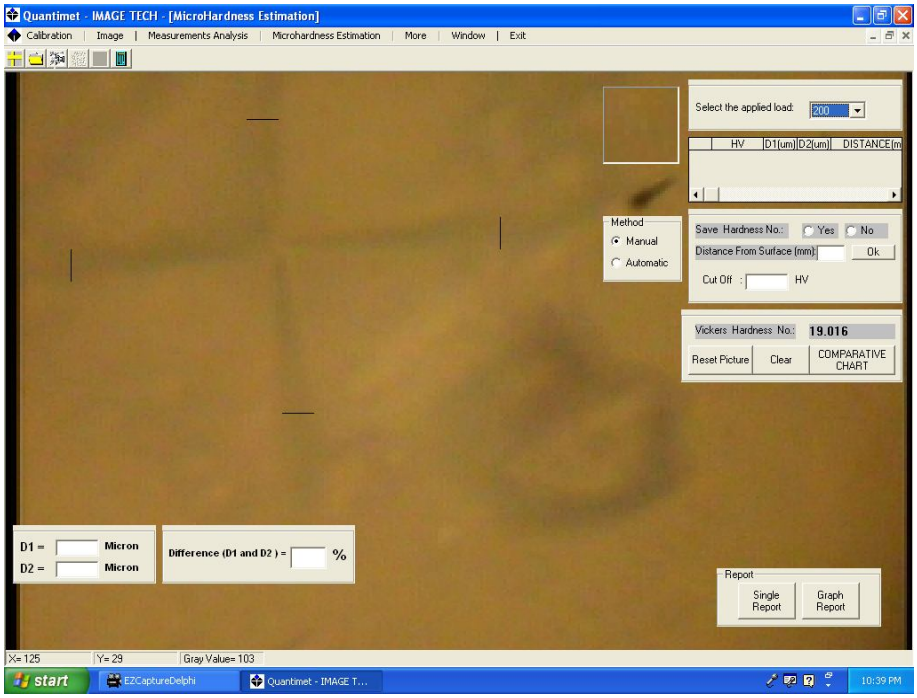

Fig 4.3.7: Vickers Hardness number of specimen

The load applied was 200 gm and VHN values were determined by applying this load by using a calibration distance of 50 units in Quantinet software as shown in Fig.4.3.7 used for image analyzing. The dwell time used during load application was 20 seconds. An indent is formed in diamond shape used for calculating VHN as shown in figure above.

4.3.4 Impact Test

An Impact testing machine shown in fig 4.3.8 was used for the testing of the PET/Epoxy composite specimen for its Impact strength. The apparatus consists of a pendulum of known mass and length that is dropped from a known height to impact a notched specimen of material. The energy transferred to the material can be inferred by comparing the difference in the height of the hammer before and after the fracture (energy absorbed by the fracture event).

Fig4.3.8: Impact Testing Machine

4.3.5 SEM (Scanning Electron Microscope)

Scanning electronic microscope was used to test Polymer fiber epoxy nano composite specimen's microstructure. The dimensioning of specimen was done according to block size of machine. The polishing of specimen was done by using Silver coating equipment. The polished specimen was used to observe the microstructure of specimen at different magnification.

SEM micrographs are helpful in viewing the micro-structure of material, hence showing any changes in physical structure of material and showing any defects like cracks, voids generated after loading of clay and hygrothermal degradation of the material. These are also helpful in calculating the area fraction of fiber and epoxy in the given specimen and the changes occurring and for also calculating the circularity of the fiber in case of Polymer fiber epoxy nano composites.

4.3.6 X-Ray Diffraction Test

X-ray scattering techniques are a family of non-destructive analytical techniques which reveal information about the crystallographic structure, chemical composition, and physical properties of materials and thin films. These techniques are based on observing the scattered intensity of an X-ray beam hitting a sample as a function of incident and scattered angle, polarization, and wavelength or energy.

X-ray diffraction was used in this study to investigate the crystallographic structure of the epoxy nano composites. XRD will enable the changes that occur to the clay due to the intercalation and/or exfoliation of the epoxy into the clay galleries to be quantified. The d-spacing of the intercalary spacing can be determined using Bragg‟s Law:

$$\lambda = 2d\sin\theta$$

Where λ is the wavelength of the incidence x-ray source, d is the spacing in question, θ is ½ of 2θ the Bragg angle or the diffracted angle of the incidence x-ray beam. Below is a schematic of the previously mentioned Bragg‟s Law (Fig. 4.3.9).

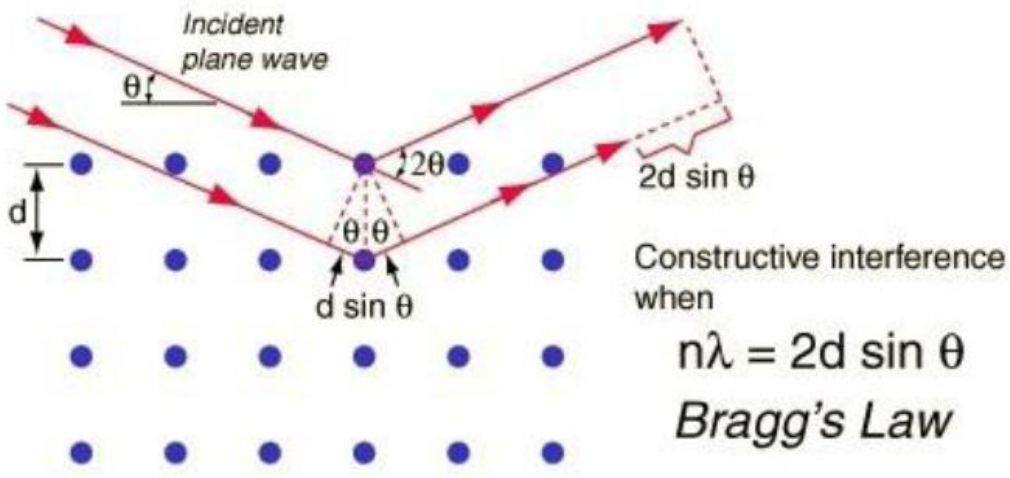

Fig 4.3.9: Schematic representation of x-ray diffraction principle and the Bragg Law

To evaluate the degree of exfoliation in the polymer, XRD measurements were carried out in a Panalytical X-ray diffract meter with Cu Kα radiation (λ=1.54Å) with a scanning speed of 10/min and at 45 kV and 40mA. During the XRD experiments,

the samples were analyzed in reflection mode. All XRD scans were through 2θ of 0^0 to 20^0.

