GLASS FIBER/EPOXY POLYMER NANOCOMPOSITES: EFFECT OF ANOTHER POLYMERIC FIBER

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Dedicated to my parents

CERTIFICATE

This is to certify that the dissertation entitled ***"Glass Fiber/Epoxy Polymer Nanocomposites: Effect of another Polymeric Fiber"*** is an authentic record of my own work carried out as per requirements for the award of degree of ***M.Tech. (Chemical Engineering)*** *at Thapar university , Patiala,* under the guidance **of Dr. Rajeev Mehta Head and Associate Professor, *Department of Chemical Engineering,*** Thapar University, Patiala during ***July 2012 to June 2013.***

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ABSTRACT

The review renders a short background on the research work carried out on epoxy clay nanocomposites. Clays are one of the ideal nano reinforcements for polymers because of their high intercalation chemistry and aspect ratio. Epoxy clay nanocomposites are finding vast applications in various industries like aerospace, defense, automobile, etc. The physical and chemical properties of the epoxy systems are influenced by the processing techniques, clay modifier and curing agents used for the preparation of nanocomposites. In the present work
Epoxy– glass fiber composites were prepared by directly blending two-pack System of Araldite (CY-230) and hardner (HY-951) with short glass fibers. The Short glass fiber content was varied from 0% to 1% by weight of the total matrix. These composites were then characterized for morphology using scanning electron microscopy, mechanical properties that is tensile test, impact test and flexural properties and Resistance toward various chemicals. The epoxy-glass fiber composites showed improved tensile and flexural properties but increased dispersion among the Properties with increasing fiber content. Several reasons to explain these effects In terms of reinforcing mechanisms were discussed.

Keywords: Short glass fibers, Epoxy composites, Mechanical properties, Polymer–matrix composites (PMCs) Nano-structures, Mechanical properties.

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NOMENCLATURE AND ABBREVATIONS

GFRP	glass fiber reinforced polymer
VLSI	very large scale integration
PNC	polymer nanocomposite
OMMT	montmorillonite organoclay
CNF's	carbon nanofibers
CNT's	carbon nanotubes
WXRD	wide angle x-ray diffraction
PAN	polyacrylonitrile
SEM	scanning electron microscope
CTE	coefficient of thermal expansion
VGCF	vapor grown carbon fiber
CAI	compression after impact

CHAPTER 1

INTRODUCTION

During the last decades, there has been a tremendous growth in the use of composite materials in various fields of application, ranging from sporting goods to structural components for the automotive and aerospace industries, where the long-term properties are of primary importance. High-performance polymer composite materials are being used increasingly for engineering applications under hard working conditions. The materials must provide unique mechanical and tribological properties combined with a low specific weight and a high resistance to degradation in order to ensure safety and economic efficiency.

Epoxy resins are widely used for matrix composites due to their excellent adhesive, dielectric, and mechanical properties and alone provide most of the properties required for composites. However, because the polymer matrix must withstand high mechanical and tribological loads, it is usually reinforced with fillers. These fillers can be chosen either as fibers (glass, carbon, and aramid) or particles such as ceramic powders. These fillers favorably stiffen the material and may also increase the strength under certain load conditions.

The fibrous composites, especially glass fiber–reinforced epoxy composites in which glass fiber is the primary load carrying element, are being increasingly used in military and aerospace applications owing to several desirable properties including high specific strength, high specific stiffness, and controlled anisotropy. The mechanical properties of composites are most important, because they can be influenced by parameters such as type of filler, type of matrix, filler concentration, filler dispersion, alignment of fibers, length of fibers, aspect ratio of fibers, the fiber matrix interphase properties or adhesion between fiber and resin matrix (Kacir et al.,1978) Glass fiber reinforcement can be of several types, such as rovings, mats, woven fabric, hybrid fibers, multiaxial fabrics, and the most important and widely used short glass fibers.

The short-fiber reinforced polymer (SFRP) composites are very attractive because of their ease of fabrication, economy, and superior mechanical properties. By combining short fibers with an appropriate polymer matrix and by controlling the production process it is possible to make composite materials featuring large specific properties. In addition, the constituent, that is the

polymer matrix and the glass fibers, are usually inexpensive and easily processed. As a consequence of these technical and economical reasons, the short-fiber reinforced polymer composites are finding more and more industrial applications where high performance per weight at a reasonable price is required.

For short fiber materials there are many more micro structural variables that affect the elastic and thermo elastic properties as compared to the continuous fiber materials: these include distributions of fiber to fiber separation, fiber length, and fiber orientation. Tensile strength is one such important property. One of the basic motivations for the use of composite materials as engineering materials is the high tensile strength that can be achieved by incorporating high-strength fibers into a matrix since the fibers carry most of the load. As indicated earlier, failure initiation and the fracture process of SFRPs depend to a large extent on the fiber volume fraction, the fiber aspect ratio, and the ratio between failure strain of fiber and matrix. In short-fiber reinforced composites, tensile strength of composites increases with increasing aspect ratio of reinforcing fibers.

1.1 FIBRE REINFORCED POLYMERS (FRP)

Fiber reinforced polymer (FRP) are composites used in almost every type of advanced engineering structure, with their usage ranging from aircraft, helicopters and spacecraft through to boats, ships and offshore platforms and to automobiles, sports goods, chemical processing equipment and civil infrastructure such as bridges and buildings. The usage of FRP composites continues to grow at an impressive rate as these materials are used more in their existing markets and become established in relatively new markets such as biomedical devices and civil structures. A key factor driving the increased applications of composites over the recent years is the development of new advanced forms of FRP materials. This includes developments in high performance resin systems and new styles of reinforcement, such as carbon nanotubes and nanoparticles.

1.1.1 ADVANTAGES OF FIBRE REINFORCED POLYMERS

- High strength to weight ratio
- Corrosion resistant
- Can be tailored for the application (both shape and type of FRP).

- FRP has a low cost considering other materials.
- Cost of installation versus replacement is low.
- Cost of installation time (both direct and indirect) is also low.

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. Gadaspow *et al.* (1993) investigated the 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.

1.2.1 MATRIX PHASE

The primary phase, having a continuous character, is called matrix.Kopeliovich *et al.* (1991) investigated the 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 embedded in the matrix in a discontinuous form. This secondary phase is called dispersed phase.

1.2.3 CLASSIFICATION OF COMPOSITE

Composites can be broadly classified in to two groups as shown in Fig. 1.

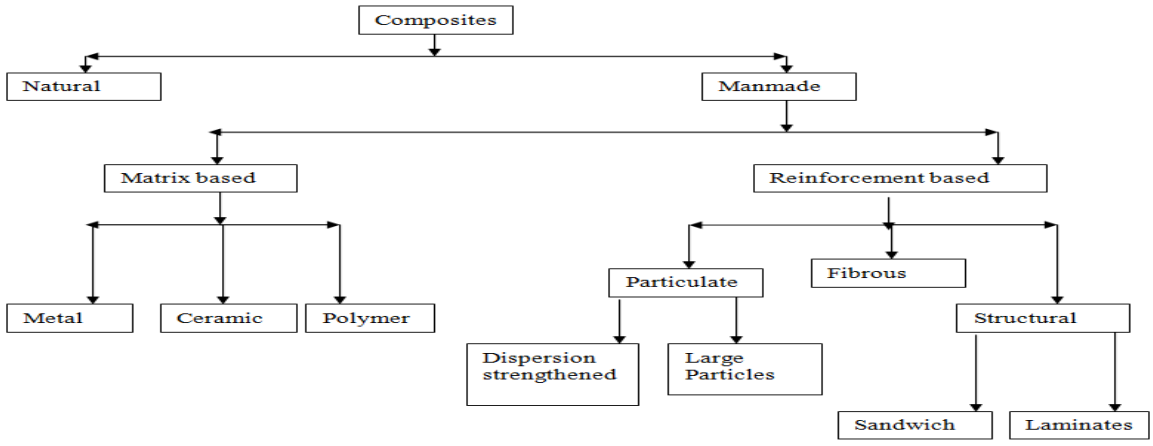


Fig. 1: Classification of composite materials (Wang, H., 2007).

1.2.4 USES OF COMPOSITE MATERIALS

- Extensively used in space technology and production of Aerospace Components (Tails, wings etc.)
- Used in the production of sport goods e.g. racing car bodies and bicycle frames etc.
- Used for general industrial and engineering structures.
- Used in high speed and fuel efficient transport vehicles.
- 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.

1.3 HOW CAN NANOTECNOLOGY HELP US?

Nanotechnology is the science of micro engineering. Micro engineering is the science of engineering that deals with particle manipulation if those particles are smaller than 100 nanometers. Atomic and molecular manipulation is the essential core of nanotechnology. This science is used to create applicable particle.

Nanotechnology may be able to create many new materials and devices with a vast range of application such as in medicine, electronics, biomaterials and energy production. At nano level, some compounds transform from inert to active, from insulator to conductors, from fragile to tough. They can become lighter, stronger and more resistant.

Transformed properties are what account for the infinite potential application of nanoparticles (Sakakiet al., 1994). The major factors of alter these properties, is the increase in the ratio of surface area to volume. Hence, due to the high surface-to volume ratio associated with nanometre sized particles it is possible to control the fundamental properties of materials through the surface/size effect.

1.3.1 NANOCOMPOSITE

Nanocomposites are found in nature, for example in the structure of the abalone shell and bone. The use of nanoparticles-rich materials long predates the understanding of the physical and chemical nature of these materials. Yacaman *et al.* (1996) investigated the origin of the depth of color and the resistance to acids and bio-corrosion of Maya blue paint, attributing it to a

nanoparticles mechanism. From the mid-1950s Nano scale organo-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).

In mechanical terms, Nanocomposites 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 nanotubes or electro spun fibers). The area of the interface between the matrix and reinforcement phase is typically an order of magnitude greater than for conventional composite materials.

In general, the nano reinforcement is dispersed into the matrix during processing. The percentage by weight (called mass fraction) of the nanoparticulates 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, or nanometer-diameter cylinder, such as PET fibers).

Table 1: Important Characteristics of Nanocomposites

Improved properties	**Disadvantages**
Mechanical properties (tensile strength, stiffness, toughness)	Viscosity increase (limits process ability)
Gas barrier	Dispersion difficulties
Synergistic flame retardant additive	Sedimentation
Dimensional stability	
Thermal expansion	
Thermal conductivity	
Chemical resistance	

Reinforcement	

1.3.2 ADVANTAGES OF NANOCOMPOSITES

- Greater tensile and flexural strength.
- Improved gas barrier properties for the same film thickness.
- Reduced weight for the same performance.
- Higher chemical resistant.
- Optical clarity in comparison to conventionally filled polymers
- Improve mechanical properties e.g. strength, modulus and dimensional stability
- Improve electrical conductivity.

