CHARACTERIZATION OF GLASS FIBRE REINFORCED ELASTOMERIC NANOCOMPOSITES WITH DIFFERENT LOADING LEVELS OF NANO FILLER

Thesis submitted in partial fulfillment of the requirements for the award of degree of

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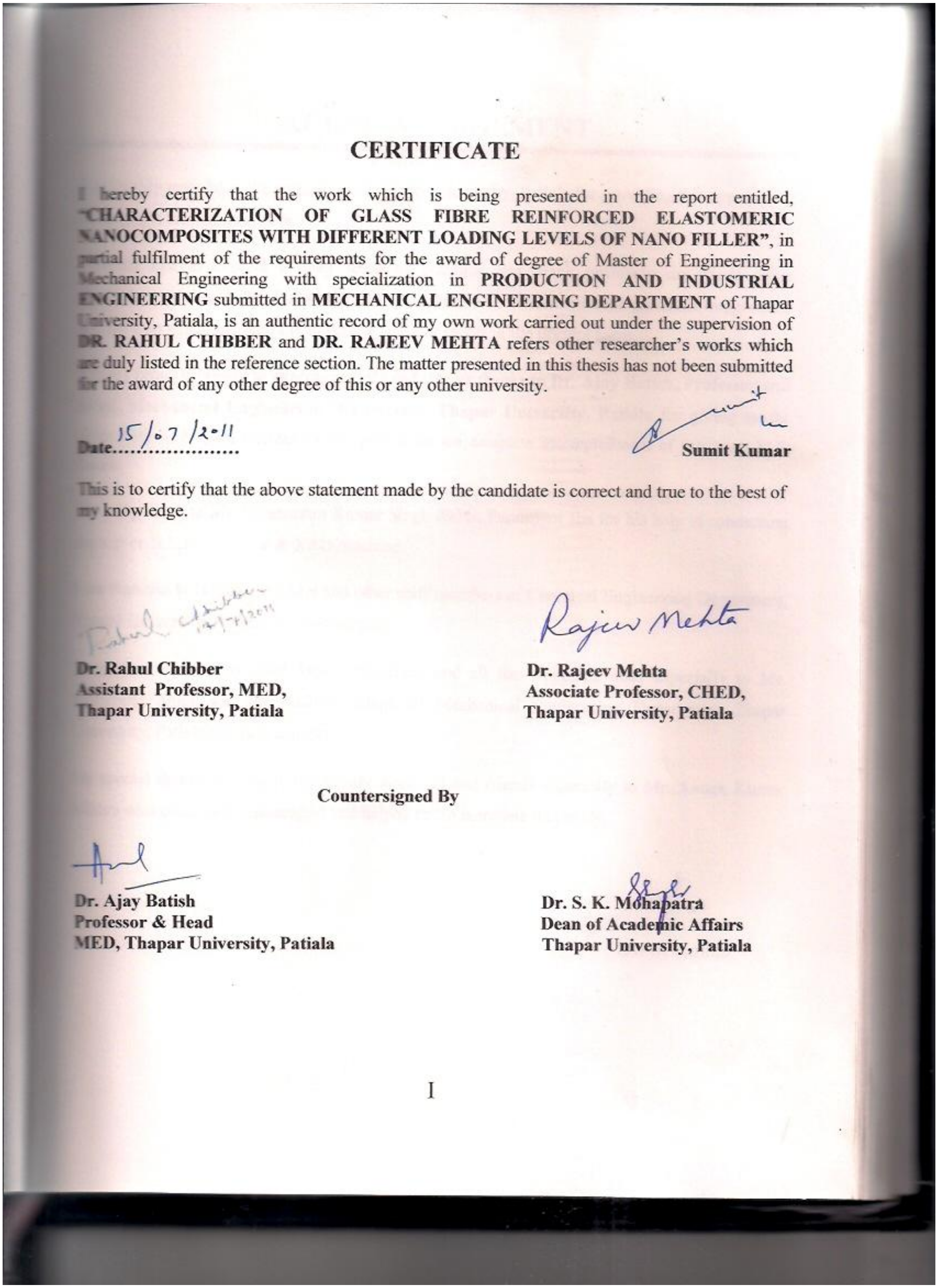

CERTIFICATE

I hereby certify that the work which is being presented in the report entitled, **“CHARACTERIZATION OF GLASS FIBRE REINFORCED ELASTOMERIC NANOCOMPOSITES WITH DIFFERENT LOADING LEVELS OF NANO FILLER”**, in partial fulfilment of the requirements for the award of degree of Master of Engineering in Mechanical Engineering with specialization in **PRODUCTION AND INDUSTRIAL ENGINEERING** submitted in **MECHANICAL ENGINEERING DEPARTMENT** of Thapar University, Patiala, is an authentic record of my own work carried out under the supervision of **DR. RAHUL CHIBBER** and **DR. RAJEEV MEHTA** refers other researcher’s works which are duly listed in the reference section. The matter presented in this thesis has not been submitted for the award of any other degree of this or any other university.

Date: 15/07/2011

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This is to certify that the above statement made by the candidate is correct and true to the best of my knowledge.

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ABSTRACT

Polymer nanocomposite is very attractive field of research and a lot of work is going on across the world in this area. But it is a considerable fact that research work on elastomers is still in its infant stage. As we know that elastomers are used in many engineering applications. So its intense investigation by intercalation of micro and nano particles can lead to valuable products which can replace the neat elastomer with improved properties at low cost.

Here we chose the most widely used rubber i.e. Ethylene Propylene Diene Elastomer (EPDM) for my research work. EPDM/OMMT clay nanocomposites have been synthesized by solution intercalation method using organically modified montmorillonite clay and then glass fibre reinforcement was done to this EPDM/OMMT clay nano composite. Characterization of the prepared specimens at different loading levels of clay (viz. 2 percentage weight, 3 percentage weight and 5 percentage weight) was done by checking the mechanical properties (tensile strength and bending strength), solvent swelling behavior, intermolecular dispersion through XRD & SEM and thermal stability through TGA apparatus. Comparative study between glass fibre reinforced pure EPDM speciemen and EPDM/ clay nano composite specimens has been done in my thesis work. It has been found that this tensile strength of 3 percentage weight clay exhibited very high gain as compared to neat EPDM specimen. The flexural strength and modulus are also higher for EPDM/clay hybrids than that of neat EPDM. Thermal stability of nano composites are also improved shown by TGA results

TABLE OF CONTENTS

Chapter 5

RESULTS AND DISCUSSIONS

Chapter 6

CONCLUSION AND FUTURE SCOPE OF THE WORK

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1 INTRODUCTION

From the past few years, we often heard about composites. Composites are combination of two or more materials (reinforcing elements, fillers, and composite matrix binder) differing in form or composition on a macro scale. The constituents retain their identities i.e. they do not dissolve or merge completely into one another although they act in concert. The properties of a composite will be different from those of the constituents in isolation and set of performance characteristics is greater than that of the components taken separately. In most of the cases a composite shows enhancement in properties (whether physical, mechanical or electrical) over its patent.

In the earlier days only metal matrix composites were there. But since in many applications metal is replaced by plastics. So in now days, a great attention is being paid to polymer matrices. The expansion of polymer industries and continuous demand for new & low cost composites with improved properties & lower particle content are some of the many new & exciting challenges for this industry & researchers.

1.1 Nano composites

Generally composites are prepared by adding micro fillers to the base matrices but it has been found experimentally that if fillers are added at nano size then same properties as in first case can be achieved with lighter weight and low cost. As demonstrated by Scholhorn, this type of insertion of nano size organic host in base matrix is called as nanocomposites. As discussed, these nano composites offer the possibility for new paradigms of material properties. In spite of the fact that clay nanocomposites are prepared for many thermoplastics and thermosetting polymers but a much less attention is given to rubber/clay nanocomposites[2].

Rubbery polymers with their low modulus stand to gain much in terms of modulus and strength from the addition of nano particles. The effect of clay on rubber can be seen by the enhancement in mechanical properties, change in electrical conductivity, improvement in barrier properties (viz. Resistance to fire, water, gases etc)[1]. These improvements are not shared by their conventional micro composite counter parts with same weight addition of the filler. In all rubber, EPDM is widely used & has great commercial importance. Hence intense investigation of EPDM (Ethylene Propylene Diene Rubber matrix) & clay nano composites should be valuable [2]. So here our main research materials are EPDM & clay and then suitable fibre for reinforcement in base matrix. Before starting description of every component, some abbreviations used in the report are as under:

EPDM- Ethylene Propylene Diene Monomer

TEM- Transmission Electron Microscopy

SEM- Scanning Electron Microscopy

XRD- X-Ray Diffraction

MMT- Montmorillonite

OMMT- Organically modified MMT

SBR - Styrene Butadiene Rubber

AFM – Atomic Force Microscopy

X% wt Y hrs – X percentage weight of clay and Y hours of post ultrasonication

wt - weight

Now description of all the component are given below

1.2 EPDM Rubber

EPDM contains small number of double bonds, external to the backbone [1] making its polymer backbone totally saturated resulting in exceptional chemical resistance.

Its physical properties solvent resistance, recommended applications are given in the table 1.1 as shown on next pages presented by Britannia rubber mfg. Ltd. ISO 9001:2000 company of Canada. EPDM is a non polar rubber by nature so it resists polar solvents. EPDM in its natural form require 5-6 hours curing at 145-150°C.

Mechanical Properties	Hardness (Shore A)	25- 90
	Tensile Failure Stress Ultimate (MPa)	25-30
	Elongation (percentage)	100-600
	Tear Resistonnce	Fair to Average
	Abrasion Resistance	Good to Excellent
Thermal Properties	Maximum Service Temperature (°C)	170-180
	Minimum Service Temperature (°C)	-60 to -50
	Glass Transition Temperature (°C)	-54
	Heat Resistance	Excellent

Table 1.1 (a) Mechanical and thermal properties of EPDM rubber [18]

Physical and Chemical Properties	Density (g/cc)	0.9-2.0
	Specific Gravity (g/ml)	0.855-0.880
	Mooney Viscosity@125 C (ML)	5-200
	Resistance to Polar Solvents like Water, acids, ketones and alcohols	Excellent
	Ozone Resistance	Excellent

Table 1.1 (b) Physical and chemical properties of EPDM rubber [18]

EPDM is widely used rubber and has great commercial importance. Its applications are found in roofing, sealing, gaskets, hoses, cable insulation, jacketing[2] and many other engineering applications like vehicles, safety equipment, solar pool panels, water pump, thermostat, radiator, air tubing in turbo charged engines, belts etc. [23]

1.3 Clay

Clay is a naturally occurring material composed primarily of fine grained minerals (basically phyllosilicate minerals with variable amounts of iron, magnesium, alkali metals, alkaline earth & other cations). Clays find wide range of applications in various areas of science & engineering due to their natural abundance and the propensity with which they can be chemically and physically modified to suit practical technological needs. Depending upon academic source, there are four main groups of clays: kaolinite, montmorillonite or smecitite, illite and chlorite. Clays have structures similar to micas and therefore form flat hexagonal sheets as shown in figure 1.1

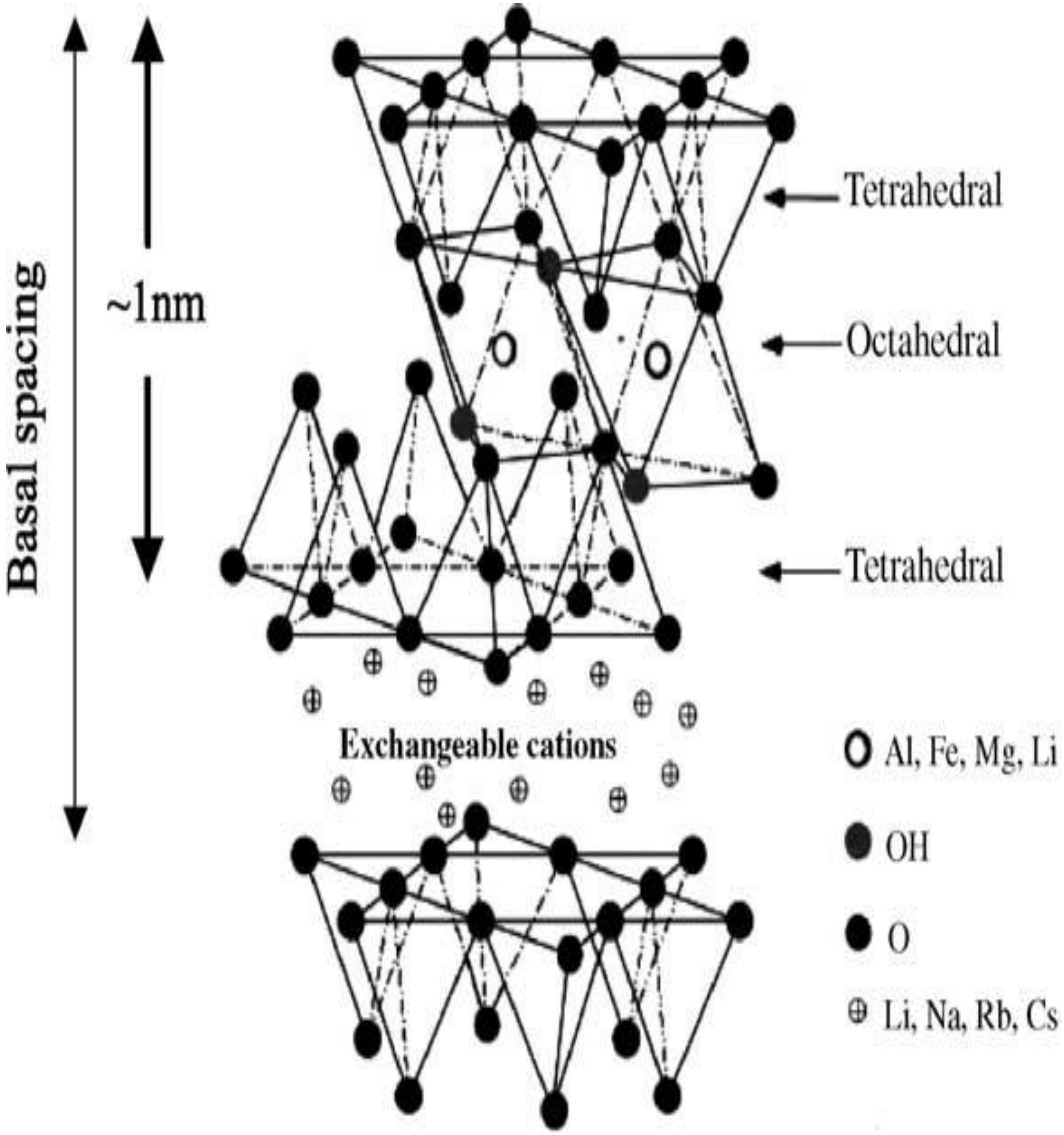


Fig. 1.1 Structure of 2:1 phyllosilicates[3].

The crystal structure consist of layers which are made up of two tetrahedrally coordinated silicon atoms fused to an edge- shared octahedral sheet of either aluminium or magnesium hydroxide. These layered silicates basically shows two types of structure

i. Tetrahedral substituted type and
ii. Octahedral substituted type

The former one can react with polymer matrix readily. This is due to the presence of negative charge on the surface of silicate layers. In many of the cases it has been seen that the physical mixture of polymers and layered silicate may not form a monocomposite and a separation into discrete phases takes place due to the poor physical interaction between the organic and inorganic components.