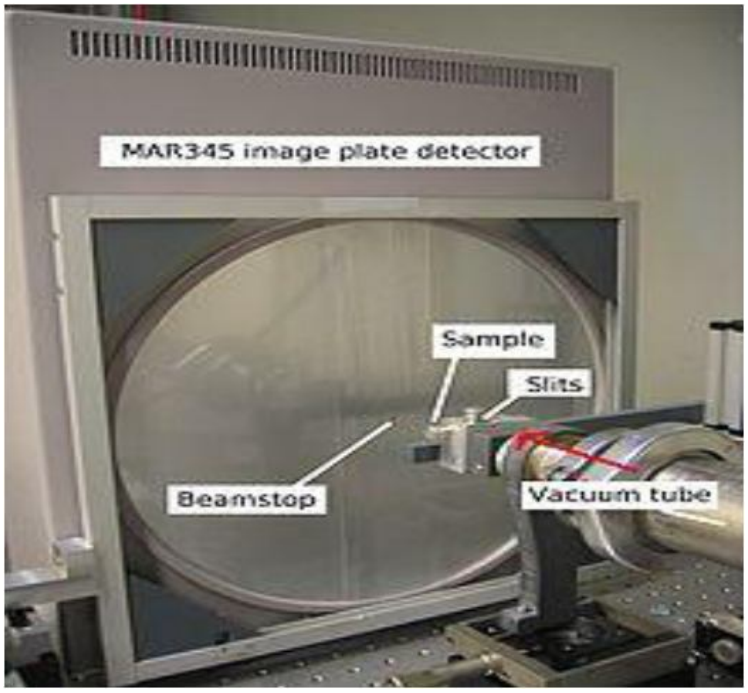

Fig 4.3.10: Schematic representation of x-ray Diffract meter principal

CHAPTER 5: RESULTS AND DISCUSSION

5.1 MICROSCOPIC BEHAVIOR

5.1.1 Micro-Hardness

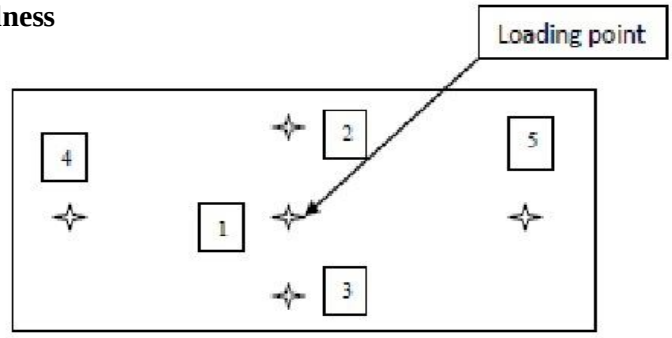

Fig. 5.1.1: Different loading points in specimen

5.1.2 Specimen for Micro Hardness

The micro-hardness of specimen at different PET loadings were measured. The table 5.1.1 shows the experimental measurements of micro hardness of the nano composites with different PET contents. An average hardness was calculated by 3 indentation measurements and a plot of the results of each type of samples is shown in Fig. 5.1.2. Primarily we have prepared 5 samples but we have taken the reading record of best three samples.

Table 5.1.1: Micro Hardness Results for Different PET loading

	Vickers Hardness Number (VHN)				
	0 %	**0.25 %**	**0.50 %**	**0.75%**	**1.00%**
Point 1	22.61	19.49	17.98	18.29	16.87
Point 2	19.15	19.69	17.39	18.15	14.84
Point 3	19.02	18.46	18.37	17.18	16.64
Average	**20.26**	**19.22**	**17.92**	**17.88**	**16.11**

From the above table it has been observed that as we increase the loading of PET the microhardness of the nanocomposite decreases when the PET loading is increased from 0% to 0.25% the microhardness decreases abruptly but when we increase content further form 0.25% to 0.5% we see average in decrease in microhardness but

less as compared to previous one. As we further increase the PET content to 0.75% we observe very less or least decrease in microhardness. Further increase in the PET content to 1% the microhardness decreases to 16.11415. So from the above discussion we can say that the microhardness of the nanocomposite decreases as we increase the PET content. The reason for this may be that PET fiber being a thermo plastic is a soft material and epoxy being the thermo setting material is a very hard material.

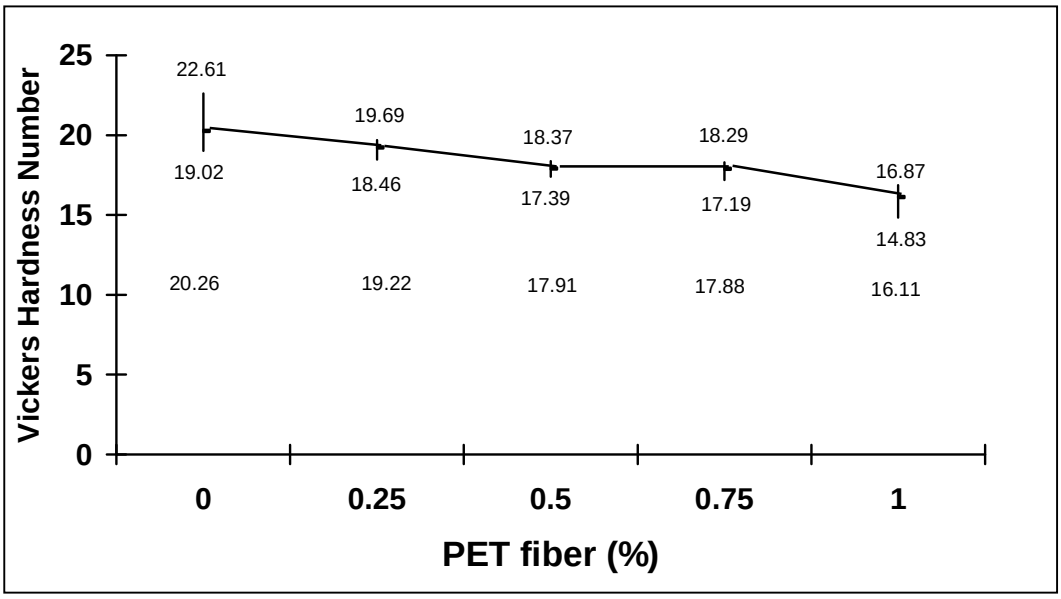

Fig 5.1.2: Micro Hardness test Results

5.2 TENSILE TEST

Following are the results that are observed for the tensile test on the test samples of different loading of PET in them.

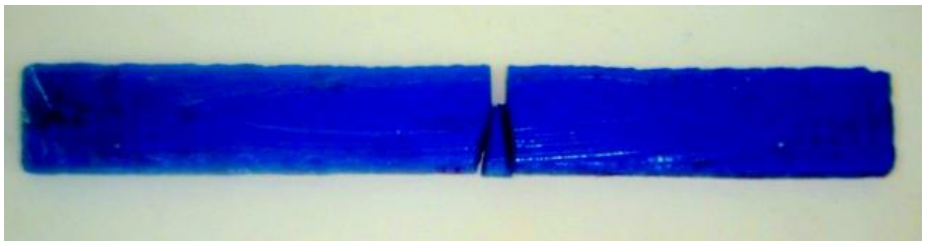

Fig. 5.2.1: Specimen breaks under tensile load

Table 5.2.1: Tensile Strength for Different PET loading

	Ultimate Tensile Strength (MPa)				
	0.00% PET	**0.25% PET**	**0.50% PET**	**0.75% PET**	**1.00% PET**
Sample 1	91.00	88.00	99.04	97.44	87.00
Sample 2	86.00	94.40	95.00	96.46	96.00
Sample 3	86.00	89.00	97.60	92.00	96.46
Average	**87.67**	**90.47**	**97.21**	**95.30**	**93.15**

With reference to the above table of tensile test it has been roughly observed that as we increase the percentage of PET the tensile strength of the nanocomposite also increases. In the graph shown below we can see that as we increase the PET content from 0% to 0.5% the tensile strength increase at very high rate that is very beneficial for the manufacturing of strong material product shows. As we further increase the PET percentage to 1% the tensile strength increases at the low rate as compared to above one. An optimum concentrate of PET fiber of 0.50% is clearly observed from fig 5.2.2.