1.4 EPOXY POLYMER NANOCOMPOSITES

The main challenge in fabrication of these polymer nanocomposites for structural applications is uniform dispersion of nanoparticles in the polymer matrix. However, good dispersion for nanoparticles in polymer composite materials is extremely difficult to achieve, since nanoparticles tend to aggregate together during fabrication. The degree with which the nanoparticles can be homogeneously dispersed in the polymer matrix would significantly influence the thermal, mechanical and optoelectronic properties of the material.

Researchers have used several techniques for dispersing nanoparticles may include:

1) Mechanical agitation, such as ball milling or magnetic stirring
2) Ultrasonic vibration
3) Shear mixing
4) Non-contact mixing
5) Using the dispersing agent.

The epoxy based thermo set polymers are generally cured using conventional heating. The manufacturing industries of these nanocomposites are also in need of quick and efficient curing method for high temperature or room temperature curing of epoxy polymers. The conventional method of curing is time-consuming, the longer it takes to complete a project, the more expensive it becomes. Several alternate curing methods have been tested and they are: UV rays,

Gamma rays, Electron Beam and Microwave (Bogdal and Karen, 2003; Clark and Sutton, 1996) microwave heating curing of room or high temperature epoxy resins.

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

- Epoxy and hardener
- Montmorillonite clay
- Glass fiber
- Polymer fiber (PET)

1.4.1 EPOXY RESINS AND HARDENER

The first commercial attempts to prepare resins from epichlorohydrin were made in 1927 in the United States. Credit for the first synthesis of bisphenol-A-based epoxy resins is shared by Dr.Pierre Castan of Switzerland and Dr. S.O. Greenlee of the United States in 1936. Dr. Castan's work was licensed by Ciba, Ltd. of Switzerland, which went on to become one of the three major epoxy resin producers worldwide. Ciba's epoxy business was spun off and later sold in the late 1990s and is now the Advanced Materials business unit of Huntsman Corporation of the United States. Dr. Greenlee's work was for the firm of Devoe-Reynolds of the United States. Devoe-Reynolds, which was active in the early days of the epoxy resin industry, was sold to Shell Chemical (now Momentive Specialty Chemicals, formerly Hexion, Resolution Polymers and others).

In 1946, the first industrially-produced epoxy resin was introduced to market. Since then, the use of thermosetting polymers has steadily increased. Epoxy resin systems are increasingly used as matrices in composite materials for a wide range of automotive and aerospace applications, and for shipbuilding or electronic devices. They serve as casting resins, adhesives, and as high performance coatings for tribological applications, such as slide bearings and calendar roller covers. The mechanical property profile of epoxy matrices can be influenced, for example, by modifying the molecular architecture and structure, i.e. by increasing the crosslink density to generate high stiffness and strength (Sue et al, 2000). Highly cross-linked epoxy matrices, however, often behave undesirably brittle because plastic deformation is constrained (Argon et al, 2003) Moreover, the local stress concentrations may initiate cracks which lead to spontaneous failure. It is therefore a primary aim of many researchers to provide epoxy with higher

toughness, but without significantly sacrificing other important characteristics such as thermo-mechanical properties and modulus, which are desired and required in many applications.

The term ‘epoxy resin’ refers to 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.

1.4.2 CLAY NANOPARTICALES

Clay is a naturally occurring, inorganic component of most soils. Chemically, clays are aluminosilicates [$Al_4Si_4O_{10}(OH)_8$] and carry negative charges. Sand, on the other hand, is composed of large, neutral particles of silicon dioxide (SiO_2).Clay is made up of tiny particles less than 0.002 mm in diameter. By comparison, silt particles range from 0.002 to 0.05 mm in size and sand particles from 0.05 to 2.0 mm. For this reason, clay soils are considered to be fine textured; silts, medium textured; and sands, coarse textured. According to Alexandre et al., (2000), Clay as nanoparticals such as smectic clays (e.g. montmorillonite) are incorporated into polymers to form resulting polymer nanocomposite, which may possess unique electrical, mechanical and optical properties.

1.4.3 MONTMORILLONITE

The most common type of nanoclay is montmorillonite (MMT), a layered aluminosilicate in the smectite family of clay. Unlike clay minerals such as talc and mica that have been used as fillers for years, MMT can be delaminated and dispersed into an individual layers only one nanometer thick by about 70 nm to 150 nm across.

Fig. 2: Montmorillonite clay

Olphen (1963) investigated the result is a radical increase in the surface area-to volume ratio: with a surface area of 750m^2/g, 20g of MMT platelets could cover a football field. Montmorillonite, can absorb 20-30 times its volume in water, and is of particular interest to the Plastics industry.

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. Members of this group include saponite. Montmorillonite is the main constituent of the volcanic ash weathering product, betonies. (Lebaron et al., 1999).

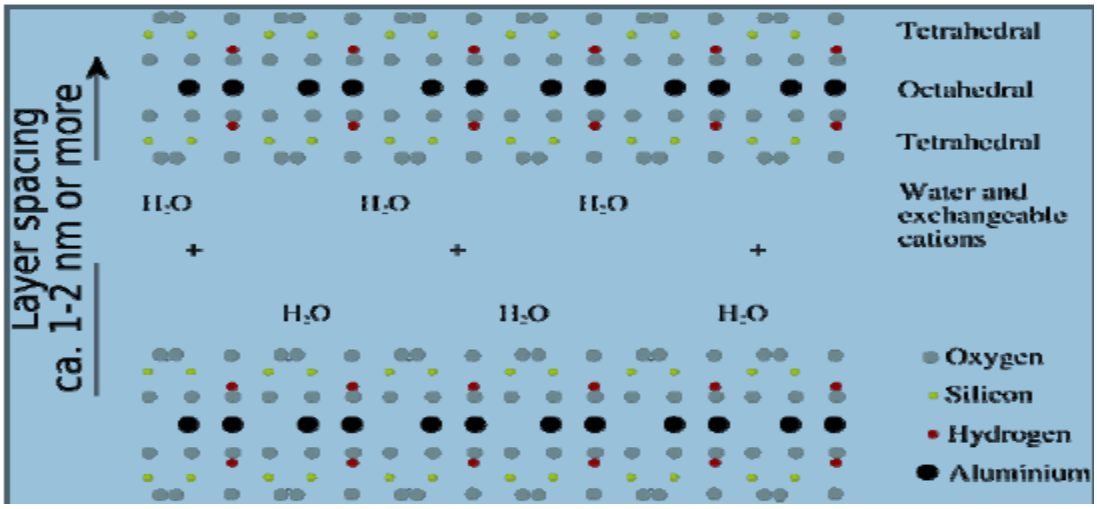


Fig. 3: structure of montmorillonite clay (Paul D.R. et al., 2008)

1.4.4 GLASS FIBER

Glass fiber can be produced by blending quarry products (sand, kaolin, limestone etc.) at 1600°C, liquid glass is formed. Glass fiber also called fiberglass. It is material made from extremely fine fibers of glass Fiberglass is a lightweight, extremely strong, and robust material. Its bulk strength and weight properties are also very favorable when compared to metals, and it can be easily formed using molding processes. Fibers have been manufactured from glass since the 1930s.

(a) (b)

Fig. 4: Glass Fibers (a) Roll of Glass Fiber, (b) Woven Fabric of Glass Fiber.

1.4.4.1 TYPES OF GLASS FIBER

According to Hartman et al. 1996 as to the raw material glass used to make glass fibers or nonwovens of glass fibers, the following classification is known as:

- **A-glass:** With regard to its composition, it is close to window glass. In the Federal Republic of Germany it is mainly used in the manufacture of process equipment.
- **E-glass (electrical):** Has lower alkali content. E-glass is the most common form of reinforcing fiber used in polymer matrix composites.
- **C-glass (chemical):** Best resistance to chemical attack. Mainly used in the form of surface tissue in the outer layer of laminates.
- **R, S or T-glass:** Manufacturer's trade names for equivalent fibers having higher tensile strength and modulus than E glass, with better wet strength.
- **AE-glass:** Alkali resistant glass.

Generally, glass consists of quartz sand, soda, sodium sulphate, potash, feldspar and a number of refining and dying additives. The characteristics, with them the classification of the glass fibers to be made, are defined by the combination of raw materials and their proportions.

1.4.4.2 PROPERTIES OF GLASS FIBER

- Mechanical Properties– similar stiffness but different strength values depending on thermal history.
- Chemical Stability– attacked by alkaline solutions, hot water.
- Thermal Properties– relatively high heat resistance.
- Electrical properties–relatively low conductivity.

Table 2: Comparison of typical properties for some common fiber

Materials	Density (g/cm^3)	Tensile Strength (MPa)	Young Modulus (GPa)
E-Glass	2.55	2000	80
S-Glass	2.49	4750	89
Alumina (Saffil)	3.28	1950	297
Carbon	2.00	2900	525
Kevlar 29	1.44	2860	64
Kevlar 49	1.44	3750	136

1.4.5 POLY ETHYLENE TEREPHTHALATE

It's a plastic resin and the most common type of polyester. Two monomers modified ethylene glycol and purified terephthalic acid –are combined to form the polymer called polyethylene terephthalate. PET was discovered and patented in England in 1941.

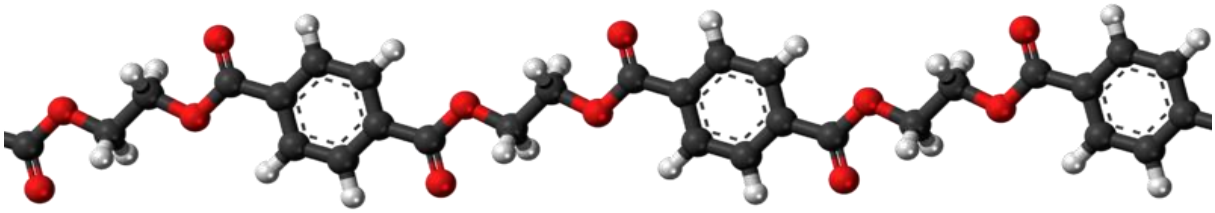


Fig. 5: A short section of a PET polymer chain (Chung et al., 1987)

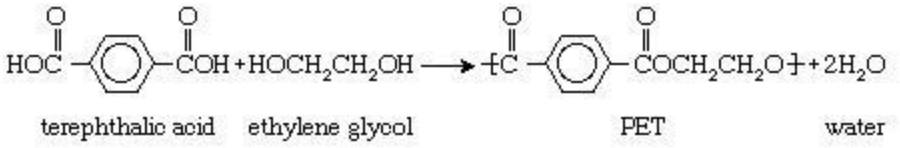
Polyethylene terephthalate (PET or PETE) is a strong, stiff synthetic fiber and resin, and a member of the polyester family of polymers. PET is spun into fibers for permanent-press fabrics, blow-molded into disposable beverage bottles, and extruded into photographic film and magnetic recording tape. (Melinte S. et al., 2001).