To render layered silicates miscible with polymer matrices, one must convert the normally hydrophilic silicate surface to an organophillic one. Generally, this can be done by ion-exchange reactions with cationic surfactants including primary, secondary, tertiary and quaternary alkylammonium or alkylphosphonium cations. These cations in the organosilicates lower the surface energy of the inorganic host and improve the wetting characteristics of the polymer matrix which result in a larger interlayer spacing and hence polymer chains find openings to enter between the silicate layers. [9]

Montmorillonite (MMT) clay is the most commonly used layered silicates due to cheapness and easily availability and also readily susceptible to organic modification due to high cation exchange capacity (110 meqiu/100gms).

It has two tetrahedral sheets sandwiching a central octahedral sheet. The particles are plate shaped with an average diameter of approximately 1µm and length approximately 100-150 nm. The chemical formula of montmorillonite is[3]

$$M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$$

1.4 EPDM/Clay nano composites:-

In recent years, rubber clay nanocomposites have attracted great interest, both in industry and in academic, since they often exhibit (at low loading levels of clay) outstanding properties as compared with unfilled rubber compounds or conventional filled composites. There are three main techniques that are used for the preparation of rubber-clay nanocomposites.

i. In Situ Polymerisation

In this method, layered silicate is swollen within monomer solution (or liquid monomer) so the formation of rubber can occur between and around the intercalated layers. The polymerisation can be initiated either by the incorporating of curing agent or initiator or by increasing the temperature if it is sufficiently reactive.

ii. Intercalation via solution :-

Acharya et al **[13]** **(2006)** has reported EPDM/ Mg Al layered double hydroxide nanocomposites by solution intercalation. **Kuila et al** **[6]** **(2009)** reported ethylene vinyl acetate(EVA)/ EPDM (50/50 by weight with layered double hydroxide as nanofillers in the nanocomposites prepared via solution blending method. This method used a solvent system in which the rubber is soluble and the layered silicate is swellable. The organically modified layered silicate is first swollen and comes apart in the solvent. The rubber is then dissolved in solvent and added to the solution. Upon solvent removal, the clay layers reassemble around the polymer resulting in rubber-clay nanocomposite.

iii. Direct melt intercalation method

This is the most promising method and it has great advantages over both previously mentioned methods being both compatible with current industrial processes and environmentally benign, due to the absence of solvents. In this method rubber and modified layered silicate mixture are blended in the molten state under shear. The rubber chains reptate from the molten mass into the silicate galleries to form either intercalated or delaminated nano composites. **Zheng et al**[1] **(2003)** reported melt intercalation method for the preparation of EPDM/montmorillonite nanocomposites using HAAKE mixer.

These techniques generate different interfacial interactions between rubber matrix and layered silicates. On the basis of strength of these interfacial interactions, rubber- clay nanocomposites are divided into three main types as given below

a. Intercalated nanocomposites:

In intercalated nanocomposites, the insertion of a polymer matrix into the layered silicate structure occurs in a crystallographic- ally regular fashion, regardless of the clay to polymer ratio. Intercalated nanocomposites are normally interlayer by a few molecular layers of polymer. Properties of the composites typically resemble those of ceramic materials.

b. Flocculated nanocomposites:

Conceptually this is same as intercalated nanocomposites. However, silicate layers are sometimes flocculated due to hydroxylated edge–edge interaction of the silicate layers.

c. Exfoliated nanocomposites:

In an exfoliated nanocomposite, the individual clay layers are separated in a continuous polymer matrix by an average distances that depends on clay loading. Usually, the clay content of an exfoliated nanocomposite is much lower than that of an intercalated nanocomposite. This is the most desirable case as it gives highest improvement in properties as compared to any other case. The structures prepared in each case is shown in figure 1.2 on the next page.

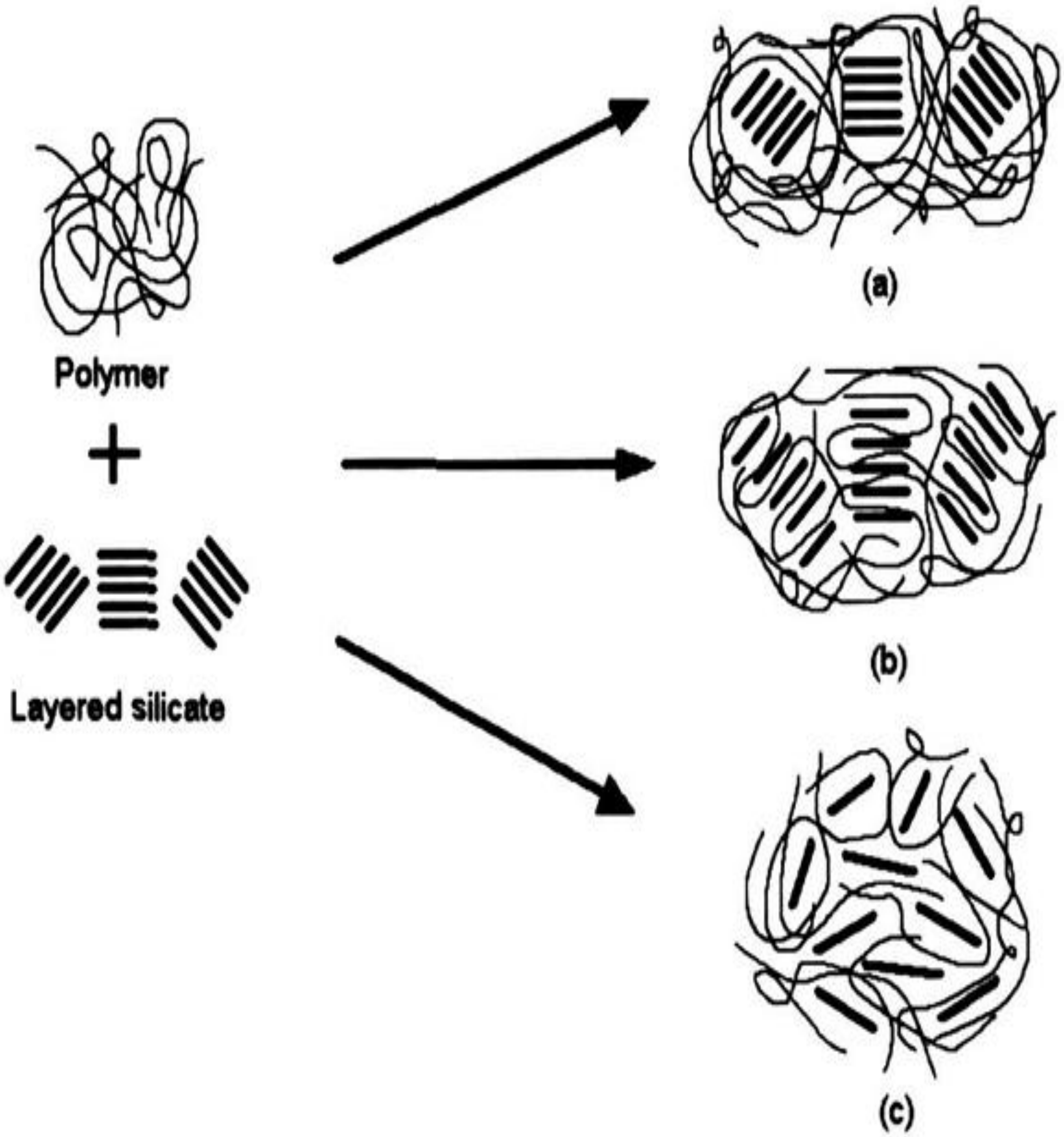


Fig 1.2 Layered silicates in (a) conventional composites (b) intercalated nanocomposites (c) exfoliated nanocomposites[15].

As already discussed EPDM is a well known general purpose rubber with a significant commercial importance. So it has been one of the main rubbers to be investigated with organo-treated layered silicates to study the effects of nano reinforcement on properties. Most EPDM nanocomposites with clays have been produces by conventional internal melt blending process . **Zheng et al** [2] **(2003)** reported preparation of EPDM/OMMT clay nanocomposite by simple static mixing in confined chamber such as HAAKE solution blending. They also reported that tensile strength and elongation at break of EPDM/OMMT nanocomposite increased respectively up to 25 MPa and 666% with increasing rotor speed due to high shear stresses produced for the addition of 15 % wt clay. Intercalation of EPDM molecules into clay galleries as well as exfoliation of clay layers in EPDM rubber matrix, leads to outstanding properties of EPDM/clay nanocomposites. The tensile strength of EPDM/OMMT nanocomposites was enhanced 3-4 times more than the pristine EPDM composites for 15 % wt clay. The tear strength was effectively enhanced (1.5-2 times higher than given EPDM vulcanized) by the incorporation of organic modified silicates in EPDM. EPDM/clay nanocomposites showed excellent gas barrier properties (the permeability of oxygen & nitrogen decreased by 60% as compared to given EPDM composites with only 10% filler content)

The effect of curing or vulcanization is also important while considering EPDM clay compounds. Since EPDM clay nanocomposites behaviour is different as compared to other rubbers when curing or vulcanization process is done. **Wu et al**[8] **(2004)** reported that vulcanization process does not affect too much in case of NR/OC and SBR/OC nano composites whereas highly intercalated or exfoilated structure of EPDM/OC formed mainly during vulcanization process, before vulcanization there is less intercalation during melt blending of EPDM with organically modified clay. These results are proved in Wu et al report by TEM images and XRD graphs. **Das et al**[7] **(2007)** reported comparison of properties, structural changes in rubber by peroxide curing system and sulphur curing system. Results of experiments of Das et al shows that peroxide vulcanization brings the silicate layers into well ordered arrangement in a particular direction as compared to sulphur vulcanization. The conceptual image of EPDM/clay hybrid formation is illustrated in figure 1.3 on next page.

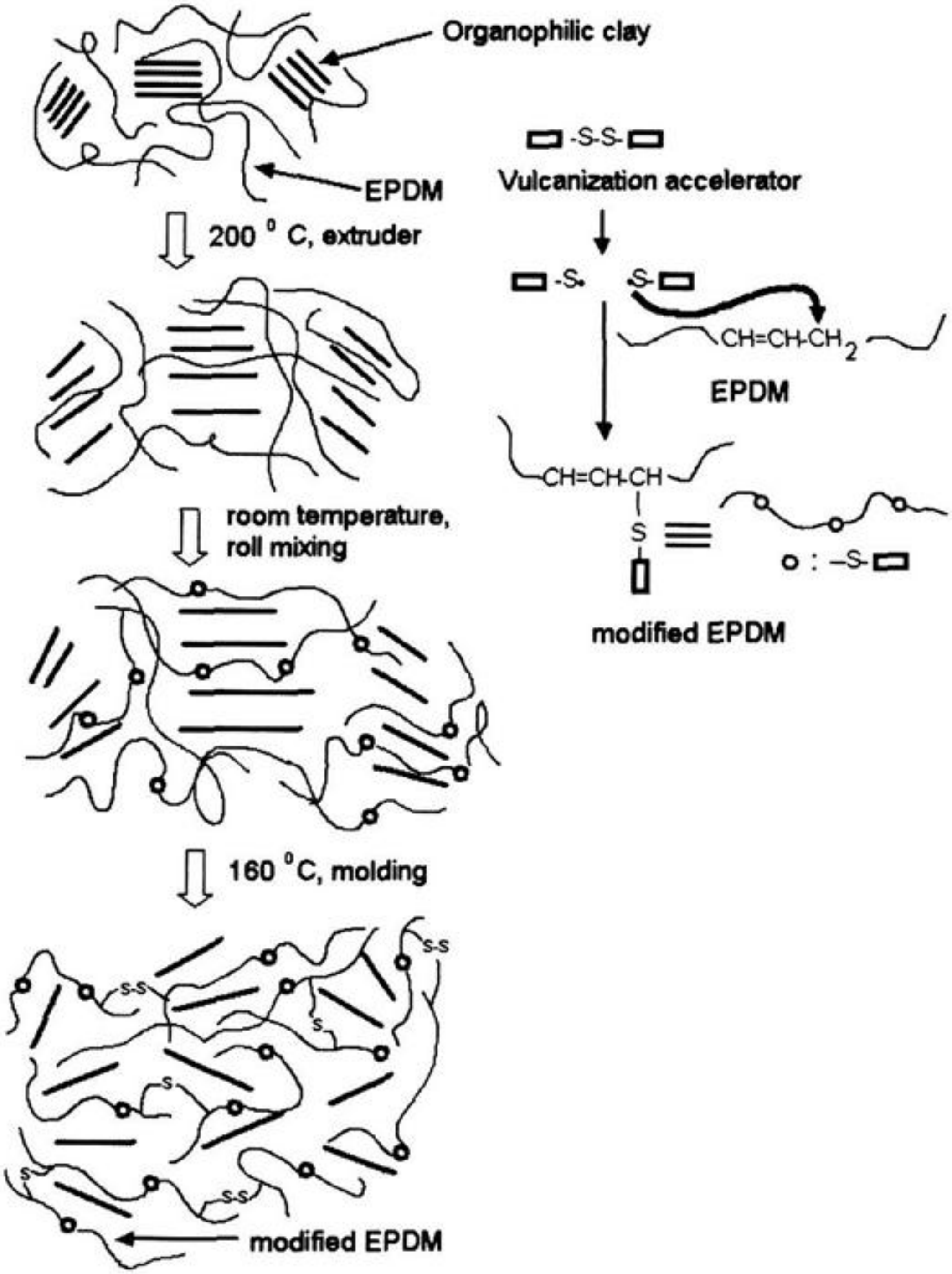


Fig 1.3 Conceptual diagram showing the vulcanization of EPDM and intercalation into clay gallery[15].

1.5 FIBRES

It is well known fact that dispersed face in the form of fibres improves strength, stiffness and fracture toughness of the material, impeding crack growth in the direction normal to the fibre. The strengthening effect is higher in long fibre (continuous fibre) reinforced composites than in short fibre (discontinuous fibre) reinforced composites. The fibres generally used are glass fibre, carbon fibre (synthetic fibre) and in some cases lingo-cellulosic fibres like jute fibre (natural fibre) are also used. Description of commonly used fibres and comparison of properties are as follows

1.5.1 Glass fibre or Fibreglass→

Fiberglass was first discovered in 1893 and was firstly made commercially available in 1936 as insulation material. It became popular in the 1950's, when some of the health hazards associated with asbestos were becoming apparent. Due to the similarity in shape between the fiberglass and the asbestos fibers, fiberglass was able to effectively replace asbestos in many applications such as electrical, thermal, and acoustic insulation and structural reinforcement. Today it is the dominant reinforcement fiber in composite construction, accounting for over 90% of worldwide consumption.[25] This is simply because it has good strength to weight characteristics, can be processed easily and sells at a low price. Glass filaments are made relatively easily by extruding molten glass. The diameters of the fibers produced range from 5 to 25 microns. Many different types and qualities of glass sell for significantly different cost. The most widespread quality is "E-glass", "E" from the word Electric implies that it is an electrical insulator. It is low cost product, used mostly in the marine industry. Others are "S glass" and "S2 glass", the letter "S" comes from the word Strength implying that it has improved mechanical properties. These types are much more expensive and used mostly in armor applications. "S" is certified as for the production parameters. "AR glass" is resistant to alkali chemical attack. "C" or "T Glass" is resistant to acid and Corrosion. "A glass" is glass with more alkali content similar to window glass, and costs a bit less. Generally, when cost is a major driving force in the selection of a reinforcing material, fiberglass is usually preferred[19]. Glass fibre is shown in figure 1.4 on next page.