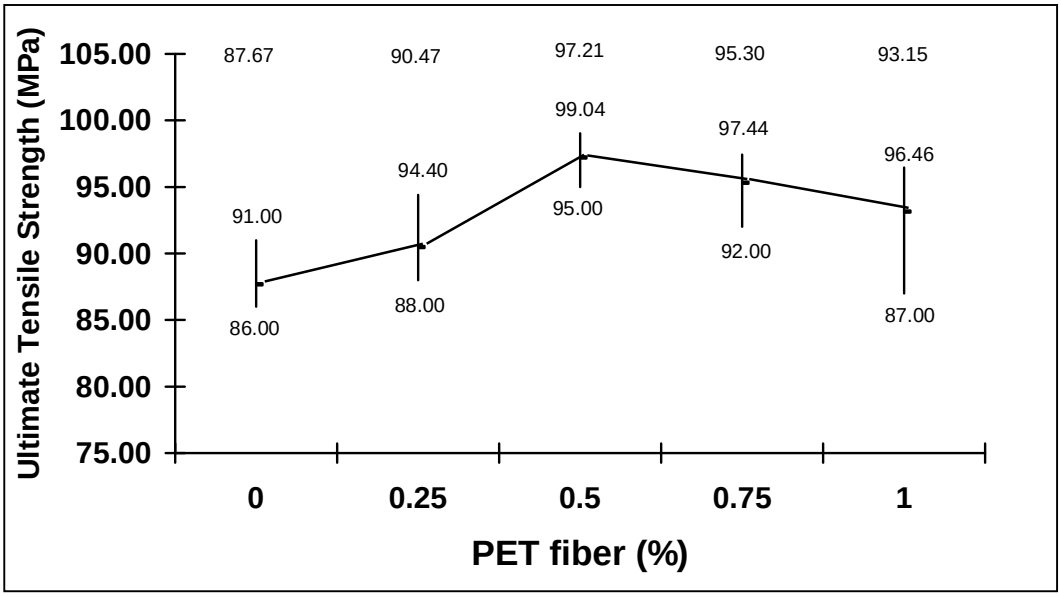

Fig 5.2.2: Ultimate Tensile Strength vs PET fiber %age

Fig 5.2.3 & 5.2.4 shows the load and elongation curve for Polymer Fiber Epoxy Nano Composites without PET & with 1% PET respectively. These graphs looks like a brittle material stress strain curve, so we can say that Polymer Fiber Epoxy Nano Composite is a brittle material. When we mix PET (thermo plastic) fiber in more quantity into the brittle material, slightly increase the elongation of composite with an increase in PET fiber content.

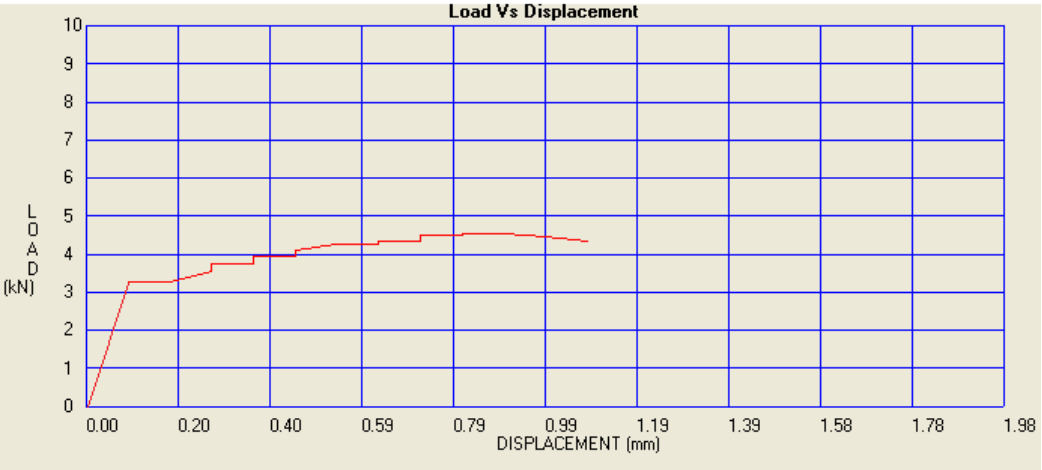

Fig 5.2.3: Load vs Displacement (without PET)

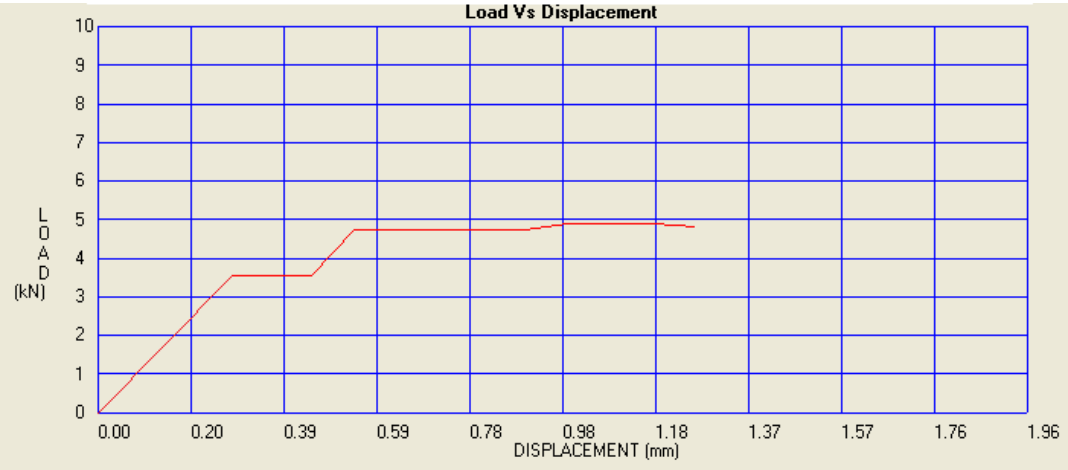

Fig 5.2.4: Load vs Displacement (with 1% PET)

In the table 5.2.2 we can clearly observe that elongation/deflection of the test sample increases as we increase the PET percentage. It can be seen firstly there is an abrupt increase as we increase the PET content from 0% to 0.5%. Further as we increase the

PET percentage to 1% we will see the average increase in the elongation in the test sample. This discussion can be easily verified by the graph shown below.