PET is produced by the polymerization of ethylene glycol and terephthalic acid. When heated together under the influence of chemical catalysts, ethylene glycol and terephthalic acid produce PET in the form of a molten, viscous mass that can be spun directly to fibers or solidified for later processing as a plastic.

Fig. 6: polyethylene terephthalate (Chen. Z et al., 1997)

In chemical terms, ethylene glycol is a diol, an alcohol with a molecular structure that contains two hydroxyl (OH) groups, and terephthalic acid is a dicarboxylic aromatic acid, an acid with a molecular structure that contains a large, six-sided carbon (or aromatic) ring and two carboxyl (CO_2H) groups. Under the influence of heat and catalysts, the hydroxyl and carboxyl groups react to form ester (CO-O) groups, which serve as the chemical links joining multiple PET units together into long-chain polymers. Water is also produced as a by-product.

The overall reaction can be represented as follows:



In the present research work, the epoxy/ glass fiber composites were made by varying the fiber content from 0 to 1% keeping the length and fiber radius constant. Mechanical properties (tensile, flexural and impact strength) have been studied for these composites and the material having best properties will be added with the treated PET fiber, which is prepared with time variation and now this material will again characterize. The fiber volume fraction was limited to 1% because of difficulty in processing beyond this concentration due to increased viscosity.

CHAPTER 2

LITERATURE REVIEW

Nano-scale materials have been the subject of research interest in recent years because of their unique properties. For this purpose, nano-sized inorganic filler are dispersed in polymer matrix offering tremendous improvement in performance properties of the polymer. In this chapter a brief review of the work done on the characterization of composites made by adding nano-fillers to matrix system. Effect of addition of pretreated PET fibers is not discussed and researched so far.

2.1 POLYMER-LAYERED SILICATE NANOCOMPOSITES

It is the one of the most promising mechanical reinforcing materials for polymeric composites. This is attributed to their high axial Young's modulus, high aspect ratio, large surface area, and excellent thermal and electrical properties.

The layered silicates were first introduced by researchers from Toyota (Okada et al., 1990) in the 1990s that discovered the possibility to build a polymer layered silicate nanocomposite from polyamide 6 and organophilic clay. Their new materials presented significant improvements of their mechanical and physical properties. Following this new approach, other researchers synthesized polymer-layered silicate nanocomposites based on epoxies (Wang et al., 1996), unsaturated polyesters (Berglund et al., 1998), polyurethanes, polyimides and polyether's (Pinnavaia T. et al. 1994), polystyrene (Moet et at., 1994), poly(ethylene) terephthalate (Long et al., 1999) and polycarbonate (Huang et al., 2000) among many others.

There are essentially three different approaches that may be used to synthesize polymer/clay nanocomposites: the melt intercalation, solution, and in situ polymerization methods. In the melt intercalation process, a polymer is mechanically mixed with organophilic clay at elevated temperatures. The polymer chains are then intercalated directly between layers of clay. In the solution method, the organ clays and the polymer are dispersed and dissolved in a polar organic solvent, respectively. The dissolved polymer chains are able to penetrate into the clay layers. A uniform mixing of polymer and layered clay is achieved after the solvent has evaporated. In the insitu method monomers are reused to intercalate directly into the clay layers. Then the monomers are polymerized in the presence of the layers.

Although the high aspect ratio of silicate monolayer is ideal for reinforcement, the monolayers are not easily dispersed in most polymers due to their preferred face-to face stacking in agglomerated tactics. Dispersion of the clay into discrete monolayer is further hindered by the intrinsic incompatibility of hydrophilic layered silicate sand hydrophobic engineering plastics.

The homogeneous dispersion of inorganic layered silicates in an organic medium like a polymer on a molecular scale is realized by treating layered silicates with organic ions in order to make them organophilic. Indeed, layered silicates such as fluorohectorite or montmorillonite have a remarkable ability to exchange ions. Their structure consists of two fused silica tetrahedral sheets sandwiching an edge shared octahedral sheet. Isomorphous substitutions in the tetrahedral and the octahedral sheets cause an excess of negative charges within the layered silicate.

These negative charges are counterbalanced by cations situated between the layers and can be exchanged for organic onium ions with long alkyl chains to render the layered silicate organophilic and therefore more compatible with the polymer-matrix. Alkyl ammonium ions reduce, also, the Van der Waals interactions between the silicate layers, which favours the penetration of the polymer or polymer precursors between these layers and therefore the formation of an exfoliated nanocomposite. So far, most of the scientific work has been focussing on the synthesis of polymer-layered silicate nanocomposites and on the study of their physical and mechanical properties.

A replacement of FRPs by nanocomposites can be regarded as unrealistic, due to the highly developed and well established conventional fiber-reinforcement of polymers and their still unmatched level of material properties. The rapid development of nano science and technology not only stimulates the research work rigorously, but also accelerates the potential applications in many fields. While most research concerning nanocomposites has been confined only to two-phase nanocomposites (for example, carbon nanotubes-dispersed epoxy), the incorporation of nano-fillers into the polymers is expected to improve the mechanical properties such as fracture toughness and the compressive strength of three-phase composites (for example, glass/carbon fiber reinforced epoxy with carbon nanotubes).

It is also believed that an addition of small amount of nanoclays into the fiber reinforced epoxy composite system can improve the mechanical properties through the reinforcement of clay particles in the matrix rich region in order to bring the improvement in interfacial and impact

properties. A number of studies have been carried out on either fiber or clay reinforces systems. However, in this present work we are only concerned with a small part of engineering application, i.e., adding nanoparticles in epoxy fiber reinforced composites to make a significant improvement in mechanical properties. Thus, the survey of literature will be limited to the related experimental research in various nanoparticles (nano fibers and nanoclays) and their corresponding properties.

2.2 LAMINATED NANOCLAY-EPOXY FRP NANOCOMPOSITES

Early research reported that nano-fillers-dispersed polymers become brittle compared with the original polymers (Schadler et al., 2004). Using Nano reinforcements in epoxy matrix, Rice and co-workers found no major improvements of the mechanical properties of carbon fiber-reinforced laminates, even though 2 wt.% of organo silicate induced a modulus improvement of 12% of the nanocomposite as compared with the pure epoxy (Chen et al., 2001). However, recent sophisticated studies indicated that fracture toughness of the nanocomposites is higher than that of the neat polymers. It should be emphasized that their work was preliminary and many variables were not explored.

For example, Haque et al. (2003) using a similar manufacturing process as used by Rice et al. (2001) (i.e. vacuum assisted resin infusion method (VARIM)) showed large improvement of the mechanical properties of their S2-glass fiber laminates and at very low layered silicate content. They showed that by dispersing 1 wt. %Nano silicates, S2-glass/epoxy-clay nanocomposites exhibited an improvement of 44%, 24% and 23% ininterlaminar shear strength, flexural strength and fracture toughness, respectively. Similarly, the nanocomposites exhibit approximately 26 ºC higher decomposition temperatures than that of conventional composites. The increased properties at low loading were associated to several factors:

(i) Enhanced matrix properties due to lamellar structures.
(ii) Synergistic interaction between the matrix, clay and fibers.
(iii) Enhanced matrix–fiber adhesion promoted by the clay.

The clays were also presumed to decrease the coefficient of thermal expansion mismatch, significantly reducing residual stresses and leading to higher quality laminates. An increased interfacial bonding, matrix agglomeration and coarse morphology were observed from the fractured surface of low loading nanocomposites. The degradation of properties at higher clay loadings was

believed to be caused by phase-separated structures and also by defects in the cross-linked structures. However, the authors acknowledged that further work is necessary in order to achieve fully exfoliated structure in clay–epoxy nanocomposites.

Gilbert et al. (2002) and Timmerman et al. (2002) demonstrated that fracture toughness and mechanical properties are increased by incorporation of metal and inorganic particles. In these studies, they have been developing the concept of La PolynanoGrESS (Layered Polynanomeric Graphite Epoxy Scaled System) which utilizes then nanoparticles effect in an epoxy matrix and scales to a continuous carbon fiber reinforced composites systems.

Typically, Timmerman et al. (2002) modified the matrices of carbon fiber/epoxy composites with layered inorganic clays and a traditional filler to determine the effects of particle reinforcement, both micro and nano scale, on the response of these materials to cryogenic cycling. The mechanical properties of the laminates studied were not significantly altered through nanoclay modification of the matrix. The incorporation of nanoclay reinforcement in the proper concentration resulted in laminates with micro crack densities lower than those seen in the unmodified or macro-reinforced materials as a response to cryogenic cycling. Lower nanoclay concentrations resulted in a relatively insignificant reduction in micro cracking and higher concentrations displayed a traditional filler effect.

Additional properties of the neat and nano-modified epoxy were also determined (partly taken from Timmerman et al., 2002) and compared. The study reported fracture toughness improvement up to about 50% and energy release rates increased by about 20% were observed for addition of 10 wt. % oforganosilicate clay.

Subramaniyan et al. (2003) observed that addition of 5 wt. % of nanoclay increased elastic modulus of epoxy resin under compression by 20% and the compressive strength of glass fiber composites with nanoclay when made by wet lay-up technique increased by 20–25%.

Karaki et al. (2004) incorporated layered clay, alumina, and titanium dioxide into an epoxy matrix and fabricated continuous carbon fiber-reinforced Polynanomeric matrices to study tension–tension fatigue behavior. They found that the number of micro cracks in each layer depended on the type of particles and their concentration.

Mohan et al. (2005) evaluated the tensile performance of S2-glassepoxy composites dispersed with alumina nanoparticles up to 1.5% weight fraction and found an increase of12% in tensile modulus and 8% in tensile strength.

Wang et al. (2005) demonstrated that the exfoliated clay with only 2.5 wt. % in epoxy showed a significant improvement in fracture toughness and concluded that an increase of the micro cracks and the fractured surface due to crack deflection resulted in the toughness increase.