Fig 1.4 Glass Fibre Sheet

1.5.2 Carbon Fibre→

Carbon has the highest strength and highest price of all reinforcement fibers used in composites today. It was invented in the UK in early 1960s at the Royal Aircraft Establishment at Farnborough, Hampshire. The most common method of making carbon fibre is the oxidation and thermal pyrolysis of an organic precursor, polyacrylonitrile (a polymer fibre based on acrylonitrile.) When heated in the correct conditions, the non-carbon constituents evaporate away. The resulting fibre is 93–95% carbon. Instead of PAN as a precursor, carbon fibre can also be manufactured from pitch or rayon. The size or thickness of Carbon tows is measured in “k” or thousands of filaments. A 3k tow has 3,000 filaments and a 12k has 12,000. Carbon fibres exhibit: substantially better strength and stiffness values than all the others, outstanding temperature performance, high electrical and low thermal conductivity. Impact or damage tolerance of pure carbon composite products can be from relatively low to very poor, and greatly depends on processing method. Despite that, when weight on a composite product is important, carbon fibre is the reinforcement to use[19]. Carbon fibre roll and woven fabric is shown in figure 1.5 on next page.

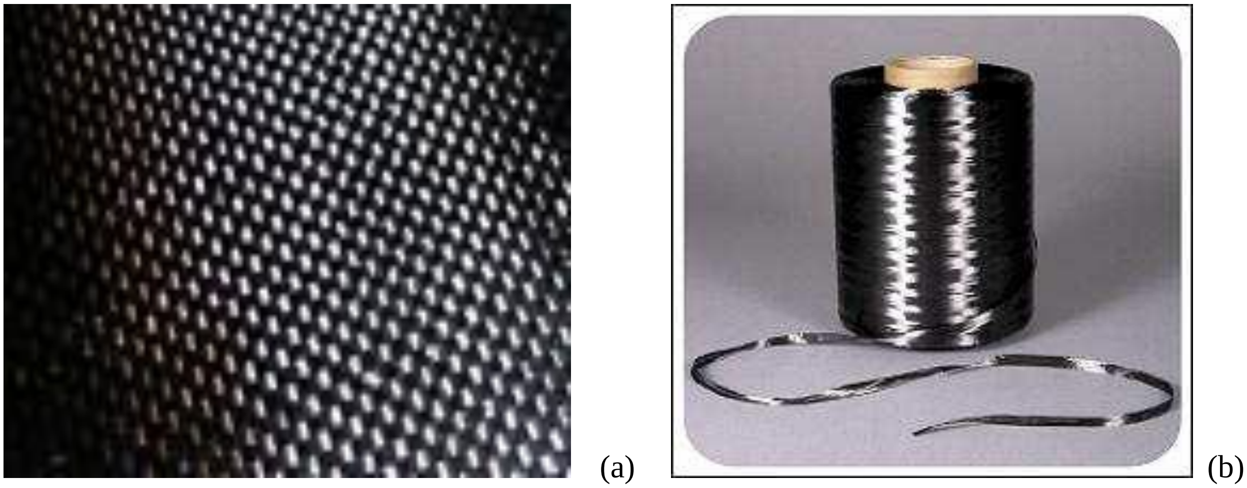


Fig1.5 Carbon Fibre (a) Woven Fabric (b) Roll[24].

1.5.3 Jute fibres→

Jute is a long, soft, shiny vegetable fibre that can be spun into coarse, strong threads. It is produced from plants in the genus Corchorus, which has been classified in the family Tiliaceae, or more recently in Malvaceae.

Jute is one of the most affordable natural fibres and is second only to cotton in amount produced and variety of uses. Jute fibres are composed primarily of the plant materials cellulose (major component of plant fibre) and lignin (major components of wood fibre). It is thus a ligno-cellulosic fibre that is partially a textile fibre and partially wood. It falls into the bast fibre category (fibre collected from bast or skin of the plant) along with kenaf, industrial hemp, flax (linen), ramie, etc. The industrial term for jute fibre is raw jute. The fibres are off-white to brown, and 1–4 metres (3–12 feet) long.

It has high tensile strength, low extensibility, and ensures better breathability of fabrics. Therefore, jute is very suitable in agricultural commodity bulk packaging. One of the cheapest natural fibres. Poor resistance against moisture, brittles under influence of light, absorbs paint easily. Jute consists of very short elementary fibers (lenth 0,7-6 mm) wich are stuck together by lignin to form long brittle fibers (length of 300-400 mm).

Some noted disadvantages include poor drapability, brittleness, fibre shedding, and yellowing in sunlight. However, preparation of fabrics with castor oil lubricants result in less yellowing and less fabric weight loss, as well as increased dyeing brilliance. Jute has a decreased strength when wet, and also becomes subject to microbial attack in humid climates. Jute can be processed with an enzyme in order to reduce some of its brittleness and stiffness. Once treated with an enzyme, jute shows an affinity to readily accept natural dyes, which can be made from marigold flower extract. Jute also responds well to reactive dyeing. This process is used for bright and fast coloured value-added diversified products made from jute[26]. Jute fibre is shown in figure 1.6.

Fig. 1.6 Jute fibres[22].

Comparison of basic properties of the discussed fibres are as given in table 1.2

Material Type	**Ultimate Tensile load (N)**	**Tensile Strength(MPa)**	**Typical Density(g/cc)**	**Elongation**
Carbon fibre	2000-5300	270-440	1.5-2	0.2-1.8
Glass fibre	2400-3700	70-85	2-2.5	4-4.5
Jute fibre	450-600	300 – 780	1.4-1.5	1-2

Table 1.2 Comparison of properties of different fibres[27].

1.6 Classification of orientation of fibres which can be used for fibre reinforcement in the composite manufacturing

i. Unidirectional

ii. Bidirectional

  - Cross ply
  - Angle ply

Illustration of unidirectional, angle ply and cross ply is shown in figure 1.7

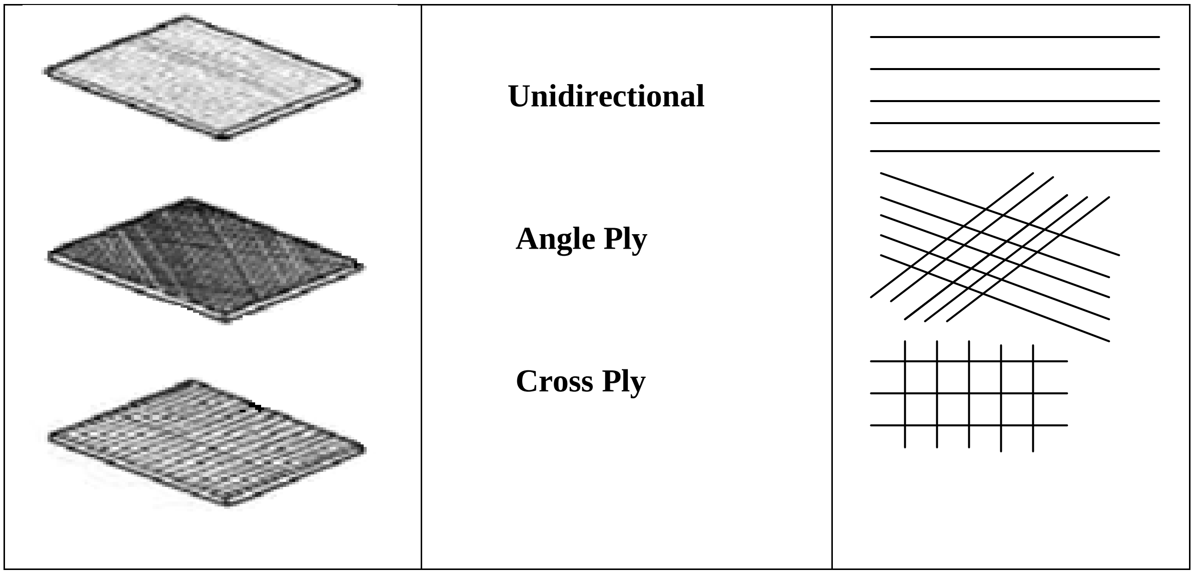


Fig 1.7 Fibre Orientations[28].

Mohammad et al[1][2006] has reviewed various rubbers, their applications and properties. Then various fibres which are often used in rubber industries. Also given that the interfacial contact area between rubber matrix and filler is controlled by the size of filler particles and filler volume fraction. The degree of bonding between rubber matrix and filler particles is a key factor in determining the degree of an elastomeric reinforcement. Also given that carbon black is most extensively used reinforcing filler in rubber composites. It is also discussed that silica fillers are chosen over carbon black. The reasons are given in the paper and then types of rubber clay nano composites, their preparation methods viz. In-situ polymerization, intercalation via solution and direct melt intercalation method. These methods are discussed in short notes in this paper. After that types of nano composites of rubber/clay nano composites structure viz. Conventional composite, intercalated nanocomposites, exfoliated nanocomposites are discussed. After that short explanation of various rubber nanocomposites viz. Natural rubber nanocomposites, epdm clay nanocomposites, SBR- clay nanocomposites, Nitrile rubber- clay nanocomposites & silicon rubber- clay nanocomposites etc. with their various properties are discussed. Finally they concluded that compared to vast literature on most of the thermoplastic or thermosetting polymer- clay nanocomposites, reports of rubber clay nanocomposites is limited & there is a lot of scope of reasearch.

Hua Zheng[2] [2004] discussed that insertion of organic molecules into layered or porous inorganic host often results in nanocomposites with improvement in the mechanical properties, heat stability, flame retardance, gas barriers properties and abrasion resistance. It has been given that EPDM is widely used rubber and has great commercial importance and intense investigation of EPDM/Clay nanocomposite should be valuable. In this paper preparation of EPDM/OMMT nano composites through melt processing is discussed and then mechanical properties are studied. A HAAKE Rheometer was used for mixing of EPDM and OMMT at a temp of 25 to 90°C with rotor speed 34, 68 or 136 rpm. It is shown with results that temperature and rotor speed had great influence on mechanical properties of the composites EPDM/OMMT composite showed a great improvement in mechanical properties after OMMT intercalation with EPDM. XRD & TEM results for composite are also shown in the paper.

RAY & Okamoto[3] [2003] reviewed the preparation,characterization ,material properties ,crystallization behavior,melt rheology &processing of polymer/layered silicate nanocompsites inontmorillonite are the most commonly used layered silicates for the preparation of nanocomposites .organic modification of layered silicates ,techniques used to modify them,chemistery involved &benefits of organic modification are also described .they also reviewed the types ofnanocompasites formed by the incorporation of polymer matrices in layered silicates after that techniques like WAXD&TEM for the characterization of nanocomposists are described. Dynamic mechanical properties of nanocomposites as a function of temperature was studied for different percentage of clay in nanocomposite. As described in it, mechanical properties are improved by the addition of modified clay into the polymer matrix. The effect of clay % is described on the properties like tensile strength, percentage elongation, temperature stability, fire retardant properties, gas barrier properties etc. Also described that improved properties are generally attained at lower silicate content(<=5 %wt) compared to that of conventionally filled systems.

Kuila et.al[4] [2009] reported the formation of EVA/EPDM nanocomposites with LDH using solution blending method .also reported that LDH have been made organophilic (DS-LDH) by intercalating dodecyl sulfate anion in the interlayer space to make it compatible with EVA/EPDM blend. EVA/EPDM was taken as 50/50 by weight for the preparation of blend. Fifteen gms of EVA/EPDM was dissolved in 100ml of toluene and stirred for 6hrs at 100c.desired amount of DS-LDH is also refluxed in 30ml of toluence for 6hrs at 100c. Finally DCP was added as curing agent to this solution and then solvent was removed under pressure. It is reported that a mixture of intercalated & exfoliated structure was seen by XRD analysis.

BLANOT et al [5] [1989] described the characterization of EPDM rubber ,polyethylene and their unfilled &filled blends .The morphology of blends and in particular ,the distribution of aluminium hydrate particles within the matrix are studied by optical and electron microscopies. It is also described that addition of aluminium hydrate particles slow down the combustion rate if used in flame retardant electrical cables. But use of large amount of inorganic filler alters some of the mechanical properties of the material. It is also shown by experimental result that polymer modified by silane can retain its mechanical properties with high filler content.

Usuki et al[6] [2002] described the successful preparation of EPDM clay hybrid via vulcunisation process. In this work, thiuram and diethiocarbamate have been used as vulcanization accelerator. Epdm pallets were melt blended at 200°c with powder of C-18-mt 7phr(parts per hundred resin) by using twin screw extruder and then zinc oxide (5 phr), stearic acid oxide(1 phr), sulphur(1.5 phr) and vulcanisation accelerator (1.5 phr) were also compounded with the blend by using a mixing roll and then EPDM was press moulded into sheets. They did the testing to check mechanical properties and permeabilities. The results were shown in which it is clarified that strength of EPDM clay hybrid is 2.0 tiimes higher than that of EPDM and gas permeability is decreased 30% as compared to perstine EPDM.

Das et al [7] [2007] reported the effect of curing systems on the orientation and dispersion of the layered silicates in rubber nanocomposite . Results of peroxide curing & sulphur curing & their comparison are studied on the structural properties of rubber clay nanocomposites. The results were obtained by using X-ray diffraction method and TEM images. Experimental methodology ,material and other parameters used for experiment during both types of curing (peroxide and sulphur)are also described ,at last they concluded that generally, sulphur curing packages are used if more dynamically elastic and flexible properties are desired, like, for example, in tire tread formulations. The peroxide curing system is useful when several other properties are desirable like compression set, abrasion etc. Peroxide vulcanization brings the silicate layers into well ordered arrangements in a particular direction. This kind of alignment of the layered silicates in the rubber matrix could be of advantage for a more effective hindering of gas permeability. The use of excess stearic acid could be a way for getting better exfoliation of the layered silicate in the rubber matrix when sulfur vulcanization will be selected for curing the rubber matrix.

Wu et al [8] [2004] prepared NR,SBR and EPDM nanocomposites with organically modified clay(OC)by melt blending process. A comparison is given in the structure shown by the three given rubbers by using X-ray diffraction &TEM observations. Effect of vulcanization process on the structure of different rubber (NR,SBR & EPDM) is also studied which gives that vulcanization process does not effect too much in case of NR & SBR nanocomposites whereas intercalated structure of EPDM/OC formed mainly during vulcanization process. Experimental methodology followed is also described & then tensile testing results performed according to ASTM standards are also shown .

Mubark[9] [2010] prepared composites by compression moulding with jute yarn reinforcement. The yarn was treated with aqueous starch solution and then composites were prepared with 5% weight of yarn content. It has been discussed that jute is cheap and easily available fibre and also reported that jute is a natural fibre so its mechanical and physical properties are highly inconsistent and is dependent upon the geographic origin, climate and growth conditions. Some other disadvantages of jute fibre are its poor weld ability, poor fibre matrix adhesion make it insufficient for proper reinforcement. To overcome these drawbacks, physical and chemical treatments are done to improve the surface structure and surface energy of the fibre.