Table 5.2.2: Elongation in Tensile for Different PET loading

	Tensile Elongation (mm)				
	0.00% PET	**0.25% PET**	**0.50% PET**	**0.75% PET**	**1.00% PET**
Sample 1	1.08	1.04	1.12	1.17	1.08
Sample 2	0.81	1.01	1.14	1.15	1.20
Sample 3	0.91	1.03	1.19	1.18	1.26
Average	**0.93**	**1.03**	**1.15**	**1.17**	**1.18**

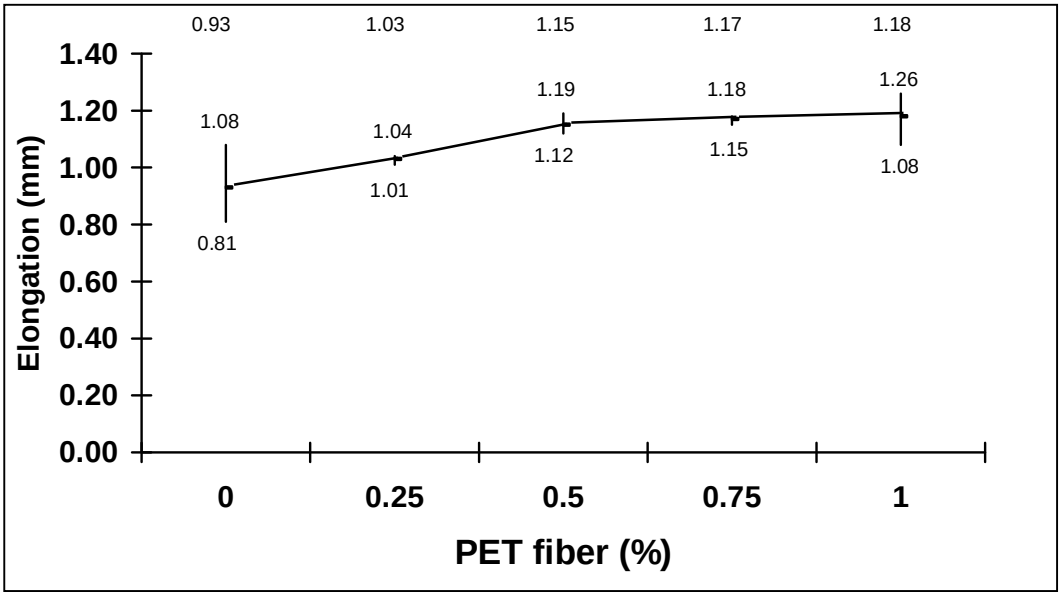

Fig 5.2.5: Elongations vs PET fiber %age

Table 5.2.3 and graph 5.2.6 shows the comparison of Modulus of Elasticity (E) for different %age of PET fiber loading. And we see Modulus of Elasticity (E) decreases with increase PET fiber contents. This is shows PET is soft material and increases the ductility of PET fiber epoxy nano composite with increases the PET fiber contents into the material, this thing clearly shows by graph also.

Table 5.2.3: Modulus of elasticity for Different PET loading

	Modulus of Elasticity (GPa)				
	0.00% PET	**0.25% PET**	**0.50% PET**	**0.75% PET**	**1.00% PET**
Sample 1	10.53	10.58	11.05	10.41	10.07
Sample 2	13.27	11.68	10.41	10.48	10.00
Sample 3	11.81	10.80	10.25	9.75	9.57
Average	**11.87**	**11.02**	**10.57**	**10.21**	**9.88**

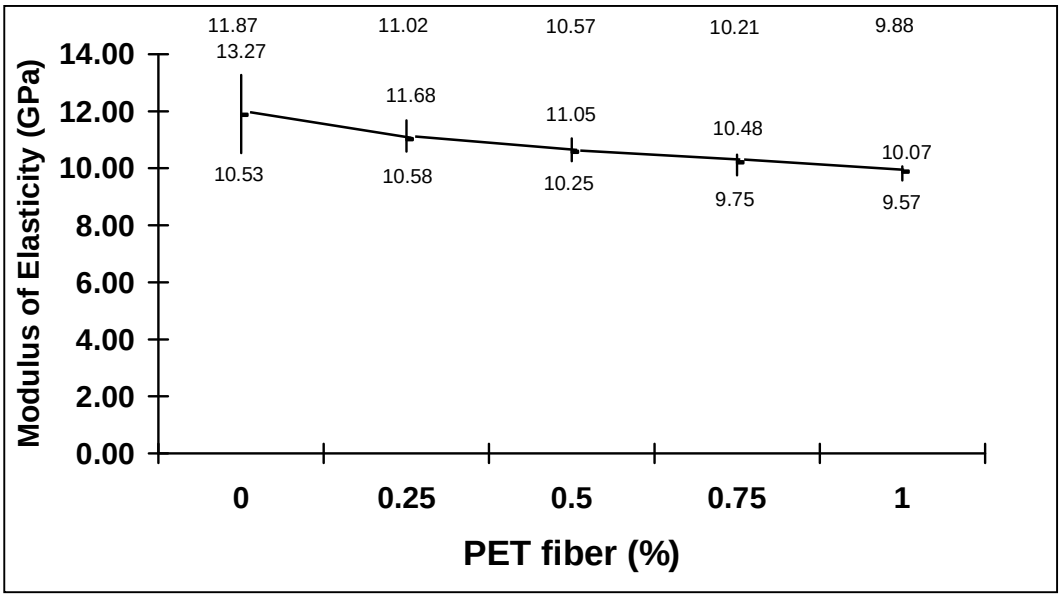

Fig 5.2.6: Modulus of elasticity vs PET fiber %age

5.3 BENDING TEST

Following are the results that are observed in the bending test on the test samples of different loading of PET fiber in it. We take five samples for each composition, but we take average of only three best results. So which results are very wide from average we neglect that sample result.

From the table 5.3.1 it can be seen that the bending strength of the nano composites increases as we increase the percentage of PET.

Table 5.3.1: Bending Strength (MPa) for different PET loading

Sample No.	0% PET	0.25% PET	0.5% PET	0.75% PET	1% PET
1	97.44	96.46	97.50	98.78	98.74
2	96.46	97.44	98.43	98.40	99.64
3	97.00	96.47	98.40	99.80	99.54
Avg.	**96.97**	**96.79**	**98.11**	**98.99**	**99.31**

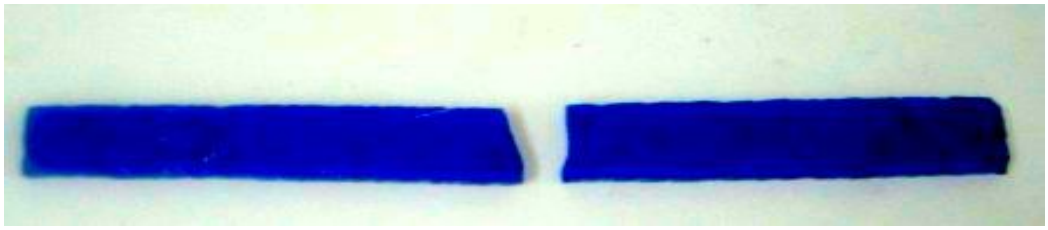

Fig 5.3.1: **Specimen breaks under bending load**

So we can say that improve the bending strength property with increase the %age of PET. These results are also shown by fig 5.3.2.