Kornmann et al. (2005) successfully synthesized epoxy layered silicates nanocomposites based on diglycidyl ether of bisphenol A and an anhydride-curing agent. A manufacturing process using hand lay-up, vacuum bagging, and hot pressing techniques was also developed to produce glass fiber-reinforced laminates with this nanocomposite matrix. Transmission electron microscopy indicated that silicate layers dispersed in the epoxy matrix present a long-range order with an interlaminarspacing of about 9 nm. X-ray diffraction analysis confirmed this nanostructure both in the nanocomposites and in the fiber-reinforced composite based on the same matrix. Scanning electron micrographs of the laminate with a nanocomposite matrix showed that nanolayers stacked at the surface of the glass fiber, improving possibly in this manner the interfacial properties of the fibers. Flexural testing of the laminates showed that the Nano layers improved the modulus and the strength, respectively, by 6% and 27%. Dynamic mechanical analyses (DMA) of the epoxy and nanocomposite plates and their corresponding laminates showed a systematic glass transition temperature decrease of the nanocomposite based materials. This, the researchers suggested, explained the larger water uptake observed at 50 °C in the plate and the laminate based on a nanocomposite matrix as compared with those based on the pristine epoxy.

Liu et al. (2005) demonstrated the improvement of fracture toughness and the reduction of water diffusivity of epoxy/nanoclay composites. Ogasawara et al. (2006) investigated helium gas permeability of silicate clay (montmorillonite) particles/epoxy nanocomposites. They reported that incorporation of increasing amounts of montmorillonite particles reduced the helium gas permeability. With the increase of montmorillonite loading, gas diffusivity decreased, while gas solubility increased.

In a recent development, Brunner et al. (2006) exploited Timmerman et al. (2002) work on use epoxy with a relatively small amount of nano-size filler as matrix in fiber-reinforced laminates. They focused on investigating 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. To start with, neat and nanomodified epoxy specimens without fiber reinforcement were prepared for a comparison of the fracture toughness of the matrix material itself.

Hackman and Hollaway (2006) studied the potential applications of clay nanocomposite materials to civil engineering structures. They concluded that the materials ability to increase service life of materials subjected to aggressive environments could be utilized to increase the durability of glass and carbon fiber composites.

The study appreciated the fact that surface modified clays are amenable to make organic/clay nanocomposites because of the weak bonding force between layers of montmorillonite 100. In the study, a typical less viscous epoxy of Epikote 807 base resin was used for better dispersion. It was shown that a loading of the nano-clay of about 4 vol. % (about 6wt. %) reduced the diffusion coefficient to 1/10, and that the theoretical predictions based on the aspect ratio of 0.001 agreed well with the experimental results.

In an interesting development, Miyagawa et al. (2006) studied the influence of bio based epoxy organo montmorillonite clay and PAN-based carbon fiber composites. A sonication technique was utilized to process the organically modified clay into glassy bio based epoxy networks. This process resulted in clay Nano platelets being homogeneously dispersed and completely exfoliated in the matrix.

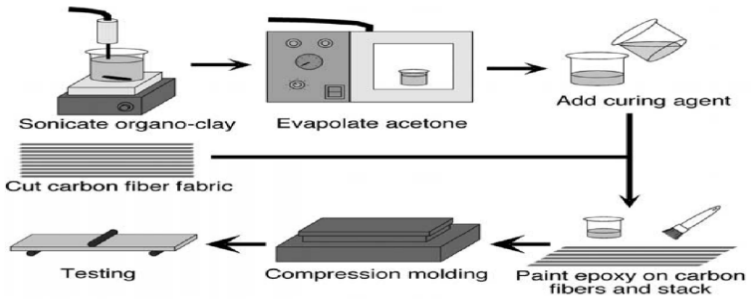


Fig. 7: Schematic drawing of processing CFRP by compression moulding (Miyagawa H. et al., 2006)

Siddiqui et al. (2007) investigated the mechanical properties of nanoclay-dispersed GFRP, and showed that the interlaminar fracture toughness of nano clay dispersed GFRP is higher than that of the conventional GFRP.

A proceeding work by Subramaniyan and Sun (2007) showed that polymers can be toughened significantly using a relatively small amount of nanoclay particles based on the three-point bending tests of the edge-notched specimens with sharp crack tips. A parallel study by the same authors reported that compressive strength of unidirectional GFRP with nanoclays increased compared to the conventional GFRP.

2.3 Montmorillonite Clay Nanocomposites

Polymer/clay nanocomposites are synthesized via melt-intercalation, common solvent mixing, or in situ polymerization (Chan et al., 1986). In the process of melt mixing, the layered silicate is mixed with a molten polymer matrix. If the silicate surfaces are sufficiently compatible with the chosen polymer, then the polymer can enter the interlayer space and form either an intercalated or an exfoliated nanocomposite. Exfoliation or a high level of intercalation is important in producing a polymer/clay nanocomposite, with such separation of individual clay sheets the high aspect ratios are obtained with the inorganic reinforcing materials. The synthesis of PET clay nanocomposites has not been as successful as compared with other polymers.

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.

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.

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.

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 whereas the other shows and increases 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.

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.

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 ultra-sonication. 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.

2.4 Polyethylene terephthalate (PET) - Nanocomposites

PET is considered as one of the most important engineering polymers in the past two decades due to rapid growth in its use. Polyethylene Terephthalate (PET) is one of the most important synthetic fibers for industrial production. The largest use of PET currently is in containers. In this area, beverage and mineral water bottles are standing in prime position. The current worldwide production of PET exceeds 6.7 million tons/year and shows a dramatic increase in the Asian region due to recent increasing demands in China and India (Kim et al., 2009). Last decade, few studies were done on mechanical behavior of PET-FRC and fiber itself.

Chang et al. (2004) studied, PET nano composites made from monomers and organoclay via an in-situ interlayer polymerization method. Nano-hybrid 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 deboning around the polymer-clay interfaces and void formation.

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.

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.

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.

Semiha A et al. (2009) investigated PET bottle granules as a light weight aggregate in mortar and reported some advantages; such as – reduction in the death weight of a structural concrete member of a building which help to reduce the seismic risk of the building, reduction in the use of natural resources, disposal of wastes, prevention of environmental pollution and energy saving.

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 transforms 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.

CHAPTER 3

RESEARCH PROBLEM

3.1GAPS 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:

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

3.2 RESEARCH PROBLEM

The present study is mainly focused upon the effect of addition of fiber to glass fiber reinforced epoxy nanocomposite and mechanical and chemical properties of these FRP laminated nanocomposites would be studied.

3.3 OBJECTIVES

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

- Synthesis of glass fiber reinforced nanocomposites with matrix, nanoclay and different concentration of fiber.
- Characterization of materials by X-Ray diffraction and Transmission electron microscopy (TEM).Determining mechanical and chemical properties of these nano composites.
- The material having best properties will be added with the treated PET fiber, which is prepared with time variation and now this material will again characterize.

CHAPTER 4

EXPERIMENTAL PROCEDURE AND MATERIALS

4.1 METHODOLOGY

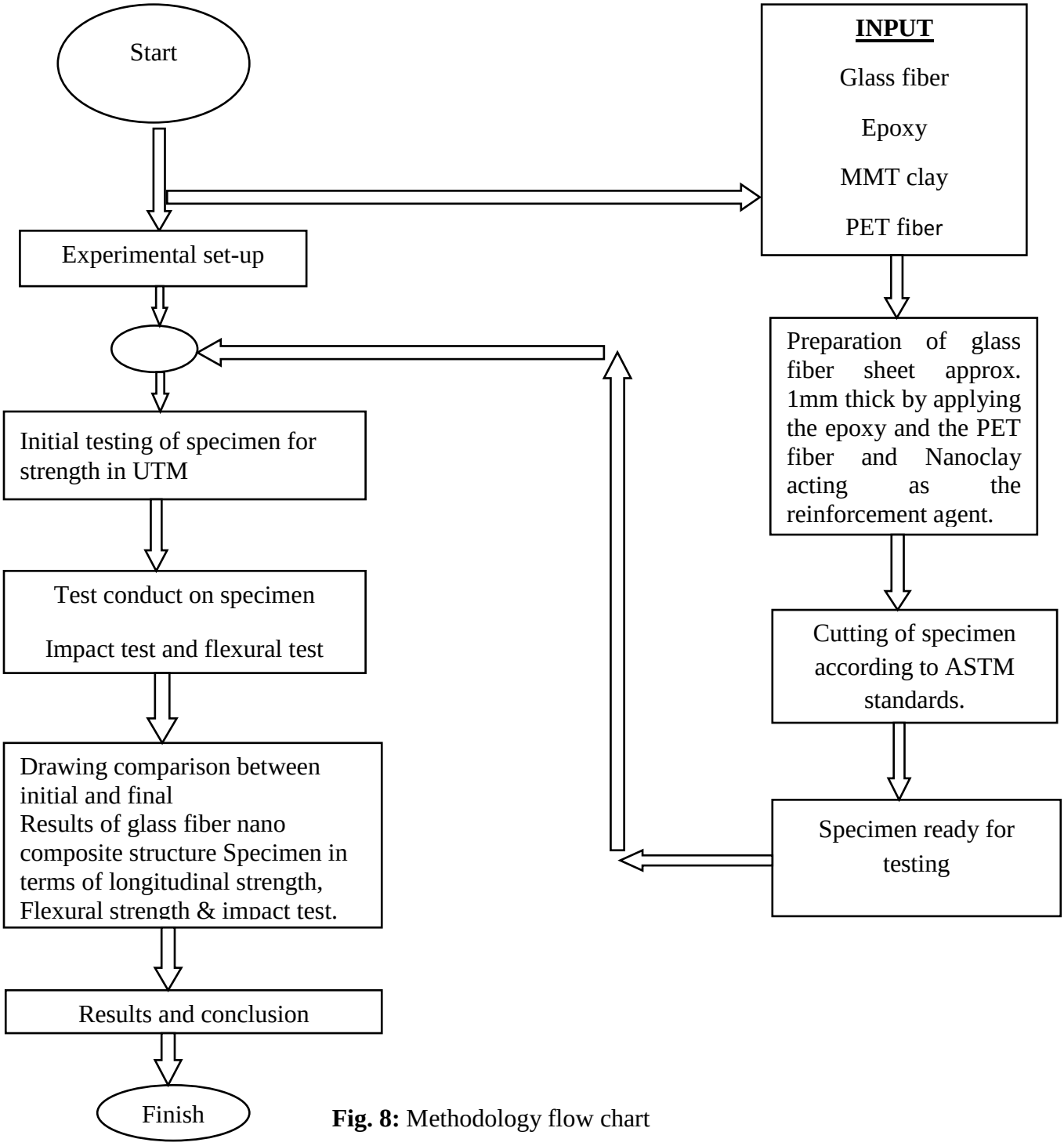


Fig. 8: Methodology flow chart

4.2 MATERIAL

4.2.1POLYETHYLENE TEREPHTHALATE FIBERS

Name of product: Recron3s© fibers

Name of the supplier: Reliance Industries Limited, India. Diameter: 15 µm

Length: 3 mm

Specific gravity: 1.36

Glass transition temperature (T_g):

180°C Dispersion in water: Excellent

4.2.2 NANOCLAY

Name of Product: Closite® 30b

Name of the Supplier: Connell Bros. Mumbai.