Kunal Das et al[10] [2009] described preparation of jute nanofibres and then composite preparation by using these jute nanofibre reinforcement. Jute nanofibre was prepared by acid hydrolysis. The prepared jute nanofibres were incorporated into bioployester matrix (BCP) by melt mixing in varying percentages of weight ranging from 0% to 15%. Melt mixing was done in barbender 30/50 E apparatus. The resultant mass was then compression molded to form sheets. Results of SEM analysis, XRD biographs and strength tests for composites under different percentage combination of constituents were shown in the study.

Singha & Thakur[11] [2010] studied on the synthesis and mechanical properties of new series of green composites involving hibiscus sabdariffent fibre as a reinforcing material in urea formaldehyde(UF) resin based matrix has been reported. Natural fibres are now considered as serious alternative to synthetic fibres for use in various fields. It has been reported that advantages of natural fibres over traditional reinforcing materials such as glass or carbon fibres etc. are their specific strength properties, easy availability, light weight, ease of separation, enhanced energy recovery, high toughness , non corrosive nature, good thermal properties, reduced tool wear and biodegradability. The experimental procedure is discussed in which weights of samples were taken and curing was done on compression moulding machine and then thermal studies were carried out. SEM micrograph was also taken. Urea and formaldehyde were mixed in NAOH solution till pH of 8 was attained at temperature of 50-60°C After that temperature was increased to 80-85°C at pH of 5.5-6 till the resinification started. Then heating was stopped and resin was cooled and samples were then cured at 130°C in compression molding machine. Composite were prepared with particle reinforcement, short fibre reinforcement and long fibre reinforcement. After this testing was done using Universal testing machine and constant strain rate of 10mm/min was applied. For wear testing, disc rotation was 500-rom and loads vary from 1 to 3 kg. For each load, wear and friction monitor run for 15 min. And readings are recorded. The results were shown graphically and analytically.

Bo Wu& Zhou[12] [2008]focused on formation of oil gels using EPDM & 4- tert- butylstyrene (tbs) cross-linked with divinylbenzene (DVB). Toulene, cyclohexane and their mixtures are found as pore forming diluents for EPDM rubber. The influence of diluents type, dosage and composition on swelling behaviour compressive properties, effective cross-link density and elastomer (EPDM) solvent interaction parameter of oil gels was studied in this work. At a temp of 80°C, the reaction was performed with in time of 8hrs and the results are discussed in which effect of diluents types on oil absorbency, then dilute composition effect on oil absorbency and then effect of diluents on compressive properties were discussed.

H. Acharya[13] [2007] conducted experiment to make EPDM/Mg Al layered double hydroxide nanocomposite by solution intercalation method. The internal structure of nanocomposites with the dispersion nature of LDH particles in EPDM matrix have been studied by TEM and AFM. LDH was organically modified to make it oraganophilic which weaker the electrostatic forces operating between the hydroxide sheets and make it compatible with non polar plastics. In this paper, the synthesis and characterization of exfoliated EPDM/LDH nanocomposites by solution intercalation method are reported. TEM and XRD analysis patterns are shown in the paper. Thermal decomposition of the prepared nanocomposite were also discussed which conclude that about 3 wt% of, LDH increases the decomposition temperature to 40 and above °C, indicating higher thermal stability.

Gatos et. al. [14] [2004] studied the characteristics of EPDM clay nanocomposites with different processing conditions. The nanocomposites were prepared by using two roll mixing mill and brabender plastic holder. They also varied the processing parameters like temperature and shear mixing and check the mechanical properties of rubber nanocomposites under these different parameters. The effect of mechanical properties of nano composites with different vulcanization accelerators like CBS, MBT and ZDEC are also studied. Among these accelerators showed the best mechanical performance. The nanocomposite formation is proved with XRD graphs and organoclay intercalation/exfoliation is shown by TEM and SEM images.

Sengupta et. al. [15] **[2007]** has reviewed various papers on rubber clay nano composites. Preparation methods (like solvent blending, latex compounding, in situ polymerization and melt intercalation) for various rubbers are discussed with reference of the researchers. Comparison of mechanical properties with variation in clay percentage is clearly shown with graphs and bar charts as produced by many scientists and researchers on different rubbers. XRD patterns for various rubbers are also discussed but not shown in the review paper. Vulcanization effect for various rubbers is also studied at the end author described that rubber/ organoclay nanocomposites are still in its infancy stage and it is of great interest due to reinforcement unisotropy and barrier properties that can be achieved by silicate layers having nanoscale thickness. Overall they showed a lot of scope exists to create novel products using nano clay as there reinforcing material in rubber matrices.

CHAPTER 3 PROBLEM FORMULATION

Compared to the vast literature on most of the thermoplastic or thermosetting polymer/clay nanocomposites ,reports of rubber clay nanocomposites are very limited. Although some researchers have done a remarkable job in this field yet much more research is needed to understand the complex nature of these nanocomposites and also to identify the factors that have the most significant influence on their physical ,thermal and specially mechanical properties, overall a lot of scope exists to create novel rubber product using nano clays as the reinforcing material in rubber matrices

Literature review shows that EPDM is most widely used rubber in engineering application and its valuable composite can be made using organically modified clay. But to the best of knowledge there is no report on the preparation or an estimation of physical & mechanical properties of fibre reinforced EPDM/clay nanocomposite.

3.1 OBJECTIVE

The objective of the present study was

(a) To prepare EPDM/clay blend

(b) To use EPDM with nano dispersed clay as a matrix in FRP

(b) To study the characterization of the prepared fibre reinforced EPDM/clay nanocomposite

4.1 **INTRODUCTION**

A set of flasks and other instruments has been used to obtain glass fibre reinforced elastomeric (EPDM/CLAY) nanocomposite. The specimen for mechanical and other testings are cut from the FRP sheet which is obtained by a well defined procedure.

4.1.1 **SET UP FABRICATION:-**

Item Name	Quantity
Round Bottom Flask	2
Conical Flask	2
Condenser	1
Heating mantle with magnetic stirrer	1
Ultrasonicator	1
Rotary evaporator	1
Toluene bottles	5
Measuring cylinder	1
Funnel	1
Weighing machine	1
Magnetic Beads	2

Table 4.1 Elements of Setup used in Expermentation

a. Round bottom flask (RB flask):-

Flasks with round bottom are used in the experimental set up to dissolve EPDM in toluene (solvent). These round bottom flasks are available with a capacity of 500ml and with socket size of 19/26. It is shown in figure 4.1.(a)

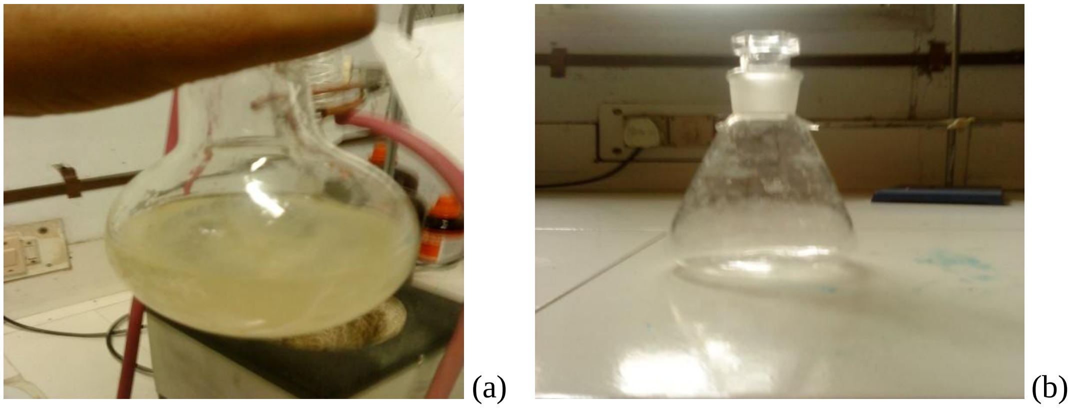

(a) (b)

Fig.4.1 (a) RB Flask (b) Conical Flask

b. Conical flask:-

Conical flask are used to suspend clay in toluene. These conical flask are flat bottom flask and are available in 250 ml capacity & with socket size of 24/29. It is shown in figure 4.2 (b)

c. Condenser:-

There is a requirement of condenser to reflush the toluene at its boiling point so that the vapourised toluene can condense back to round bottom flask. Condenser can be air condenser, Liebig condenser or coil condenser. In our experimental set we have used coil condenser with socket 19/26 & effective length of 200 mm. It is shown in figure 4.2(a)

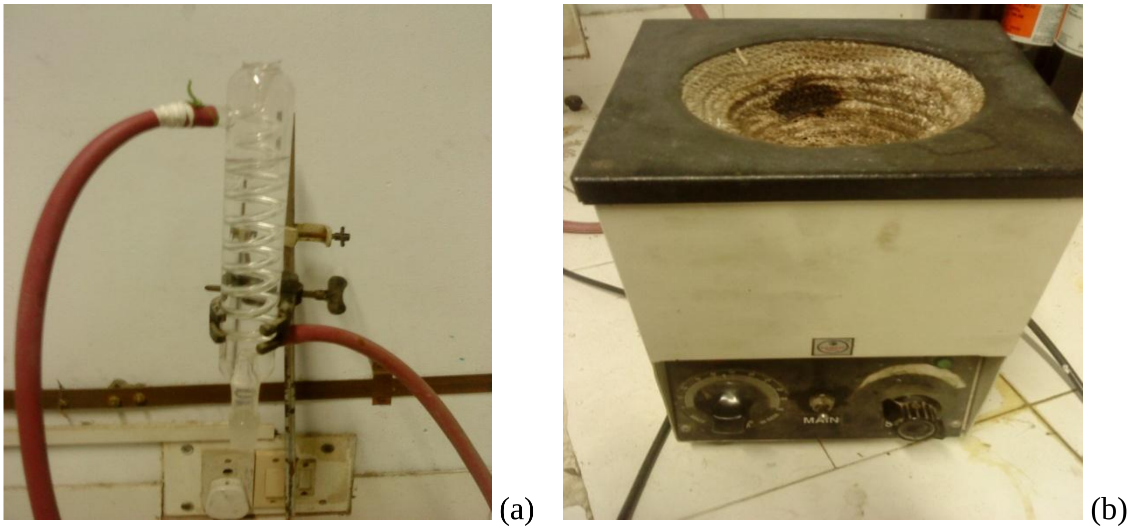

(a) (b)

Fig.4.2 (a) Condenser (b) Heating Mantle

d. Heating mantle with magnetic stirrer:-

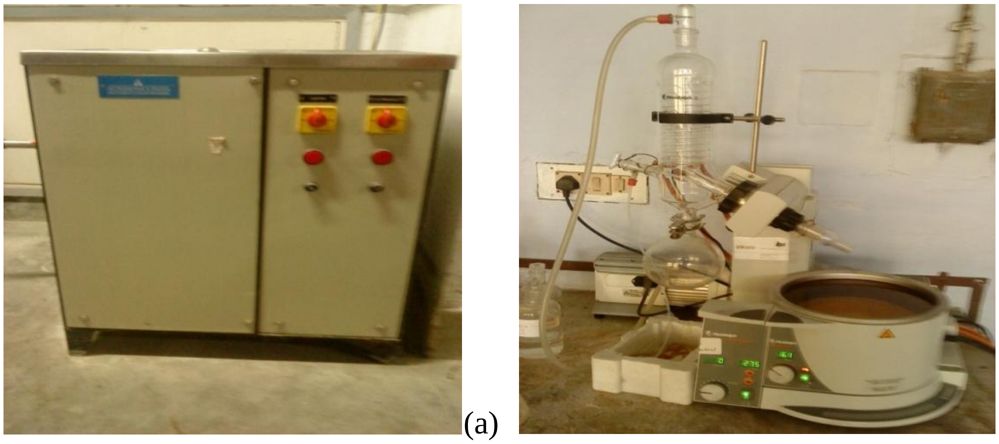
A heating mantle of capacity 500 ml & a power of 200 watts with magnetic stirring is used to stir the rubber & toluene mixture as EPDM rubber is dissolvable in toluene only at high temperature of 100°C with continuous stirring for at least 6 hrs. It is shown in figure 4.2(b)

e. Ultrasonicater:-

The main element of the system is ultrasonicater with a heater and with ultrasonic frequency of 33 ± 3 kHz and a capacity of 1.5 litre with a size of 7” × 4”×3”. Sonicator is mainly used for ultrasonic suspension of clay & ultrasonic suspension of EPDM/clay mixture. It is shown in figure 4.3(a)

f. Rotary evaporator:-

Rotary vacuum flash evaporator fitted with 40 W, AC motor, continuously frequency variable speed control 20-200 rpm, digital display, oil or water bath with room temperature to 100°C temperature control, with heater 1.5 kw, Jack lifting up to 150mm, boiling flask 2000ml, vertical coil condenser, receiver flask with ball cup joint etc. Rotary evaporator is mainly used to evaporate solvent out of EPDM/ clay mixture to generate sheets for XRD testing. It is shown in figure 4.3 (b).



(a) (b)

Fig 4.3 (a) Ultrasonicator (b) Rotoryevaporator

g. Toluene Bottles:-

Toluene bottles are available with different capacities viz. from 250 ml to 2.5 litres we used 500 ml capacity bottles in our experiments as shown in figure 4.4.

h. Measuring cylinder :-

Measuring cylinder is used for measuring the amount of liquid solvents. Here we used a measuring cylinder which can measure upto 100ml capacity as shown in figure 4.4.