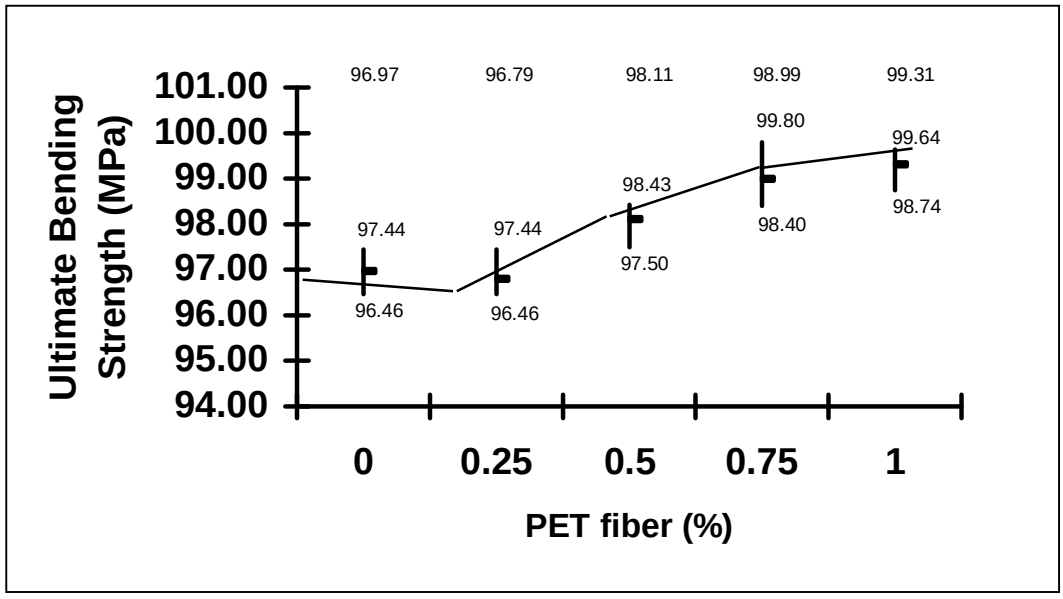

Fig 5.3.2: Bending Strength vs PET fiber %age

Fig 5.3.3 & 5.3.4 shows the load and deflection curve for Polymer Fiber Epoxy Nano Composite without PET & with 1% PET respectively. These curves look like a brittle material stress strain curve, so we can say that Polymer Fiber Epoxy Nano Composite is a brittle material. When we mix PET (Thermo plastic) fiber in more quantity into the brittle material, slightly increase the deflection of composite with increase the %age of PET fiber.

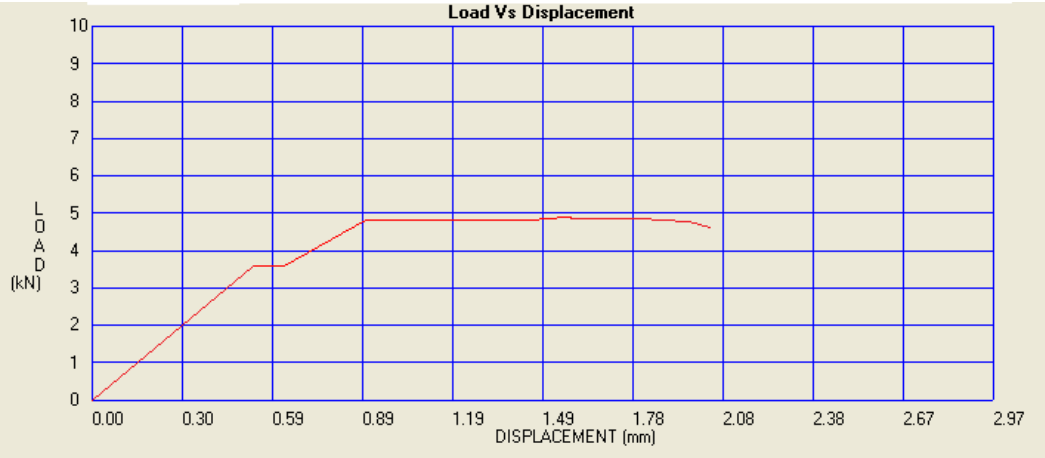

Fig 5.3.3: Load and Deflection Curve (without PET)

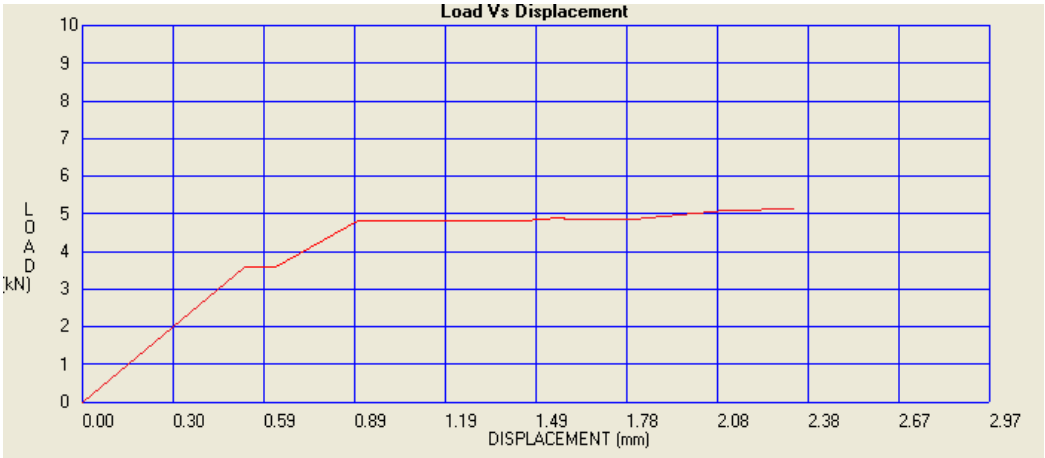

Fig 5.3.4: Load and Deflection Curve (with 1% PET)

In the table 5.3.2 we can clearly observe that deflection of the test sample increases as we increase the PET percentage from the graph it can be seen firstly there is abrupt increase as we increase the PET content from 0% to 0.5% .Further as we increase the

PET percentage to 1% we will see the average increase in the elongation in the test sample. This discussion can be easily verified by the graph 5.3.5.

Table 5.3.2: Deflection vs PET contents

Sample No.	0% PET	0.25% PET	0.5% PET	0.75% PET	1% PET
1	1.77	1.86	2.02	2.17	2.17
2	1.81	1.80	2.12	2.16	2.27
3	1.80	1.96	2.16	2.26	2.26
Avg.	**1.79**	**1.87**	**2.10**	**2.20**	**2.23**

From the results of bending strength results, we can say that is an increase in the material softness with increase in the %age of Polyethylene Terephthalate (PET). Another one deflection results also show this is good flexible material and also changes the flexibility with change the %age of PET for desire properties.