Moisture: <3%

Typical Dry Particle Size: <10µm (D50)

Color: Off White

Packed Bulk Density: 365g/L

Density: 1.98 g/cc

4.2.3 EPOXY RESIN

Name of Product: Araldite® CY 230 and Hardener HY 951

Name of Supplier: Huntsman Advanced Materials, India.

Density at 25^0C (77^0F): 1.15 g/cm^3

Viscosity at 25°C: 10 – 20 mPa

4.2.4 GLASS FIBER

45^o Orientation E-Glass Fiber

Width: 150mm

4.3 PROCESSING

4.3.1CUTTING GLASS FIBER SHEET

For the experimentation unidirectional roll of glass fibre was purchased having 150mm width having 45^0 fibre orientations woven with polymer fibres. The sheets were initially cut from roll

in lengths of 600 mm.

4.3.2 MIXING OF NANOCLAY INTO EPOXY (BASE)

PREPARATION OF NANOCLAY

Before mixing the nanoclay into the epoxy base, Nanoclay was dried at 120^0C for 2 hours in a vacuum oven.

MECHANICAL STIRRING

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. 9). Oil bath was used to heat up the epoxy to desired (80^0C) 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 80^0C for 1 hour.

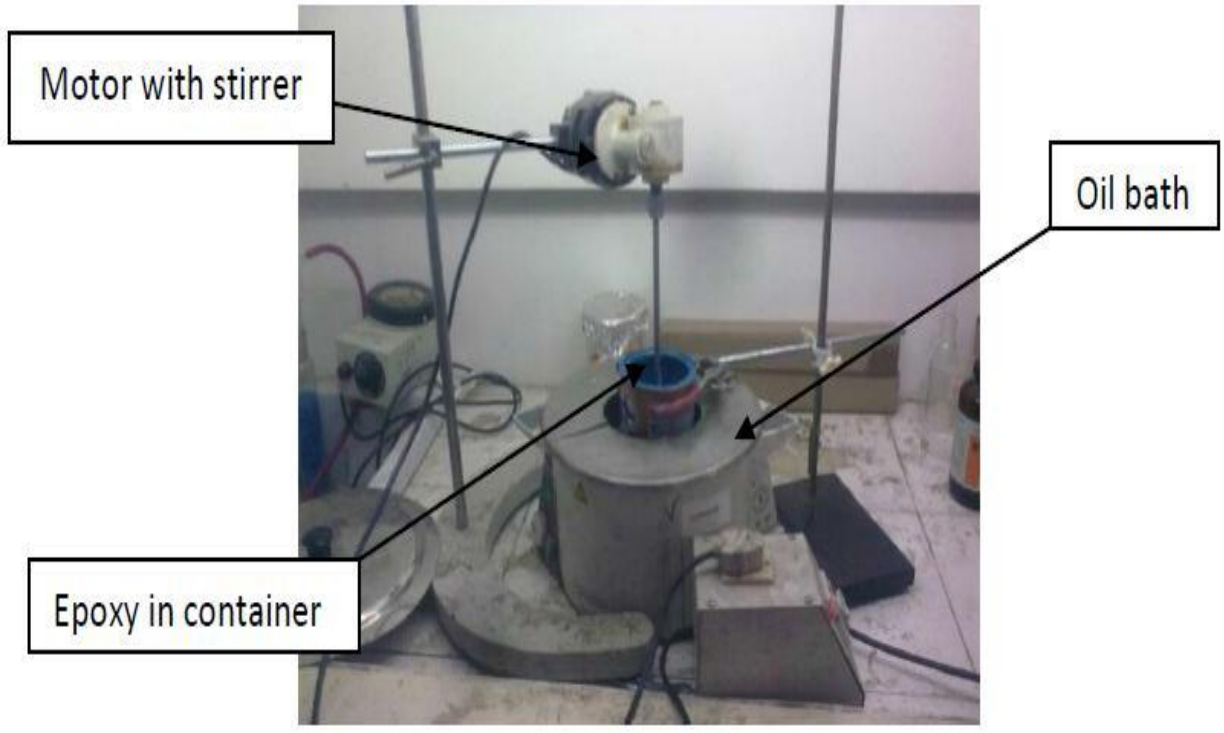


Fig. 9: Oil bath set-up with mechanical stirrer

4.3.3 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 ultra-sonication bath for up to 3hours at 30^0 temperature (Fig.10)

Fig. 10: Ultrasonication bath

4.3.4 MIXING OF EPOXY BASE SOLUTION WITH 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. 11).

Fig. 11: Mixing of PET fiber Epoxy solution

4.3.5 MIXING OF EPOXY BASE & PET SOLUTION WITH HARDENER

After Ultrasonication, the solution is mixed with the hardener in the ratio 10:1by volume. After mixing, manual stirring for 5 to 10 minutes was done. The whole procedure is shown in Fig.12

.

Fig. 12: Mixing of hardener to the solution

4.3.6 COATING OF NANOCLAY AND PET FIBER MIXED EPOXY TO GLASS FIBER SHEETS

The mixture was then poured on to the glass fiber mat and applied uniformly using the hand layup method. For this, steel scraper was used to maintain uniformity of the solution. The composite sheet was then cured for 24h at room temperature, and post cured at 70^0C for 9-10h.

Fig. 13: Glass Fiber Sheet

After the Characterization of materials by X-Ray diffraction and Transmission electron microscopy (TEM) ,mechanical and chemical properties of these nano composites are determined and the material having best properties will be added with the treated PET fiber, which is prepared with time variation and now this material will again characterize.

PREPARATION OF TREATED 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 2.5min.5 min.10min.15min., 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.

4.4 SPECIMEN SPECIFICATIONS

The specimens had been cut and prepared as per the ASTM standards D3037/3039, D790 and D 695 for tensile, bending tests and impact testing respectively. The dimensions of specimens are shown below.

Table 3: Specimen specification for testing

Parameters for specimen	**Specimen for tensile testing**	**Specimen for flexural testing**	**Specimens for Impact Testing**
Length	250mm	250mm	65mm
Width	25mm	25mm	10mm
Thickness	2.5mm	2.5mm	4mm

4.4.1 SPECIMEN DIMENSIONS

- **For flexural test**

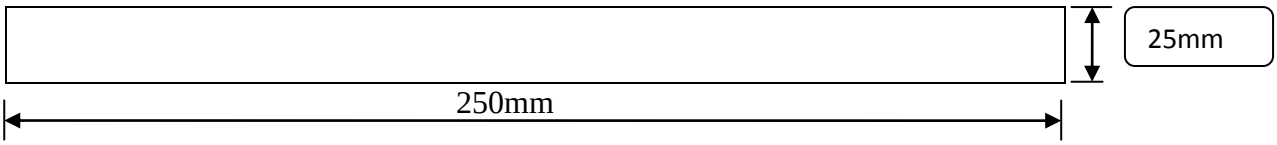


Fig.14: Specimen dimensions for flexural test

Fig. 15: Nanocomposite flexural specimen

- **For tensile test**

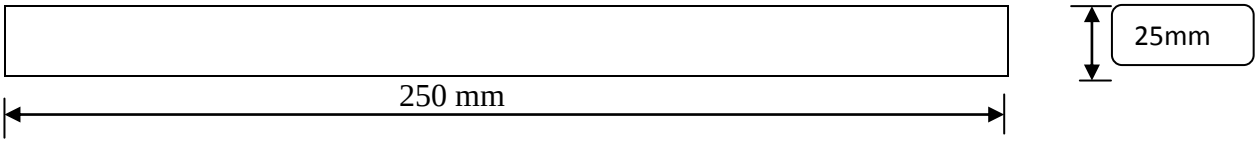


Fig. 16: Specimen dimensions for tensile test

- **For impact test**

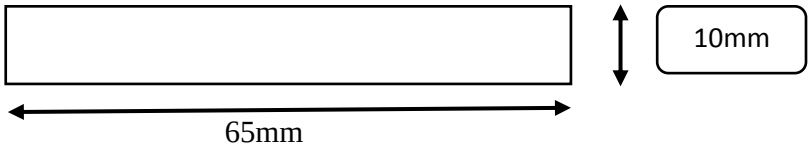


Fig.17: Specimen dimensions for impact test

Table 4: Record of specimens

PET Loading	**No. of Specimen**			**Specimen**
	Tensile	**Flexural**	**Impact**	
0 wt%	3	3	3	9
0.25 wt%	3	3	3	9
0.50 wt%	3	3	3	9
0.75 wt%	3	3	3	9
1.0 wt%	3	3	3	9
Total Specimen				45

4.5 METHODS USED IN EXPERIMENTATION

4.5.1 TENSILE TESTING

A Universal Tensile Testing machine shown in Fig.18 and Fig.19 was used for the testing of the PET/Epoxy composite specimen for its tensile strength.

Fig. 18: UTM testing machine

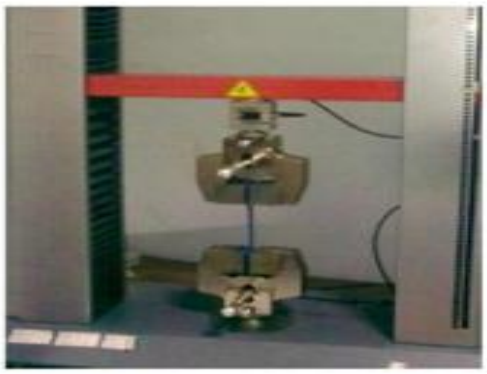


Fig. 19: Specimen in jaws

The test specimen had been prepared according to ASTM standards D3037/3039. 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.

4.5.2. THREE POINT FLEXURAL TEST

Three point bending tests of specimen were carried out in Zwick / Roell using the arrangement as shown in Fig. 20. The test specimen had been prepared according to ASTM standards D3037/3039.