Fig 4.4 Measuring cylinder & Toluene Bottle

i. Weighing machine :-

It is used for measuring weight of various susbstances. Its least count is 0.001 gms.and has a maximum limit of measuring of 310 gms as shown in figure 4.5 (a).

j. **Magnetic Bead:-**

These are always used with magnetic stirrer to give rotation to any fluid or matter inside the flask as shown in figure 4.5 (b)

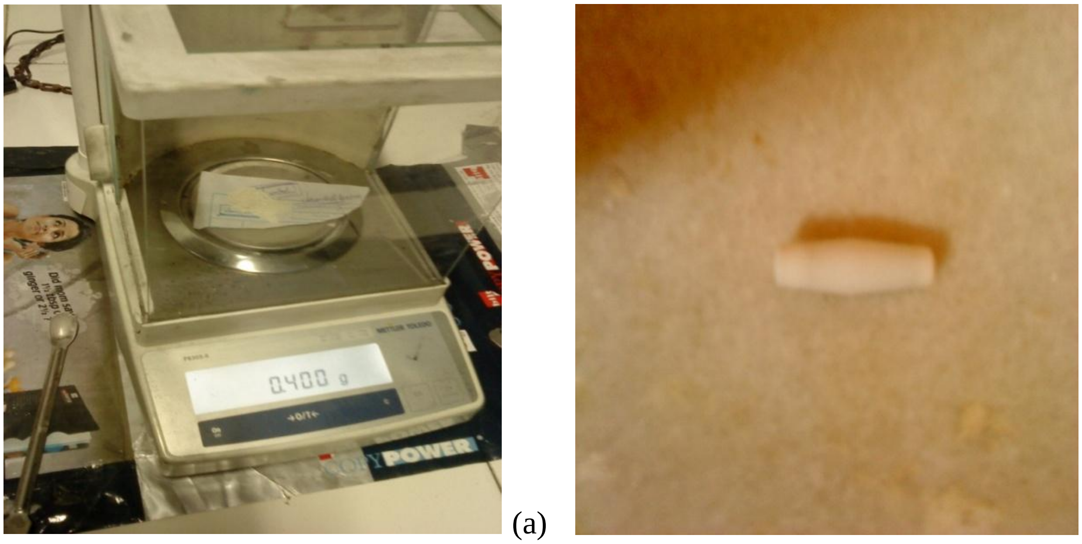
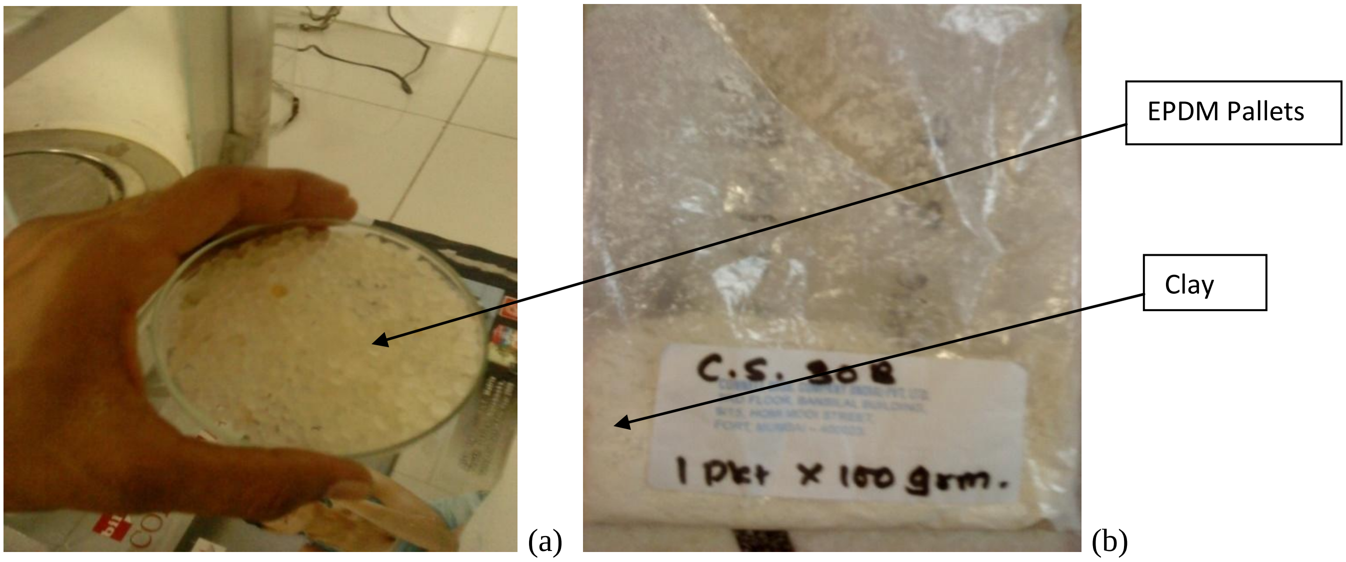

(a) (b)

Fig 4.5 (a) Weighing machine (b) Megnetic bead

4.1.2**. MATERIAL SPECIFICATIONS**

a. **Base Elastomer**

We are using EPDM as base elastomer which was purchased from Silica House India Pvt. Ltd. New Delhi. This base elastomer is in pallets form as shown in figure 4.6 (a)



(a) (b)

Fig 4.6 (a) EPDM rubber in the form of pallets (b) Clay powder used in experimentation

b. Clay

We are using Closite-30B clay which was purchased from Connell brothers India Pvt. Ltd. Mumbai as shown in figure.4.6

c. Glass fibre

We have used glass fibre for fibre reinforcement and it was purchased from BASF construction chemical India pvt. Ltd.

4.2 EXPERIMENTAL PROCEDURE

A) Cutting GFRP Sheet

For the experimentation we had purchased the unidirectional woven fabric roll of GFRP of 50cm width having 0° fibre orientation woven with polymer fibres. The sheets were initially cut from roll in length of 200mm. Glass Fibre sheet is shown in figure 4.7

Fig. 4.7 Uncoated GFRP sheet used for making specimen

B) Dissolving of EPDM in toluene

In this step, we take desired amount of EPDM (in our case it is 10gm for each case) and dissolved it in toluene (taken 100ml for each case) by stirring it continuously for 6 hours in a round bottom flash with the help of magnetic stirring as shown in figure 4.8

Fig 4.8 EPDM Stirring & reflushing with toluene

C) Suspension of clay in toluene

In this step, we take clay by some weight percentage of base polymer (i.e. EPDM) and suspend it in toluene for 4 hours. It is taken in conical flask on which ultrasonic waves strikes which are produced inside an ultrasonicator apparatus as shown in figure 4.9. These two steps are performed in such a manner that the first step (i.e. dissolving of EPDM in toluene for 6 hours) and the second step (i.e. suspension of clay in toluene for 4 hours) completes at the same time.

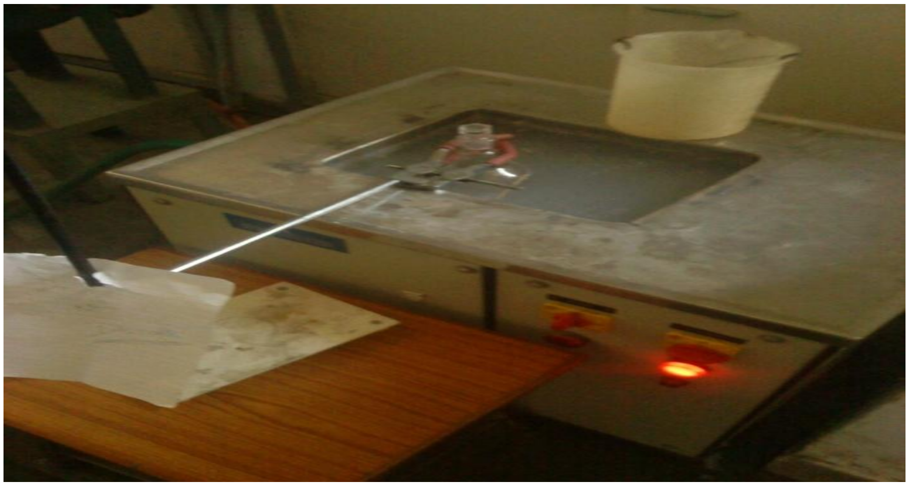


Fig 4.9 Clay suspension in toluene

D) Mixing of suspended clay in dissolved EPDM

After the above steps, we mix up the suspended clay in dissolved EPDM and then continuously stir and reflush for 12 hours. Finally an ultrasonic suspension is given to this EPDM/CLAY mixture in ultrasonicator machine.

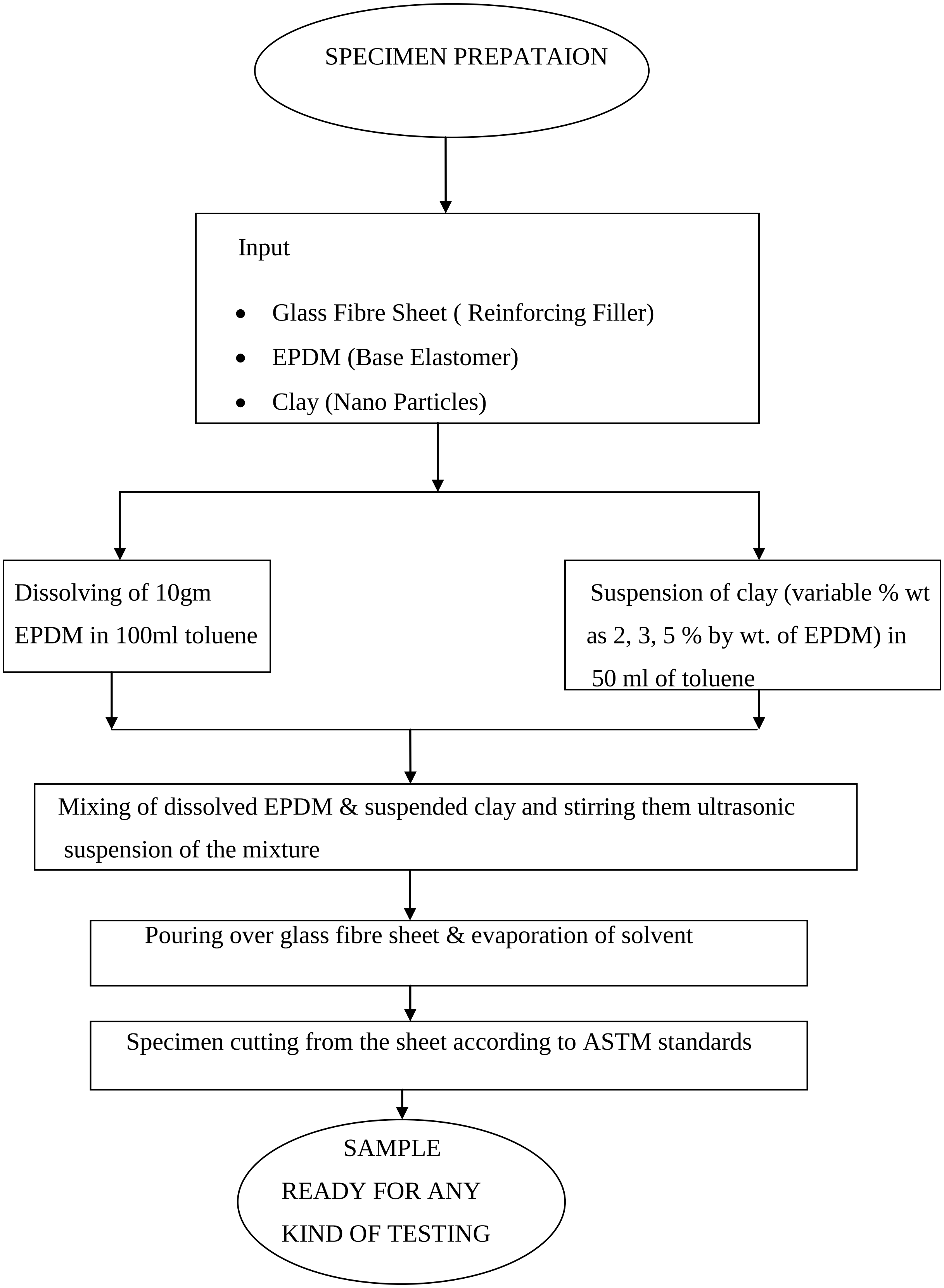
E) Pouring of Mixture

After this above freshly prepared mixture is poured in a sheet mold in which glass fibre that is already placed as shown in figure 4.10 and finally solvent is evaporated by putting the sheet mold on hot plate as shown in figure 4.11 and thus GFRP elastomeric nano composite is prepared.

Fig 4.10 Pouring of EPDM/Clay mixture on Glass Fibre Sheet

Fig 4.11 Solvent Evaporation on hot plate

4.3 FLOWCHART OF EXPERIMENTAL WORK



4.4 SPECIMEN SPECIFICATION

Following were the specifications of specimen:

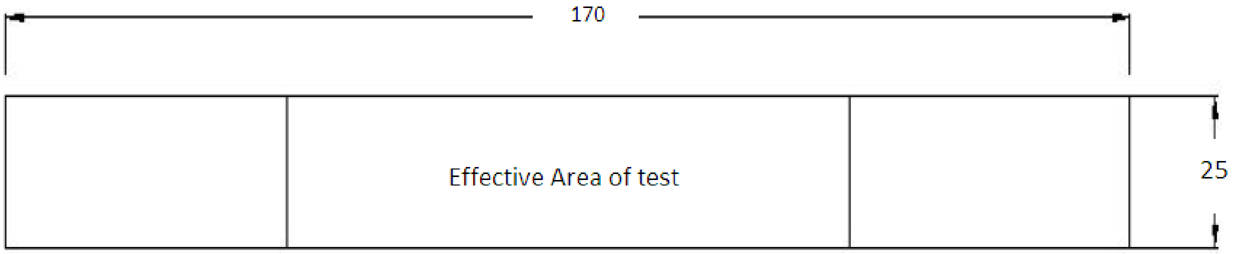
Length of the specimen: 170mm (5mm more than the actual test specimen for test)

Breadth of the specimen: 25mm (6mm more than the actual test specimen)

Thickness of the specimen: t+ h mm (approx.)

where t is the thickness of EPDM/ clay nanocomposite sheet and h is the thickness of glass fibre sheet. Dimension & Image of the specimen is shown in figure 4.12

Dimension of the specimen



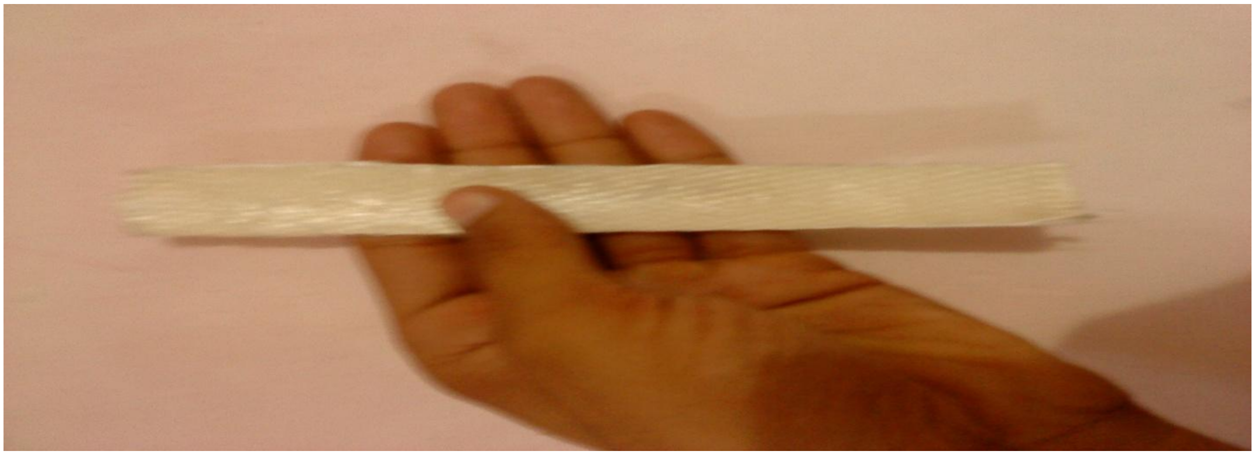


Fig 4.12 Actual Image of the specimen

4.5 TEST MATRICES

Matrix of number of specimen for final testing prepared under different conditions are shown below

Specimen types	Number of specimen at different weight percentage of clay				Number of specimen for each testing	Number of specimen for all testing
Post ultrasonication time (In hours)	% WT OF CLAY				Tension test and bending test	Total Specimens
	0 % wt	2% wt	3% wt	5% wt		
4	2	2	2	2	4	8
6	2	2	2	2	4	8
Total pieces at particular % of clay	4	4	4	4	Total specimens	16

Table 4.2 Test specimens for mechanical testing

Specimen types	Number of specimen at different weight percentage of clay				Number of specimen for each testing	Number of specimen for all testing
Post ultra sonication time (In hrs)	% WT OF CLAY				Solvent Swelling, TGA, XRD and SEM	Total Specimens
	0 % wt	2% wt	3% wt	5% wt		
4	2	2	2	2	4	16
6	2	2	2	2	4	16
Total pieces at particular % of clay	4	4	4	4	Total specimens	32

Table 4.3 Test specimens for other testings

4.6 TESTING METHODS USED IN THE EXPERIMENTATION

4.6.1. Tensile testing

Tensile test was performed on universal testing machine as shown in figure 4.13(a) For tensile testing, specimens are cut into dumb bell shape according to the standard **ASTM D638-08** Type I specimen for reinforced composites as shown in fig 4.13(b) & 4.14.