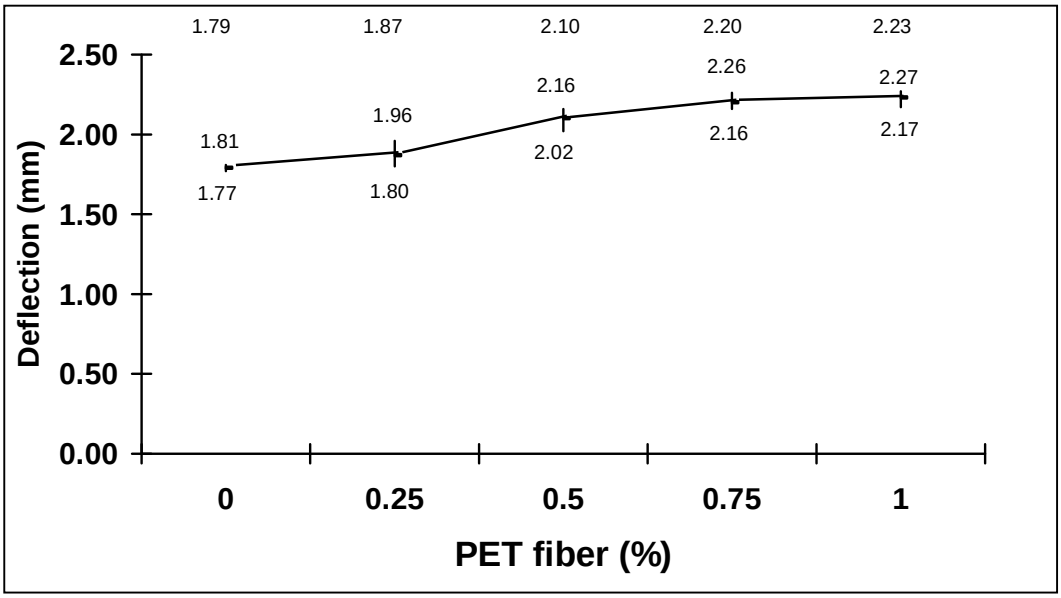

Fig 5.3.5: Deflection vs PET fiber %age

5.4 IMPACT TEST

Impact strength or toughness is the main property of materials.

Table 5.4.1 shows the results that are observed while doing the Charpy Impact test on the test samples with different loading of PET fiber.

Table 5.4.1: Toughness (ft - lb/in^2) vs PET contents

Sample No.	0% PET	0.25% PET	0.5% PET	0.75% PET	1% PET
1	5.70	6.30	6.50	6.80	7.10
2	5.60	6.05	6.55	6.92	7.63
3	5.34	6.36	6.75	6.83	7.23
4	5.42	6.14	6.82	6.95	7.42
5	5.26	6.42	6.63	7.04	7.45
Avg.	**5.46**	**6.25**	**6.65**	**6.91**	**7.37**

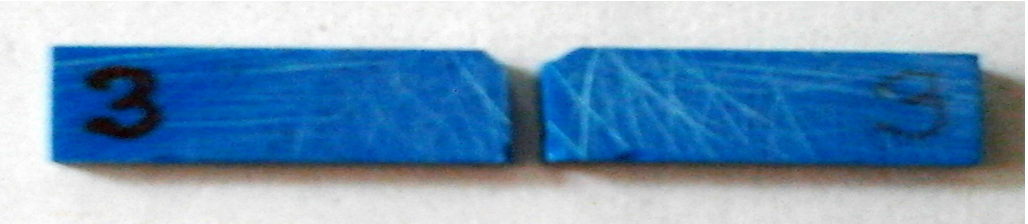

Fig 5.4.1: Specimen breaks under impact load

Form the table 5.4.1 we can say that the impact strength increases with an increase in the PET content. Fig 5.4.2 shows the actual view of the specimen that broke from the V notch under impact load. Below shown graph clearly shows that as we increase the PET content from 0% to 1% the impact strength increases by 35%.

According to **Teh et al (2005)** the fracture toughness of neat epoxy increases by about 33% from 0.70 to 0.93 MPa!m1/2 upon incorporating 1 wt% untreated PET fibers. When incorporating only 1 wt% PET fibers treated by NaOH for 2.5 min, compared with neat epoxy, the fracture toughness of the composite increases by about 80%,

indicating a significant toughening effect using the surface-modified PET fibers (for 2.5 min surface treatment by NaOH), probably due to improved interfacial adhesion between the fiber and the matrix.

But we have used the Epoxy and Clay material which is different used by the Teh et al (2005). So our material toughness increases 35% when added 1% PET modified fiber.

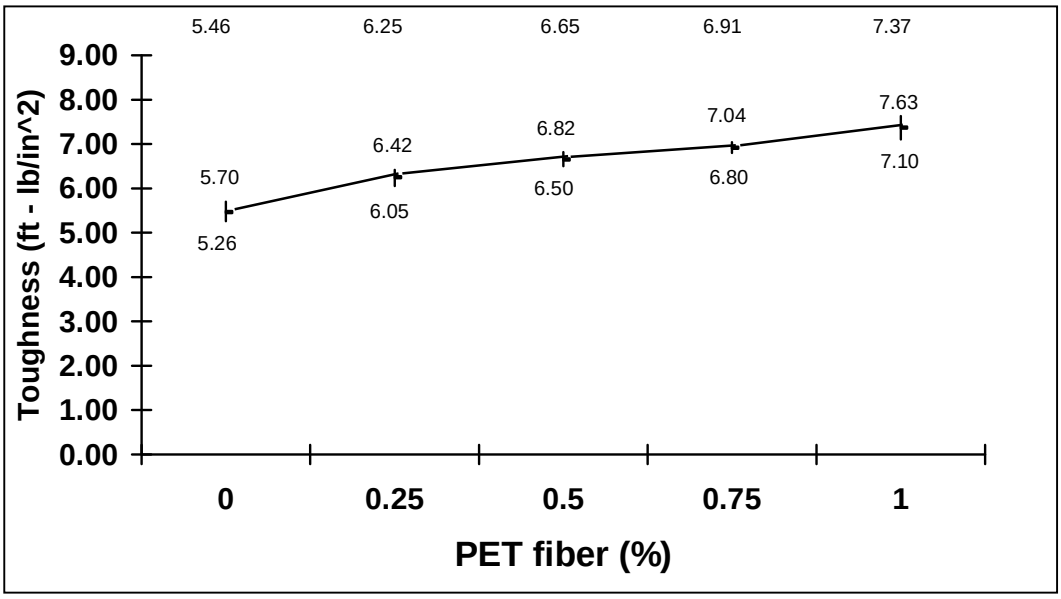

Fig 5.4.2: Toughness vs PET fiber contents

5.5 X-ray Diffraction Test

The X-ray Diffraction experiments were conducted on the samples having different nanoclay loading. But our all samples are made by same amount (3% wt) of nano clay, so we perform X-ray Diffraction test only on one sample. X-ray diffractometer gives the values of d-spacing and 2θ nano composites.