Fig. 20: Three points bend test machine

4.5.3 IMPACT TEST

An Impact testing machine shown in Fig.21 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).

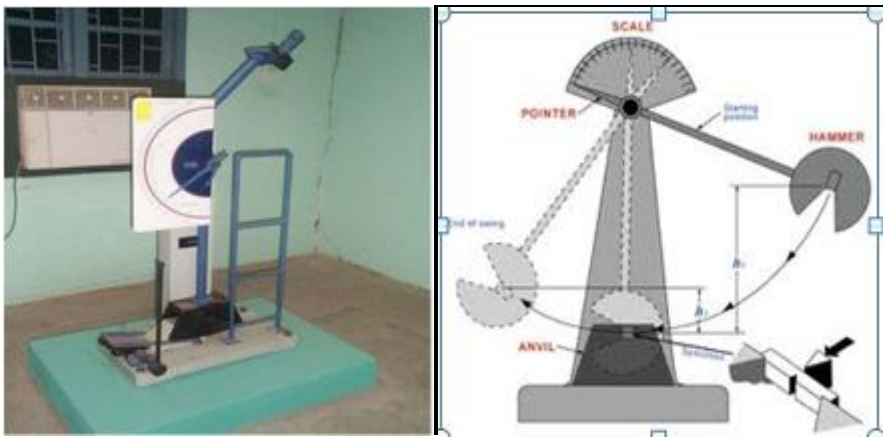


Fig.21: Impact Testing Machine

4.5.4. 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 nanocomposites. 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 intergallery 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 beams. Below is a schematic of

the previously mentioned Bragg's Law (Fig. 22).

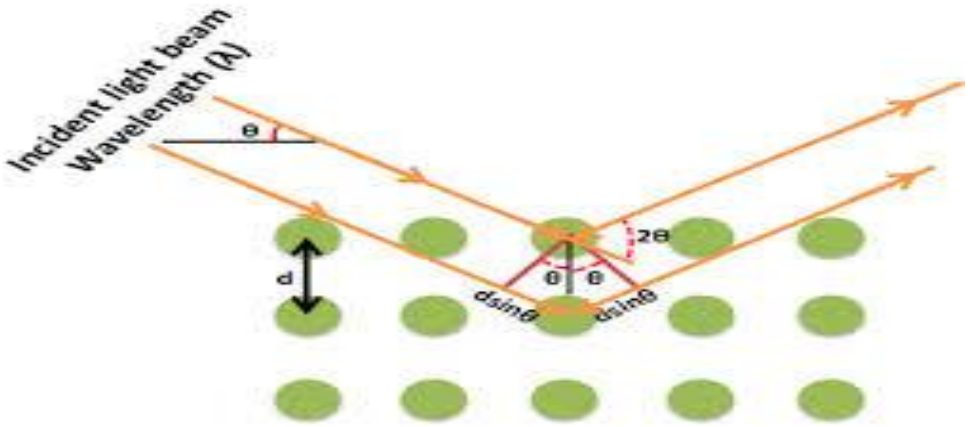


Fig. 22: Schematic representation of x-ray diffraction principle

To evaluate the degree of exfoliation in the polymer, XRD measurements were carried out in a Analytical X-ray diffractometer with Cu Kα radiation (λ=1.54Å) with a scanning speed of 1^0/min and at 45 kV and 40mA. During the XRD experiments, the samples were analysed in Reflection mode. All XRD scans were through 2θ of $3^0$to 5^0.

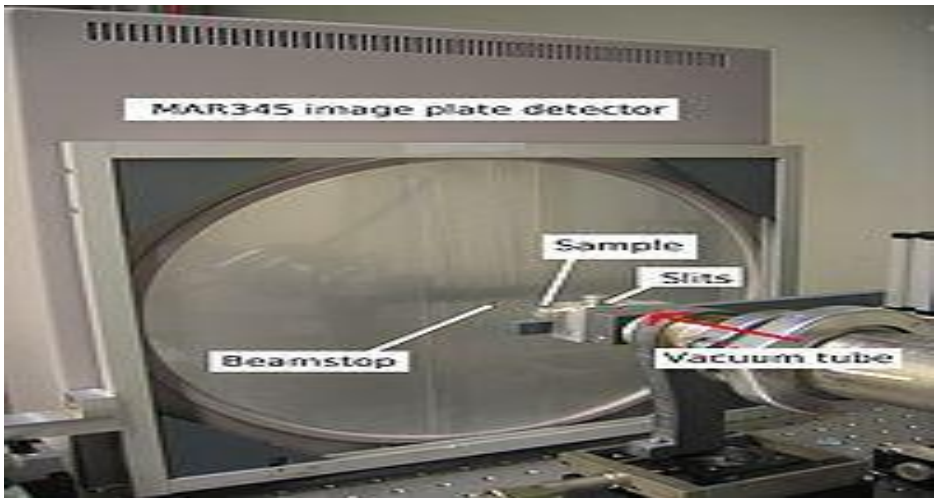


Fig. 23: Schematic representation of x-ray diffractometer principle

4.5.6. Transmission Electron Microscopy (TEM)

TEM is a vital characterization tool for directly imaging nanomaterials to obtain quantitative measures of particle and/or grain size and morphology.

TEM functions involve four basic operations:

- A stream of electrons is formed and accelerated towards the specimen using a positive electrical potential,
- This stream is confined and focused using a metal aperture and magnetic lenses into a thin, monochromatic beam, (magnetic lenses are circular electro-magnets capable of projecting a precise circular magnetic field in a specified region,
- The focused beam is impinged on the sample by a magnetic lens,
- The energetic electrons then interact with the irradiated sample. These interactions and effects are detected and transformed into an image.

A schematic of a TEM is illustrated in Fig. 24.

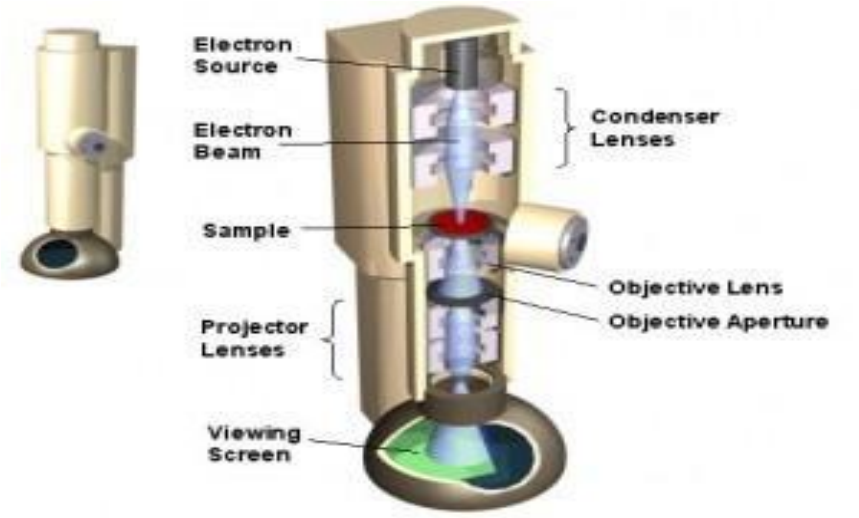


Fig. 24: Schematic of transmission electron microscope

We used a HITACHI transmission electron microscope operating at an accelerating voltage of 80KV is used in this study to test the morphology and particle size. Sample in powder form is prepared for imaging by drying nanoparticles on a copper grid that is coated with a thin layer of cabon.

Fig. 25: H-9500 300kv Transmission Electron Microscope

CHAPTER 5

RESULTS AND DISCUSSION

5.1 TENSILE TEST

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

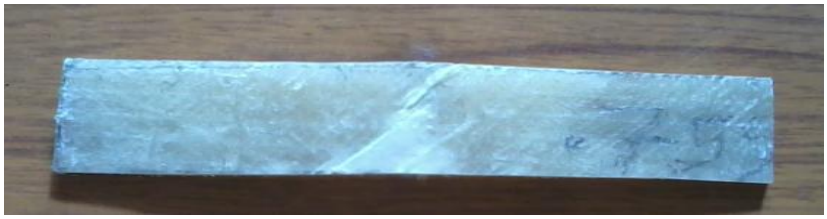


Fig.26: Specimen breaks under tensile load

Table 5: 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	61.4	62.8	60.2	65.5	78.6
Sample 2	60.8	60.6	63.8	72.7	89.2
Sample 3	62.4	63.5	60.5	70.2	68.7
Average	61.53	62.3	62.27	69.46	78.93

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. This is the graph which is drawn between % of pet fiber & tensile strength. I have taken three best specimens which are having maximum tensile strenght.Since these samples are developed on the variation of content on PET fiber starting from 0 up to 1 %. Here in the graph, first the tensile strength will be improved very little from 0 to .25 % PET fiber content. Now the tensile strength will decrease drastically from .25 to .50 % PET fiber content then again tensile strength goes strengthen almost linearly from .50 to 1 % PET fiber content contain sample.

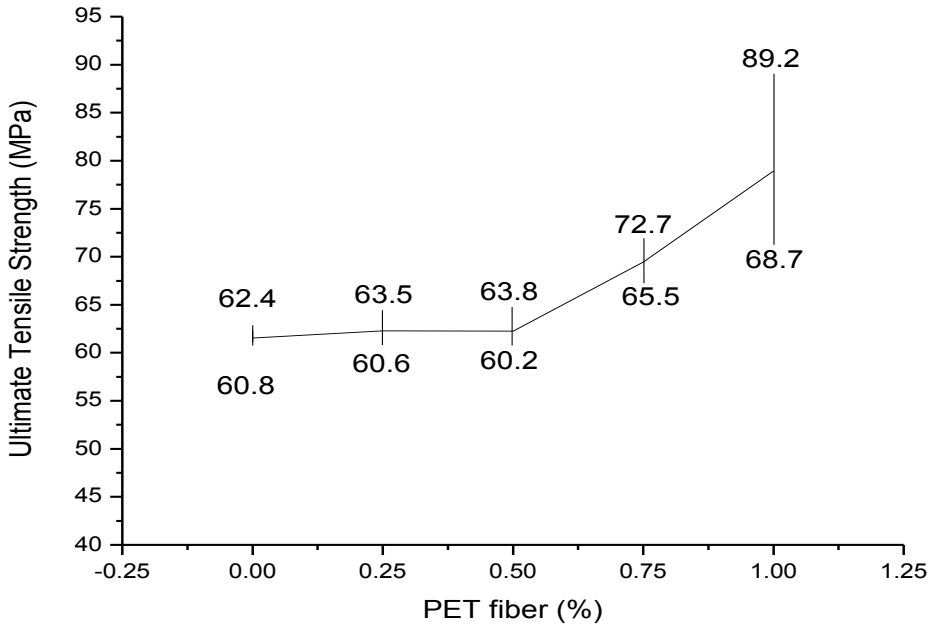


Fig.27: Ultimate Tensile Strength vs. PET fiber %

5.2 FLEXURAL BEHAVIOR

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.