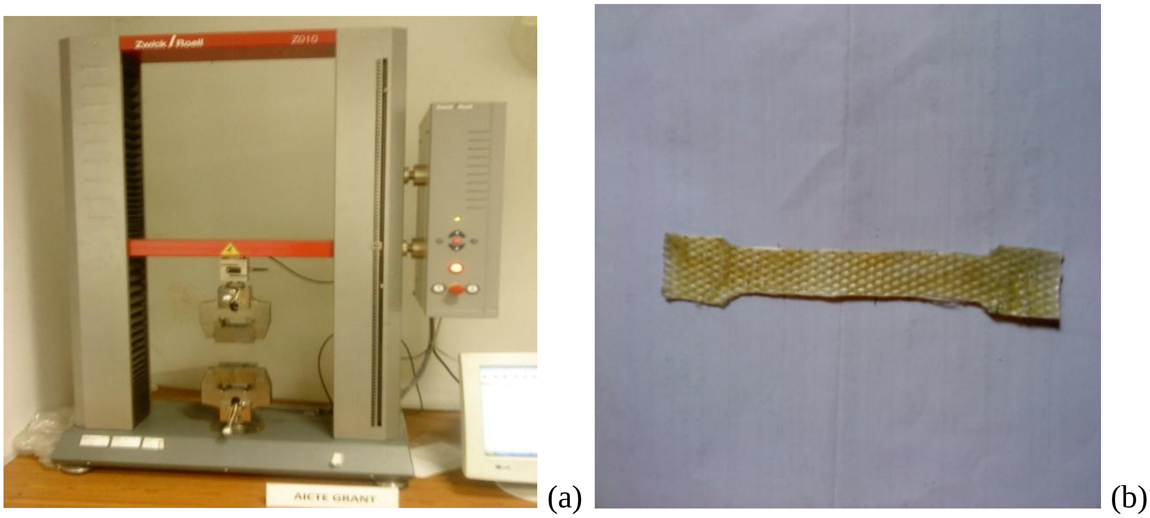


Fig 4.13 (a) Zwick/Roell UTM (b) Tensile test specimen

The test graphs, tensile strength, strain and ultimate tensile load were obtained for each specimen from the testing machine. Computer display to interpret the results through testXpert II software is shown in figure 4.15

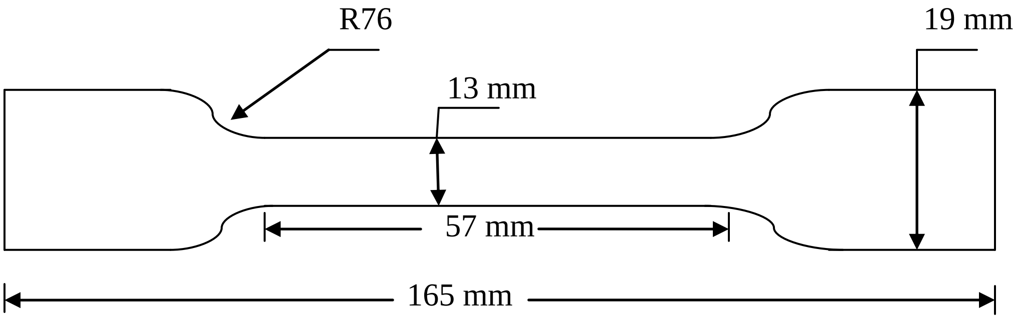


Fig 4.14 Dimensions of test specimen for tensile test

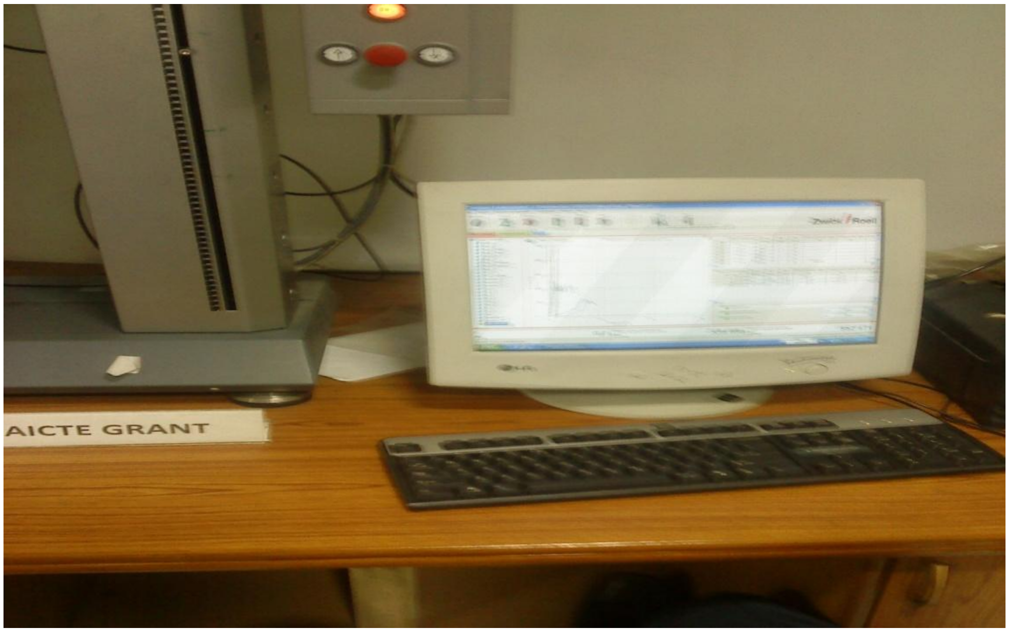


Fig 4.15 Computer display of UTM

4.6.2 Scanning Electron Microscope (SEM) testing

SEM was used to study the condition of clay dispersion in elastomeric base matrix. Apparatus used for SEM are shown in figure 4.16

Fig 4.16 Gold Coating apparatus & SEM Tester with display

4.6.3 X-Ray Diffraction (XRD) testing

XRD test was used to check the peaks available in EPDM clay mixture to find out the amount of intercalation of clay with EPDM. Apparatus used for XRD is shown in fig 4.17

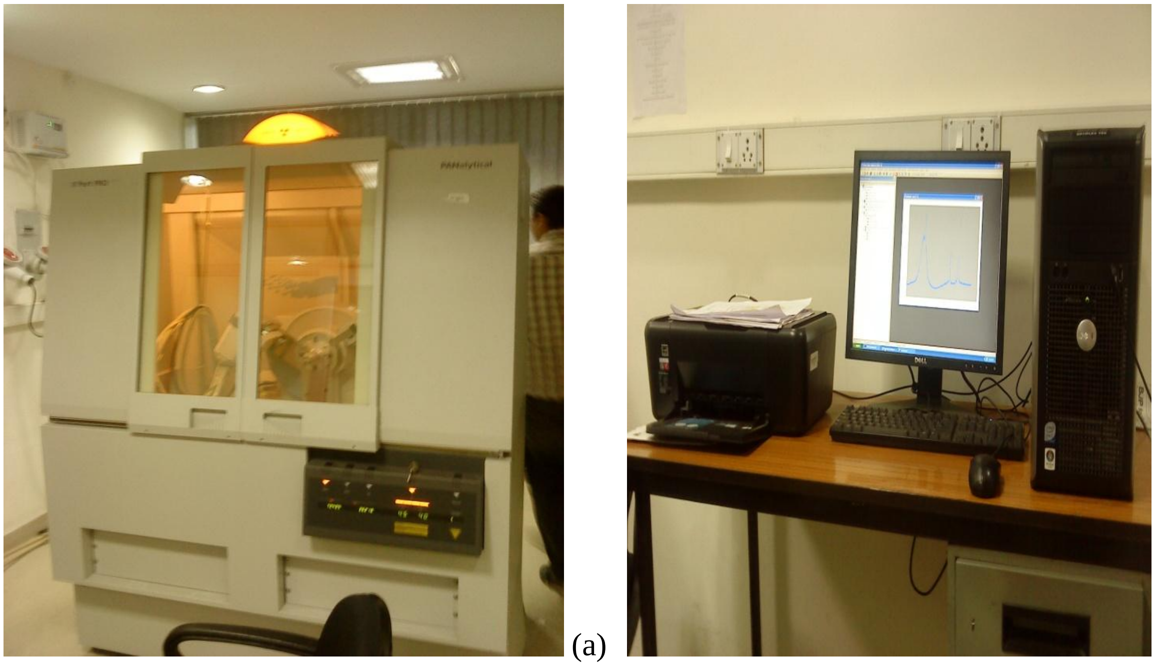

(a) (b)

Fig 4.17 (a) XRD Tester (b) Corresponding display device

4.6.4 Solvent swelling measurements

Solvent swelling measurements are done to check the solvents uptake by the specimen at different loading levels of play. In our case study is done with two solvents (toluene and water). Readings are taken after every hour for toluene while these are taken after every 6 hours for water. Set up used for solvent study is shown in figure.4.18 as shown on next page. It consists of a vacuum bag which do not allow the air to evaporate the solvent till the study is completed as shown in figure 4.18.

Fig 4.18 Solvent Swelling Arrangement

4.6.5 Thermo gravimetric analysis (TGA)

This study is always conducted to investigate the thermal stability of rubber nano composite at high temperatures. In this study, change in sample weight is recorded with the change in temperature. Set up used in TGA is shown in figure 4.19

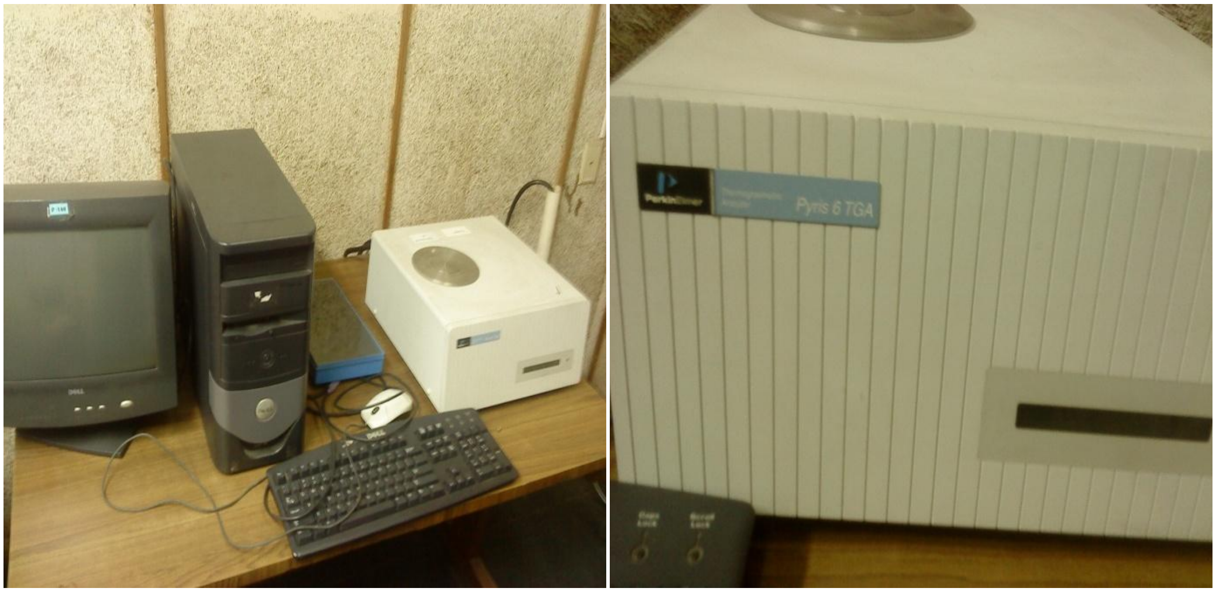


Fig. 4.19 TGA Apparatus

4.6.6 Flexural Testing

Flexural or Three Point Bending tests of nanocomposite specimens were carried out in using instrument as shown in Fig.4.20 (a). The test specimen had been prepared according to **ASTM D-790** standard as shown in figure 4.20 (b). Dimensions of test specimen is shown in figure 4.21 which was cut from the specimen shown in figure 4.12

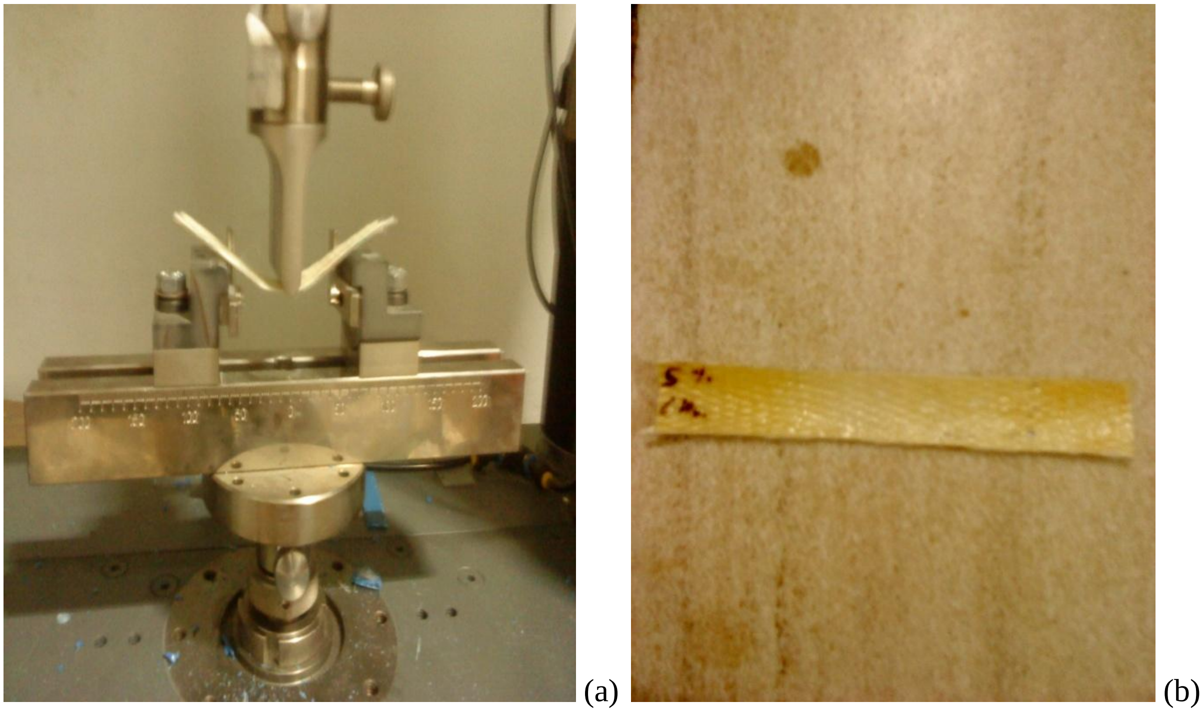

(a) (b)