XRD result clearly shows that the epoxy chains have intercalated into the nano clay layers. This has been inferred from the peak at 4.854 as shows in graph visa we the 2 theta is equal to 1148 for pure Closite 30B

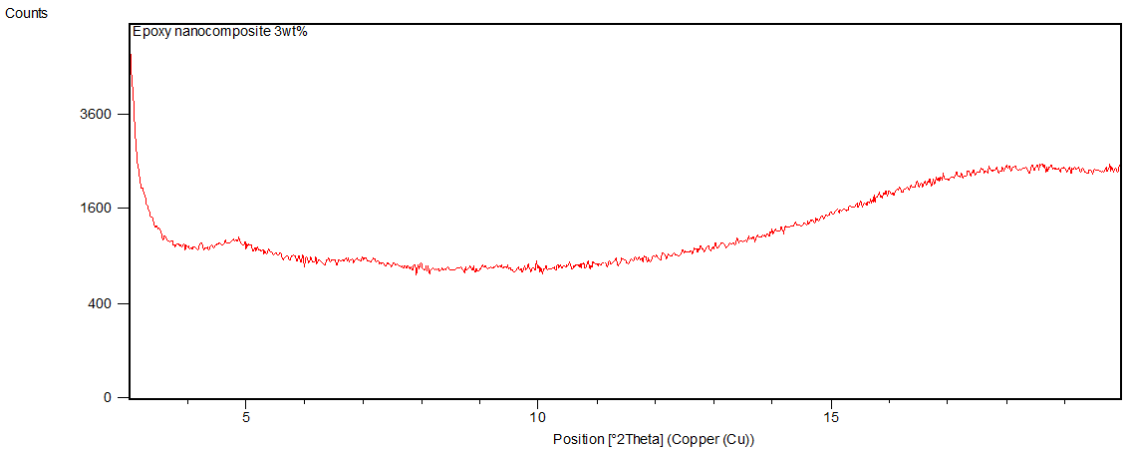

Fig 5.5.1: X-ray diffractogram for 3% wt nano clay

5.6 Scanning Electron Microscope (SEM)

SEM was used to determine size and distribution of particles in the samples for the five polymer nanocomposite systems. The primary goal of using SEM was to determine particle dispersion.

Scanning electron microscopy was used in this study to obtain high magnification photos of the polymer fiber epoxy nano composites to observe their structures in order to relate with the resulting properties. Images of several different clay loading samples were obtained at 5000X magnification.