Table 6: Modulus of elasticity (GPa) for Different PET loading

Sample No	**0% PET**	**0.25% PET**	**0.50% PET**	**0.75% PET**	**1% PET**
1	234	276	239	278	245
2	258	188	229	269	336
3	236	300	167	186	329
Average	242.66	254.66	211.66	244.33	303.33

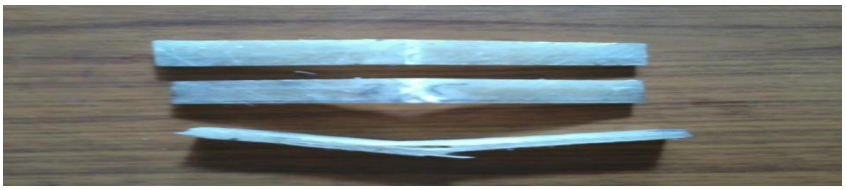


Fig. 28: Specimen breaks under bending load

Table 6 and Fig.29 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. These results are also shown by fig.

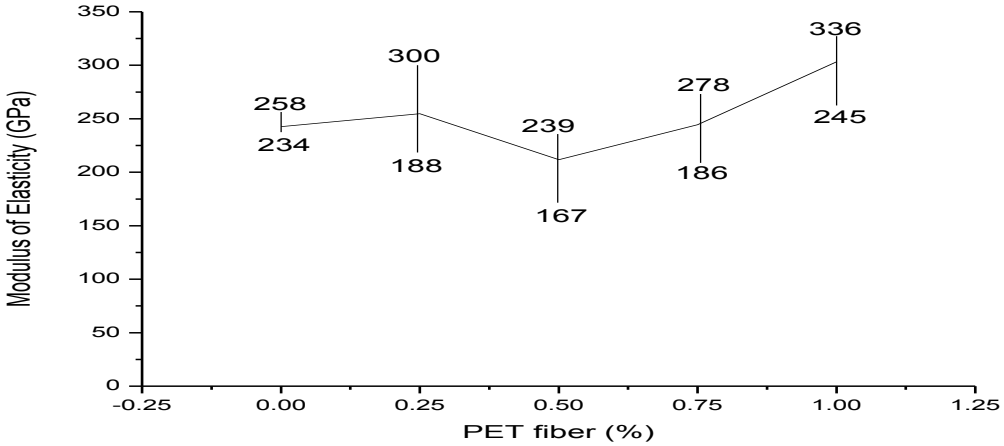


Fig. 29: Modulus of elasticity vs. PET fiber %

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 percentage of PET for desire properties.

Table 7: Deflection of max. Force for Different PET loading

Sample No	0% PET	0.25% PET	0.50% PET	0.75% PET	1% PET
1	1.4	2.1	1.4	2.2	2.3
2	1.5	1.8	1.5	1.7	2.1
3	2.0	2.2	2.4	2.3	2.2
Average	1.6	2.03	1.76	2.06	2.13

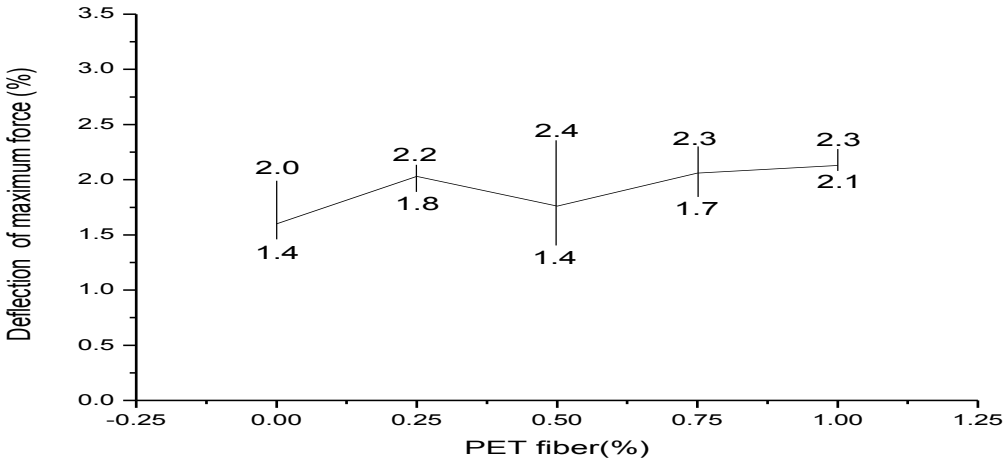


Fig. 30: Deformation of max. Force vs. PET fiber %

5.3 IMPACT TEST

Impact strength or toughness is the main property of materials. Table 8 shows the results that are observed while doing the Charpy Impact test on the test samples with different loading of PET fiber.

Table 8: Toughness (lb/ft) vs. PET contents

Sample No.	0% PET	0.25% PET	0.5% PET	0.75% PET	1% PET
1	2.68	3.52	4.03	4.02	4.16
2	2.68	3.70	4.09	4.09	4.36
3	2.75	3.35	4.19	4.09	4.35
Average	2.70	3.52	4.10	4.06	4.29

Form the Table 8 we can say that the impact strength increases with an increase in the PET content. Fig. 32 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 58%.

Fig. 31: Specimen breaks under impact load

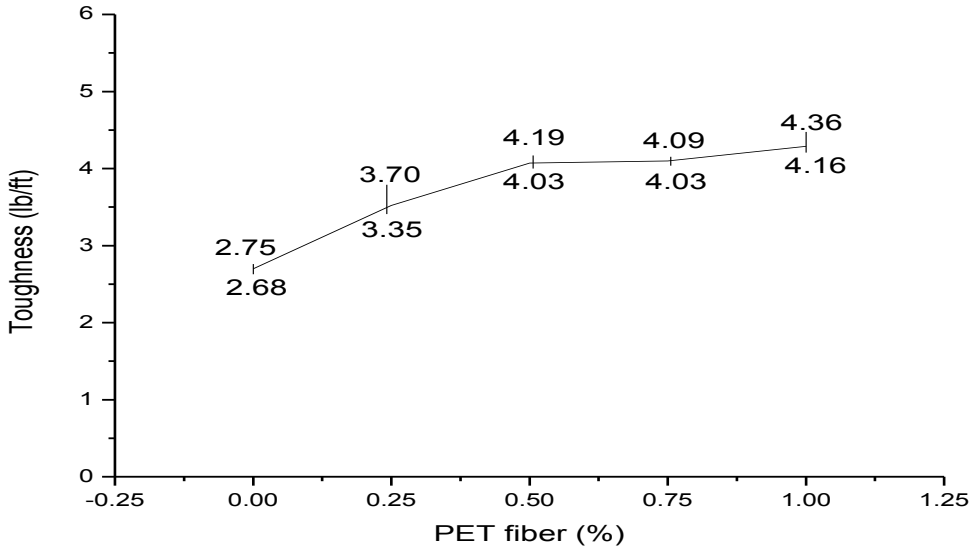


Fig. 32: Toughness (lb/ft) vs. PET fiber %

Table shows the results that are observed while doing the Charpy Impact test on the test samples with different time variation of modified PET fiber. Form Table 9 we can say that the impact strength increases with an increase in the time variation of PET fiber.

Table 9: Toughness (lb/ft) vs. Time (min)

Sample No.	2.5min	5min	10min	15min
1	3.35	3.69	4.11	4.56
2	3.29	3.52	3.09	4.46
3	3.42	3.62	4.19	4.63
Average	3.35	3.61	3.79	4.55

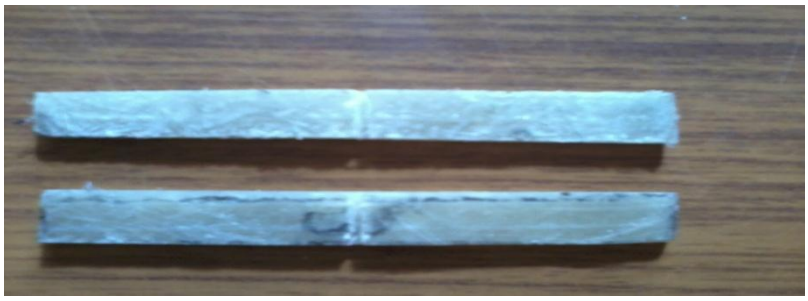


Fig. 33: Specimen breaks under impact load

According to Teh et al. (2005) the fracture toughness of neat epoxy increases by about 33% from 0.70 to 0.93 MPa 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.

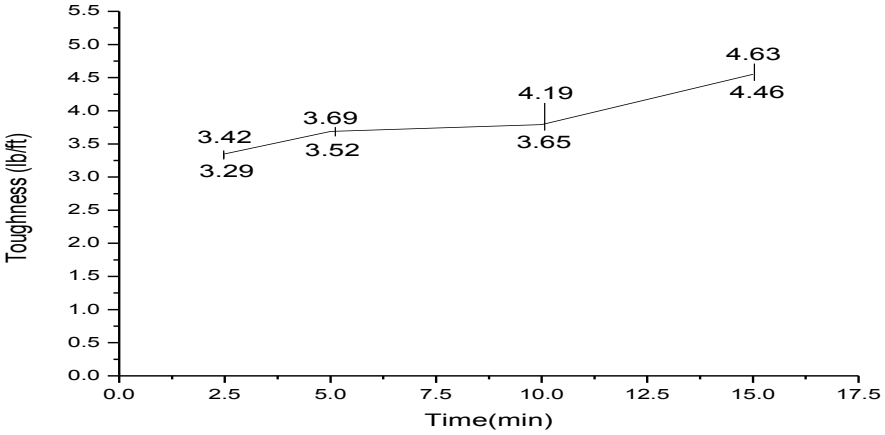


Fig.34: Toughness (lb/ft) vs. Time (min)

5.4 TRANSMISSION ELECTRON MICROSCOPY (TEM)

Sample in powder form was dissolved in ethanol and sonicated for 1 hour prior to dispersion onto a copper grid using a porous carbon film. The morphological detail of the sample was determined at various magnifications.TEM images, shown in Fig.35 illustrates the morphology of nanocomposites containing 3wt% clay loadings. The image shows a uniform dispersion of

nanoclay particles. The particles appear to be agglomeration-free and the individual nanometer thicknesses dispersed in the polymer matrix are clearly visible.