Fig 4.20 (a) Flexural Testing Arrangement (b) Testing Specimen

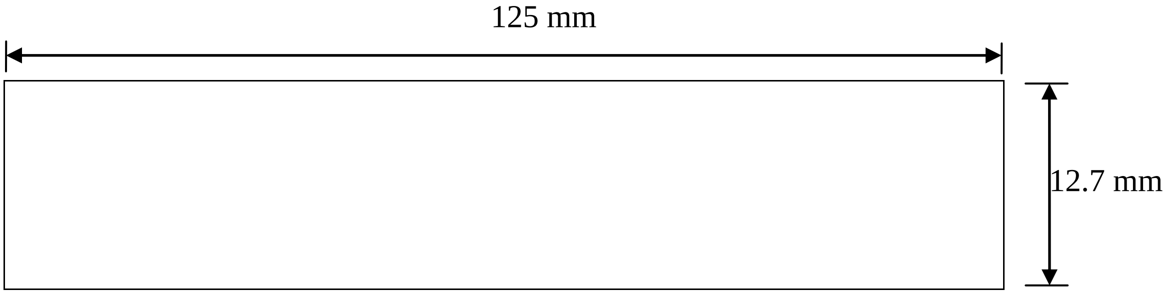


Fig 4.21 Dimensions of flexural test specimen

CHAPTER 5 RESULTS AND DISCUSSIONS

5.1. MACROSCOPIC VISUAL OBSERVATION OF THE SHEETS

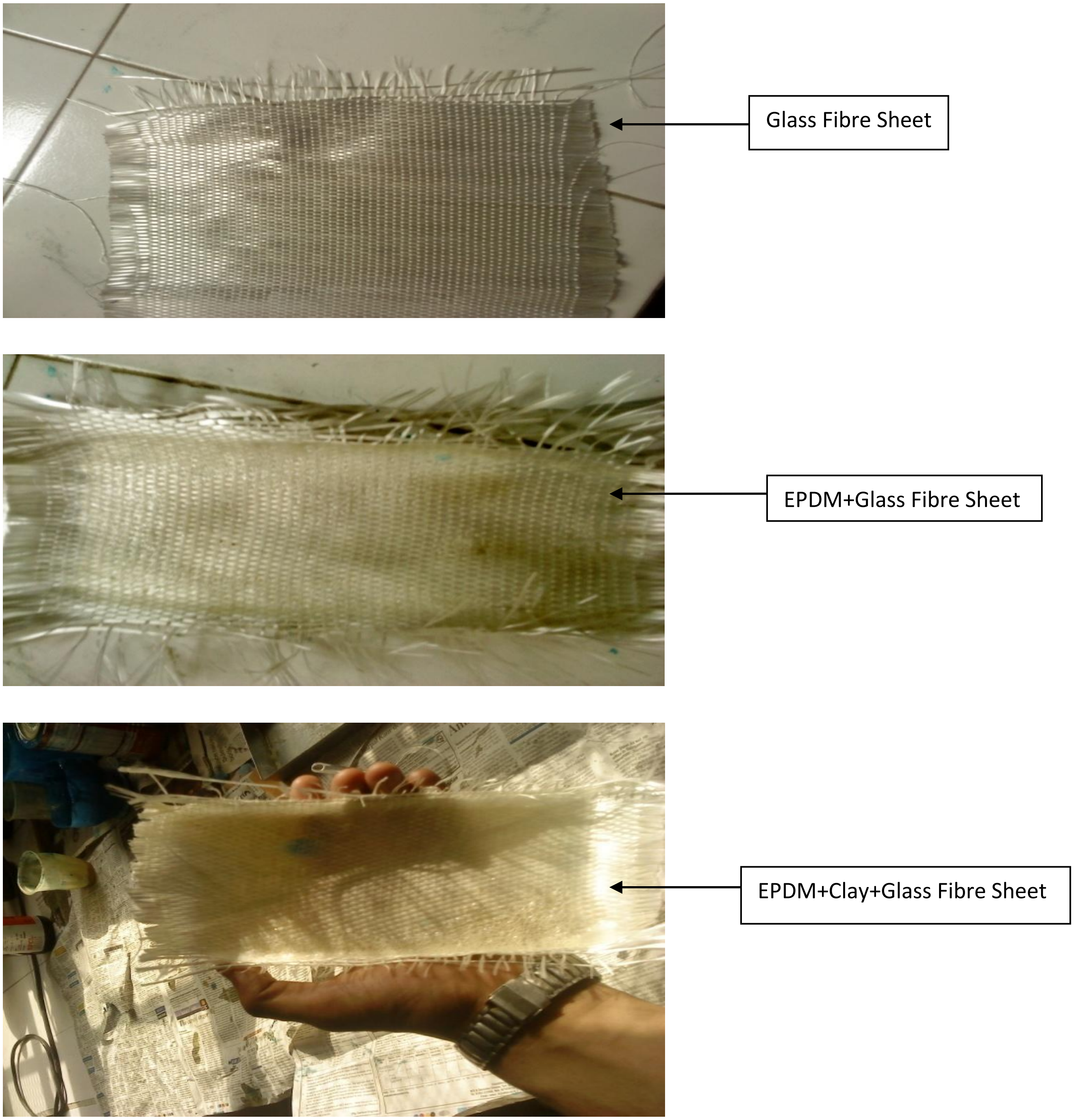


Fig. 5.1 Comparison of nanocomposite sheet with EPDM+Glass fibre sheet & glass fibre sheet

5.2 RESULTS OF TENSILE TESTINGS

Actual picture of the graph of force v/s strain as obtained from the software testXpert II for each specimen while performing the tensile testing on Zwick Roell UTM machine are shown in figure 5.2

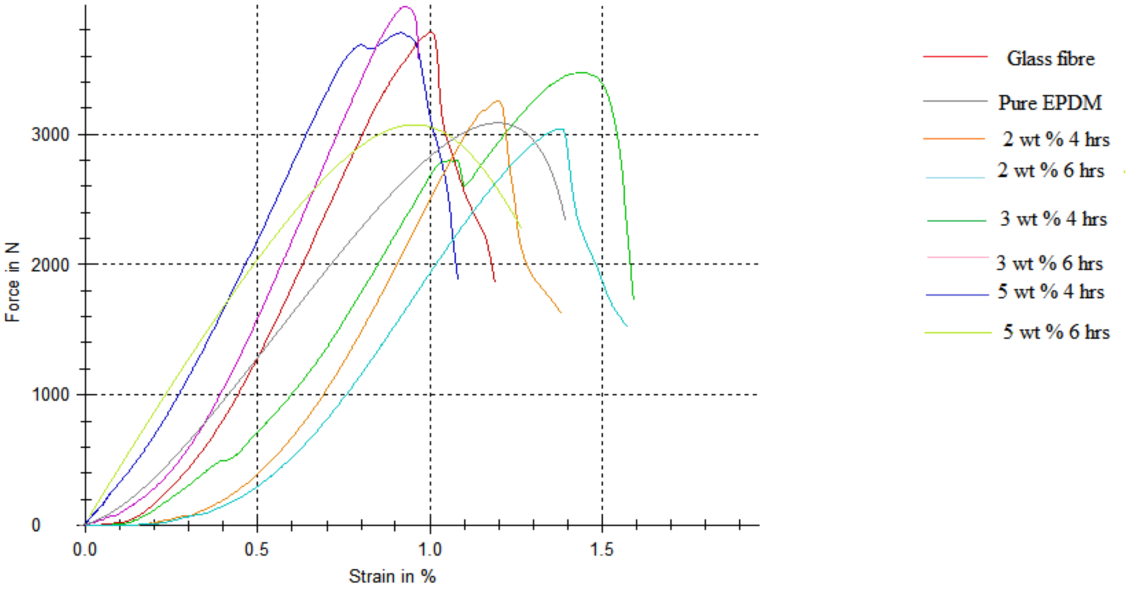


Fig. 5.2 Pictorial representation of the force v/s strain graphs of each specimen during the tensile testing

The data obtained from the machine for each specimen after performing the test is shown in the table 5.1 as shown on next page.

Specimen type/ Flexural properties	Tensile Strength (Mpa)	Ultimate tensile load (N)	Elongation(dl) at F_{max} (mm)	Percentage elongation at break
Glass Fibre	75.6	3780	5.4	1.2
0%wt(EPDM+Glass Fibre)	137	3087	5.3	1.2
2 % wt 4 hrs	145	3254	6.5	1.4
2 % wt 6 hrs	135	3042	7.6	1.6
3 % wt 4 hrs	154	3474	7.9	1.6
3 % wt 6hrs	177	3977	5.1	1.0
5 % wt 4 hrs	168	3777	5.0	1.1
5 % wt 6 hrs	136	3060	6.8	1.3

Table 5.1 Tensile properties of various glass fibre reinforce specimens

These data are represented individually on bar chart as shown in the following figures (5.3, 5.4, 5.5, 5.6)

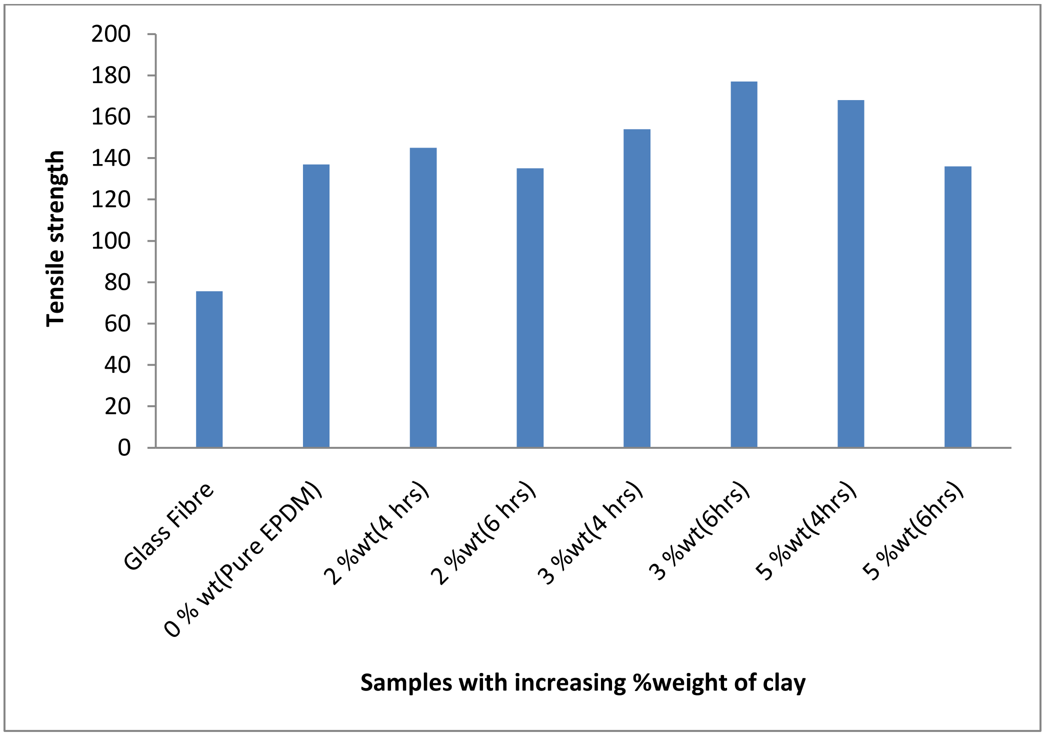


Fig.5.3 Bar chart showing tensile strength variation of the specimens

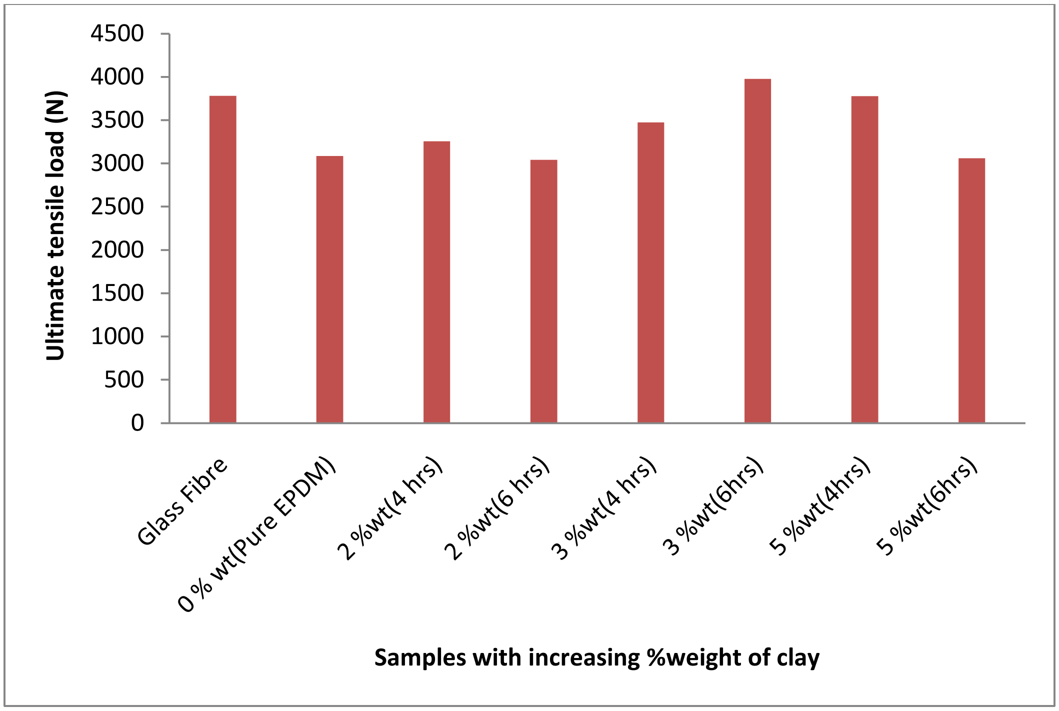


Fig.5.4 Bar chart showing the variation in ultimate tensile load of the specimens

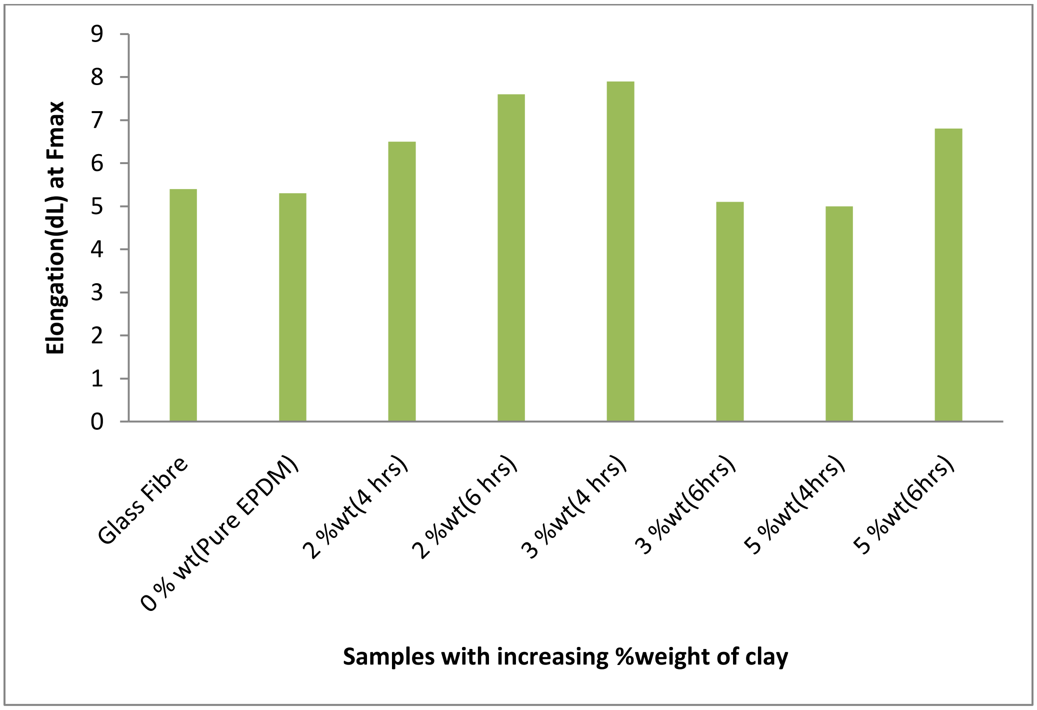


Fig.5.5 Bar chart showing the variation in Elongation(dL) at F_{max} of the specimens