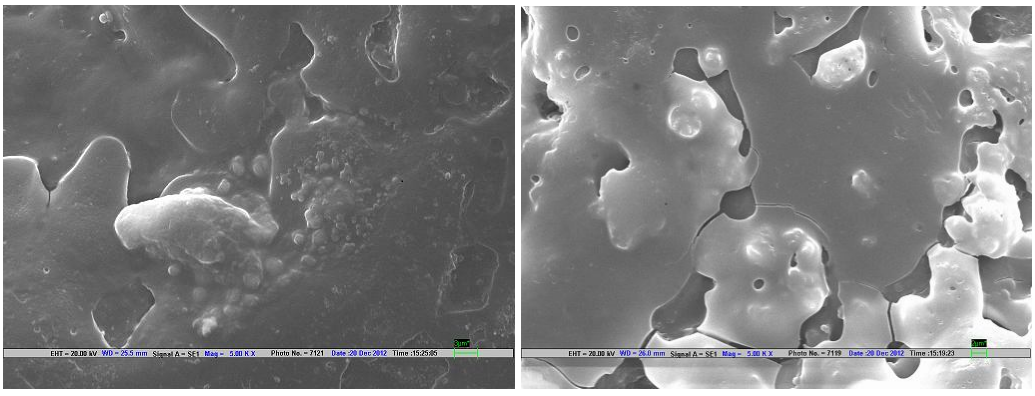

Fig 5.6.1: SEM image of nanocomposite having 0% wt PET fiber loading

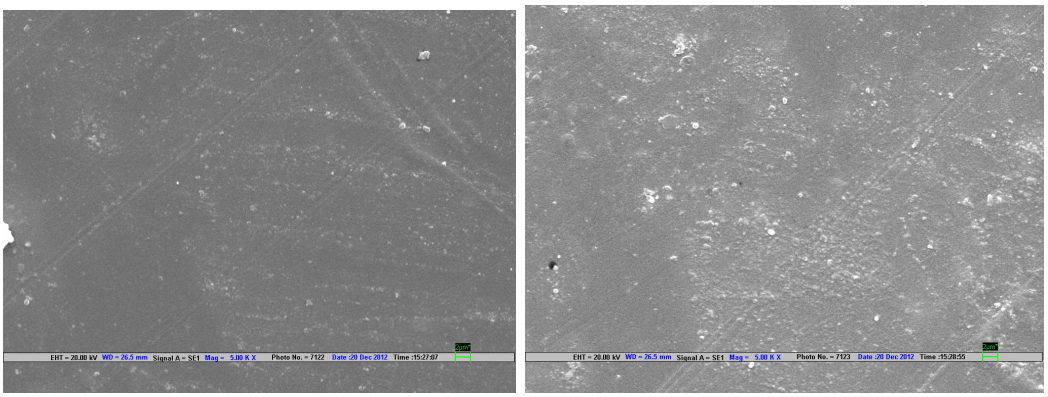

Fig 5.6.2: SEM image of nanocomposite having 0.25% wt PET fiber loading

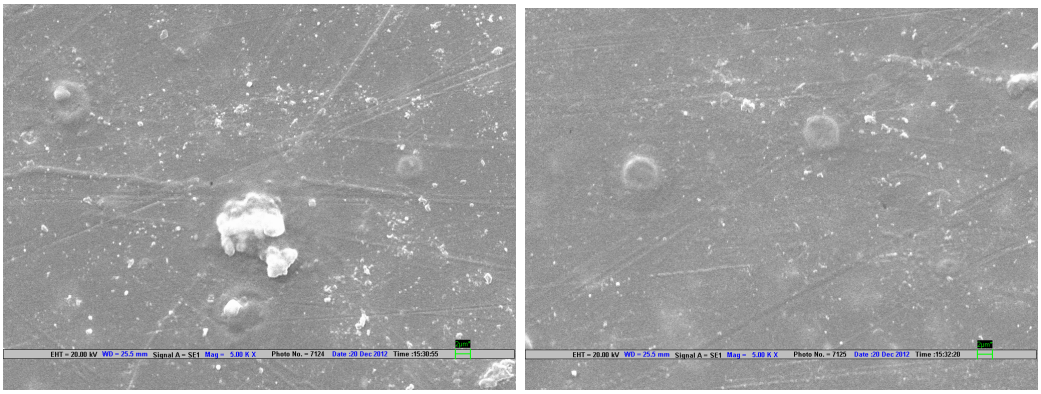

Fig 5.6.3: SEM image of nanocomposite having 0.50% wt PET fiber loading

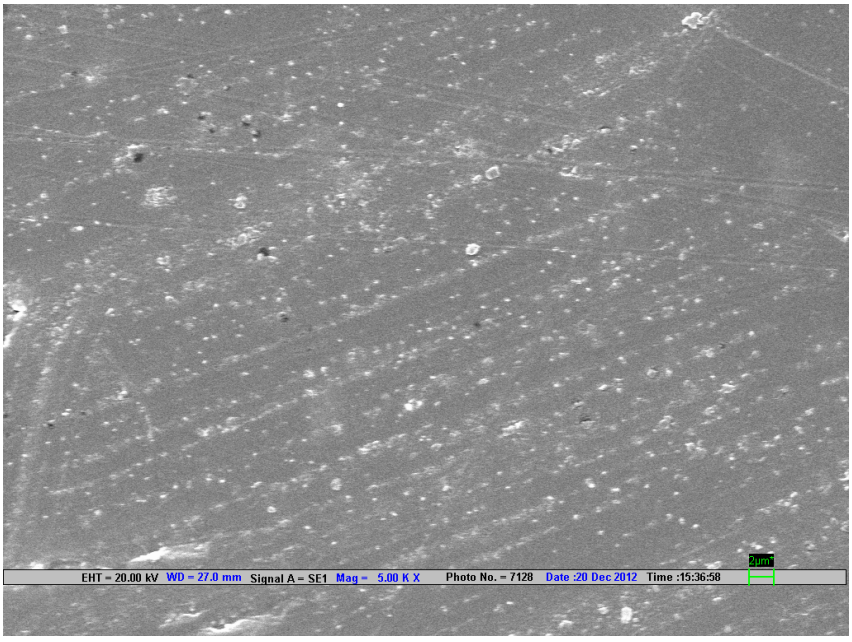

Fig 5.6.4: SEM image of nanocomposite having 0.75% wt PET fiber loading

Fig 5.6.1 shows the structure of nano composite without mixing the PET fiber. We show without PET fiber epoxy have not proper bond, so don't make plane layers. Fig 5.6.2 shows the image of nano composite with mixing of 0.25% PET fiber. In fig white spots are shows the PET fibers. Some holes are also shows in image, which show fiber, remove from that place during tensile test.

Fig 5.6.3 & fig 5.6.4 shows the image for nano composite with mixing 0.50% & 0.75% PET fiber. In image shows some white straight lines that are PET fiber in horizontal position. And we also show with increase the %age of PET fiber increase the white area in the image.

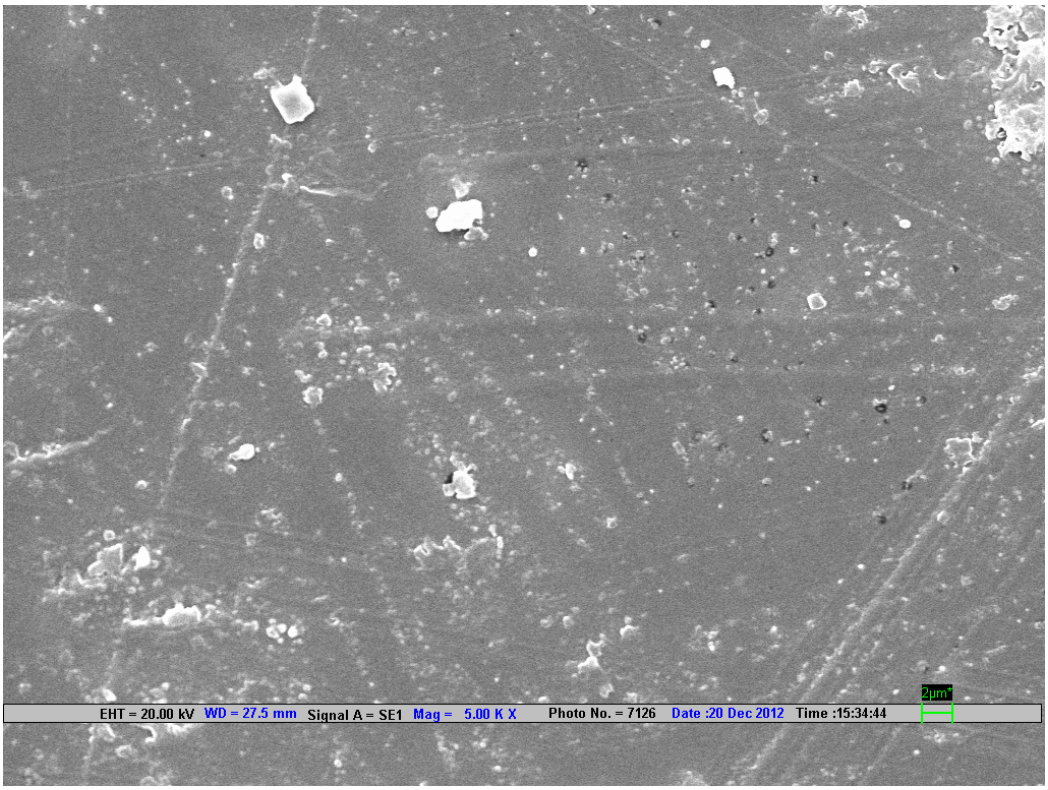

Fig 5.6.5: SEM image of nanocomposite having 1% wt PET fiber loading

Fig 5.6.5 shows the image of nanocomposite with mixing of 1% PET fiber. In this image some white spot are large which show the PET fiber are in vertical position and straight lines shows the PET fiber in horizontal position.

In all images we clearly see with mixing of PET fiber into the nano composite, matrix make the proper bond and also make the plane layers.

CHAPTER 6: CONCLUSIONS AND FUTURE SCOPE

PET introduced nano composites have been manufactured using epoxy as matrix. PET was added to epoxy in different weight percentage (1 wt%, 0.75 wt%, 0. 5 wt%, 0.25 wt % & 0 wt% of weight of resin). For the processing of epoxy-PET mechanical stirring and ultrasonication was done. The composites were manufactured using hand layup method and characterized using Tensile, Bending, Microhardness & Impact Tests. Tensile, bending and Impact tests were performed on nano composites as per ASTM standards.

It was found that the hardness of the nano composites decreased with increasing PET content. The Tensile strength of the sample piece increases with the increase in the PET content, but after 0.50 wt% start decreases the tensile strength. Bending strength firstly decreases as we increase the PET strength to 0.25 wt% & after that the bending strength increases as we increase the PET content. Impact strength increases with the increase PET content.

6.2 Future Scope

1. The experiment can be performed on polyester as matrix system, since with this matrix the barrier properties of composites can be enhanced.
2. Clay loading can also be varied more than 3 wt%.
3. The duration of current experiment can be increased to see the effect in long term.
4. PET loading can be increased to 2-3 wt% if PET loading is done mechanically.
5. PET stickiness can be increased to large extent by washing the PET fiber for more time in NaOH, to get other properties.

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