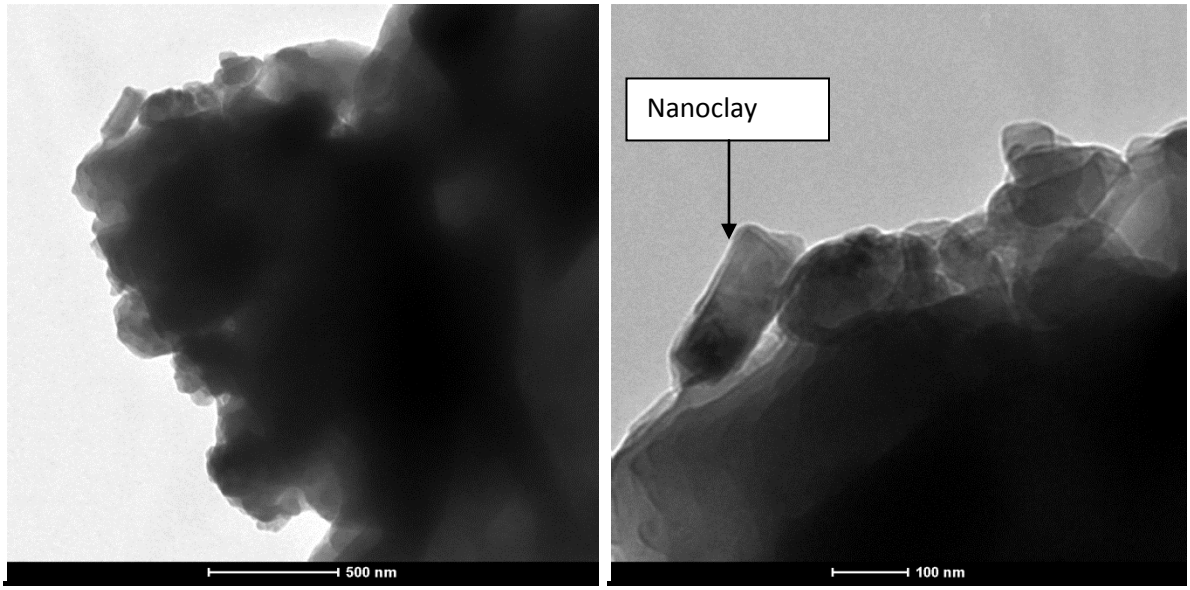


Fig. 35: TEM micrograph of 3 wt% nanoclay

5.5 X-RAY DIFFRACTION

X-ray diffraction has played a central role in identifying and characterizing solids since the early part of this century. X-ray diffraction pattern of amorphous polymer will not show any sharp and highly intensed peaks whereas the nanocomposites of amorphous polymer show sharp and highly intensed peaks. This is due to the development of crystallinity in the amorphous polymer.

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 the test samples of different loading of PET fiber in it. X-ray diffractometer gives the values of d-spacing and 2θ nano composites.

The characteristics peak of clay as illustrated in fig.36, fig.37, fig.38, fig.39 and fig.40 are not visible. This may be due to the exfoliation of clay during the polymerization of resin. The exfoliated structure does not show any peak in the X-ray diffractogram.

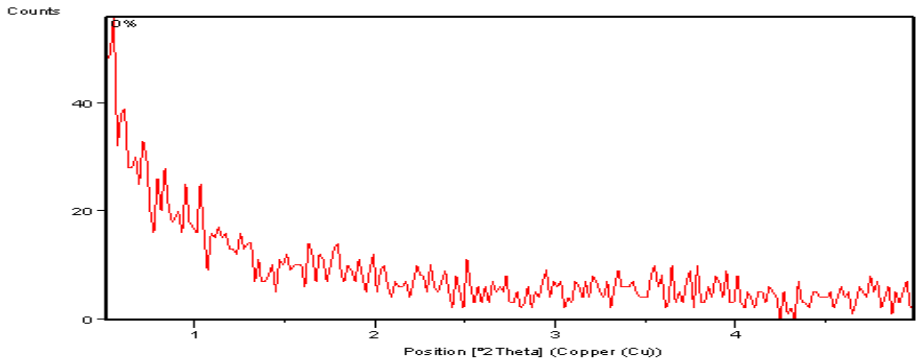


Fig. 36: X-ray diffractogram image of nanocomposite having 0% wt PET fiber loading

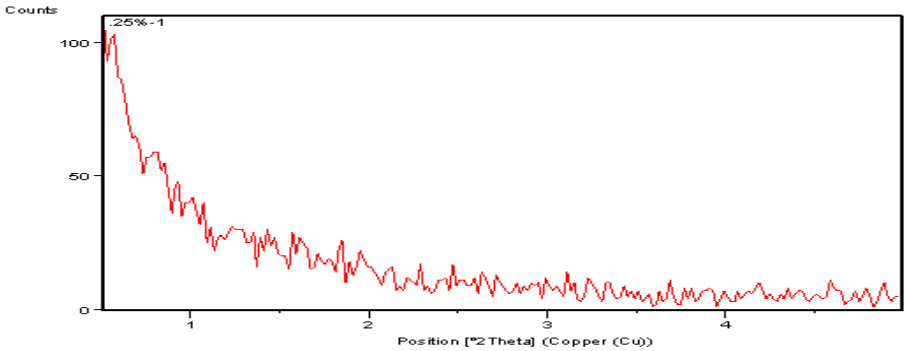


Fig. 37: X-ray diffractogram image of nanocomposite having .25% wt PET fiber loading

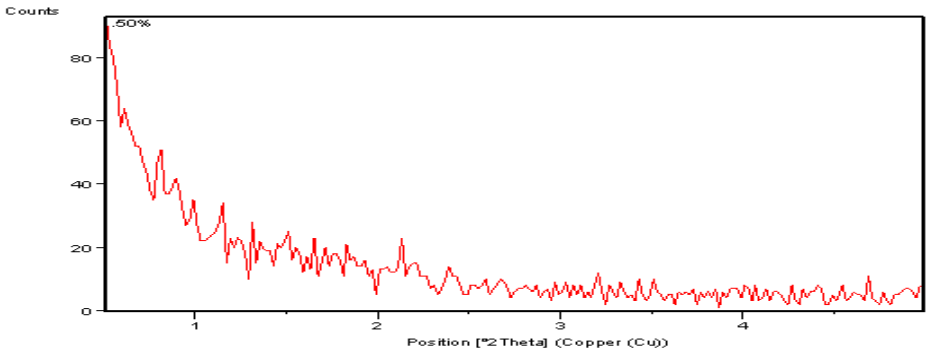


Fig. 38: X-ray diffractogram image of nanocomposite having .50% wt PET fiber loading

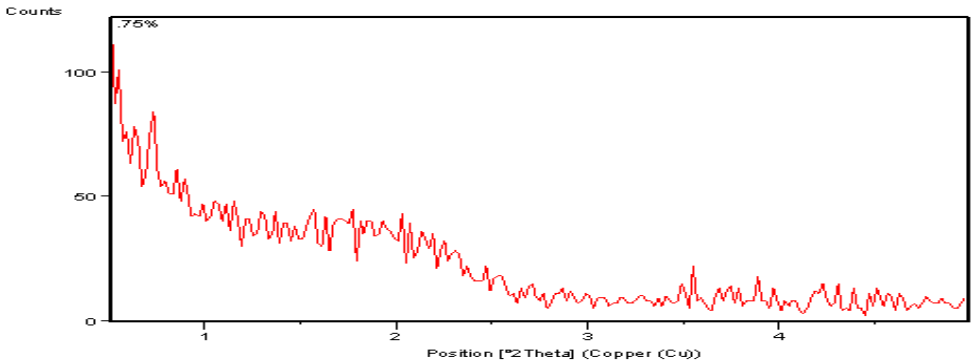


Fig. 39: X-ray diffractogram image of nanocomposite having .75% wt PET fiber loading

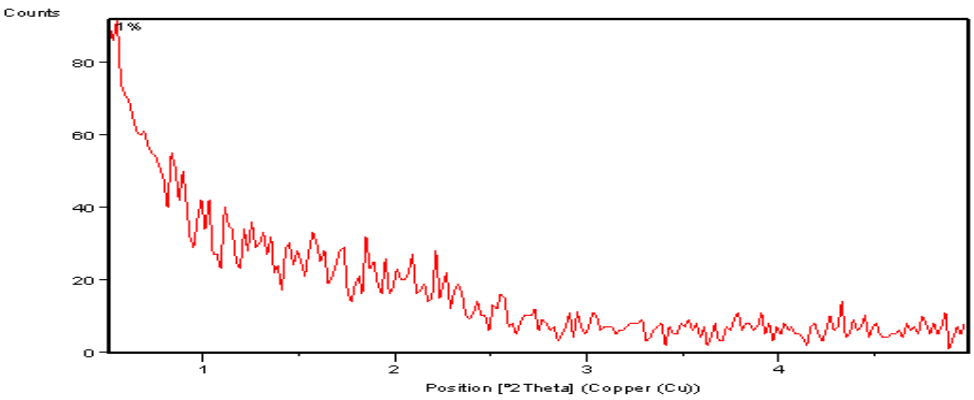


Fig. 40: X-ray diffractogram image of nanocomposite having 1% wt PET fiber loading

CHAPTER 6

CONCLUSIONS AND FUTURE SCOPE

CONCLUSION

In this study, the effect of addition of another polymeric fiber like PET fiber content on mechanical behavior and morphology of the polymer epoxy-organoclay nanocomposites was investigated and the following conclusions were derived:

- Tensile strength and flexural modulus increases with increase in fiber content and was maximum for 1% fibers. The study could not be extended beyond this fiber fraction because of limitations in processability.
- XRD patterns indicated exfoliation for 3wt. % clay and a decrease in d-spacing in higher clay loadings after that.
- The impact strength of the nanocomposites exhibit marked improvement with addition of Closite 30B. Adding of 3 wt. % Closite 30B improved the impact strength, flexural modulus, and tensile modulus.

Future Scope

- The experiment can be performed on polyester as matrix system, since with this matrix the barrier properties of composites can be enhanced.
- Clay loading can also be varied more than 3 wt%.
- The duration of current experiment can be increased to see the effect in long term.
- PET loading can be increased to 2-3 wt% if PET loading is done mechanically.
- 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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