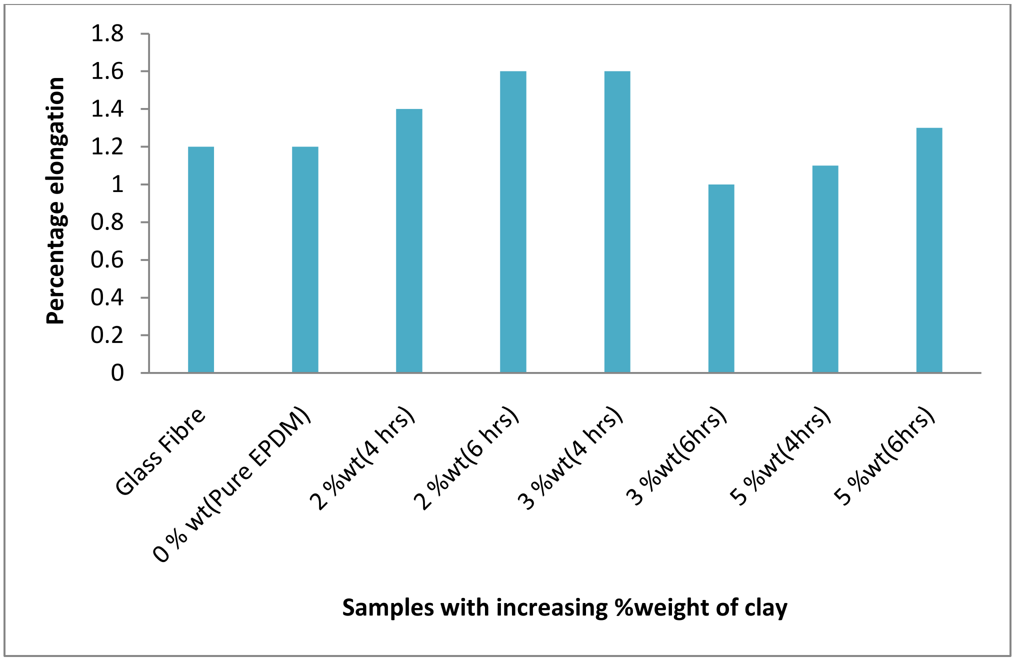


Fig.5.6 Bar chart showing the variation in %age elongation of the specimen

5.2.1 Discussion of results of tensile testing

Random pattern is shown by the tensile properties of the specimens. Although all properties are increased by the addition of nano clay particles but different property showed a different manner of increment increased in different manner at different percentage weight of clay and with different hours of post ultrasonication. There is no particular specimen which show increase in all the tensile properties.

Tensile strength increased with the addition of clay particle as compared to EPDM+Glass fibre+Glass fibre and glass fibre sheet. Specimen with 3 percentage weight clay and 6 hours post ultrasonication showed a high gain in tensile strength as compared to EPDM+Glass fibre+ glass fibre. It may be due to proper intercalation of clay particles with the elastomer whose evidence is given by the XRD data which has shown the peak shifted to lower angle indicating proper intercalation of clay particles with the elastomers by increasing the d-spacing between the molecules and ultimately also increasing the strength. Overall tensile strength is increased with the addition of nano clay particles except in one or two occasion.

Ultimate tensile load shown by 3 percentage weight clay and 6 hours post ultrasonication is maximum in all the specimens and it may be due to the same reason as explained for tensile strength.All the other specimens showed a decrease in capacity to take the load as compared to alone glass fibre specimen. The reason behind it is not very clear, it may be due to that rubber is not very compatible with the glass fibre and a poor physical bonding takes place between them.

Elongation(dL) at F_{max} has shown almost opposite pattern as shown by the ultimate tensile load. It may be due to the same reason as explained for ultimate tensile load. Elongation(dL) at F_{max} is more in cases where physical bonding between glass fibre and nano composite layer is less so that nano composite layer stretches more as compared to the cases in which the physical bonding is high where the layer and the glass fibre stretches equally and due to the rigidness of glass fibre the value of Elongation(dL) at F_{max} becomes low.

Percentage elongation has the same pattern as shown by Elongation(dL) at F_{max} and the reason may be the same as for the pattern of Elongation(dL) at F_{max}

5.3 RESULTS OF FLEXURAL TESTING

Similar to tensile testing, the representation of force v/s deformation graphs for the specimens as obtained from the machine display is shown in figure 5.7

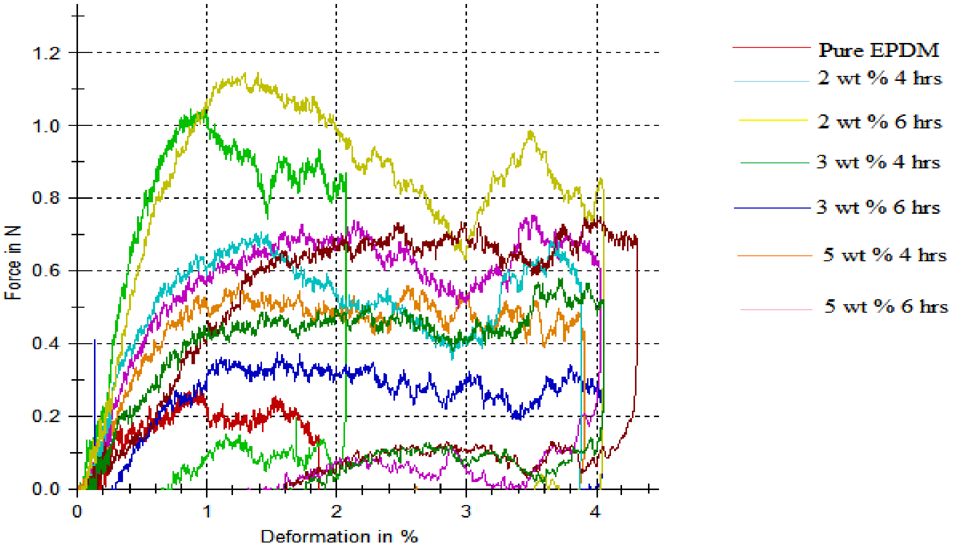


Fig 5.7 Pictorial representation of the force v/s % deformation graphs of each specimen during the tensile testing

The data obtained from the machine for each specimen after performing the test is shown in the table 5.2

Specimen type/ Flexural properties	Flexural Modulus (Mpa)	Flexural Strength (Mpa)	Ultimate flexural load (N)
0%wt (EPDM+ Glass fibre)	260	3.42	0.35
2 %wt & 4 hrs	448	6.19	0.70
2 %wt & 6 hrs	571	4.80	0.55
3 %wt & 4 hrs	687	4.70	0.55
3 %wt & 6 hrs	716	6.24	0.75
5 %wt & 4 hrs	1170	5.84	0.67
5 %wt & 6 hrs	1090	9.48	1.10

Table 5.2 Flexural properties of various glass fibre reinforced specimens

These data are represented individually on bar charts as shown by the following figures (5.8, 5.9, 5.10)

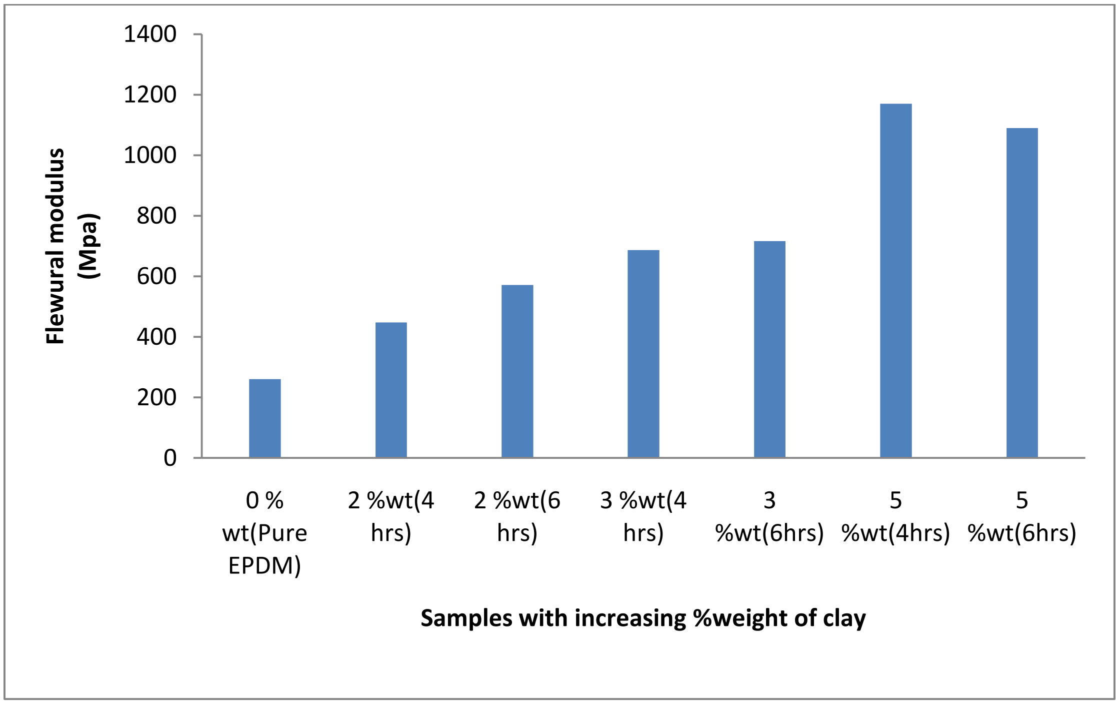


Fig.5.8 Bar chart showing the variation on flexural modulus of the specimens

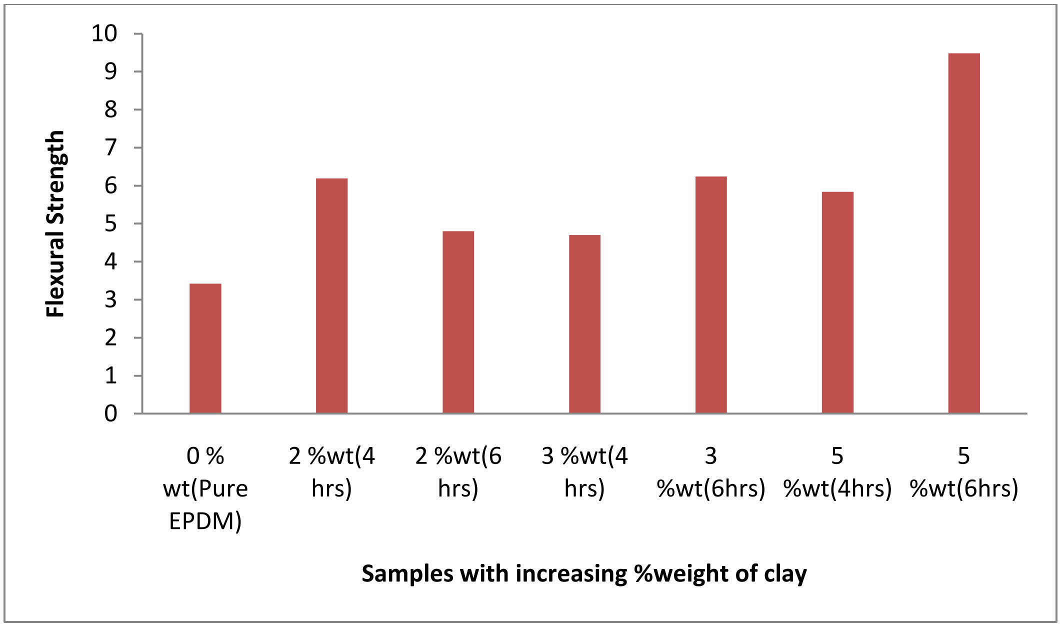


Fig.5.9 Bar chart showing the variation of flexural strength

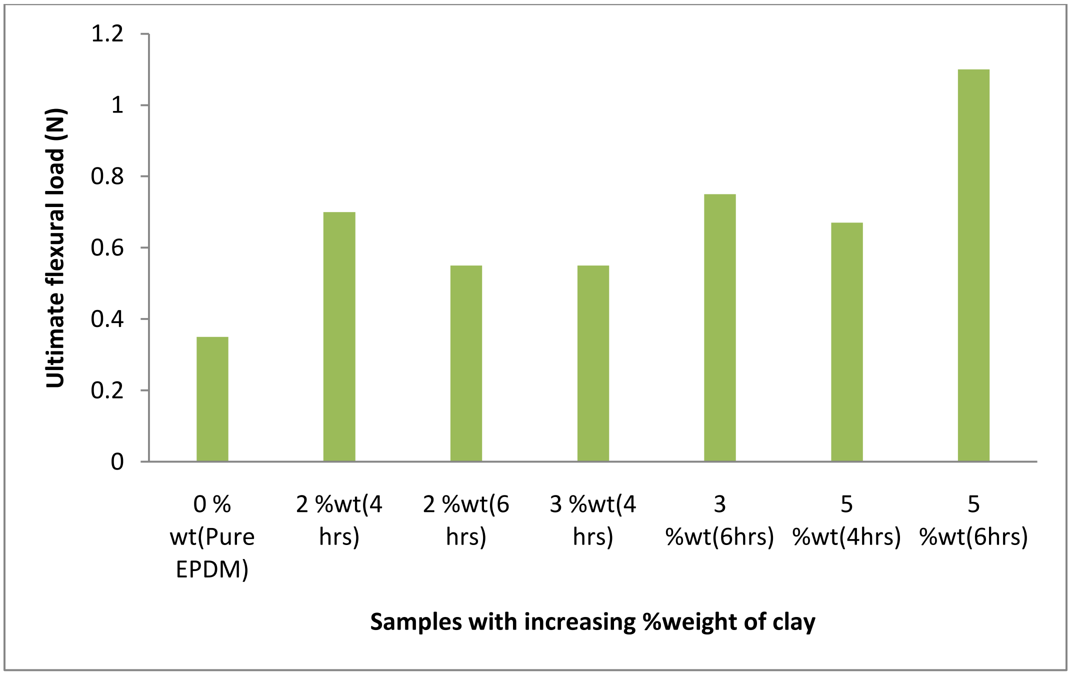


Fig.5.10 Bar chart showing the variation of ultimate flexural load taken by the specimens

5.3.1 Discussion of results of flexural testing

Flexural properties are increased by incorporating clay particles inside the elastomeric molecular chains. Flexural modulus follows almost a linear increasing trend with increasing percentage weight of clay and with increase in post ultrasonication time. But flexural strength and ultimate flexural load followed almost the same pattern which is very random in nature Although increase is shown by both of the properties with incorporation of clay particles as compared to EPDM+ Glass fibre yet the increase is irregular in nature as specimen with 5 percentage weight clay and 6 hours post ultrasonication showed a hike in both of the properties. Except it all other nanocomposite specimens showed a normal range for these properties. The reason which can be concluded about hike in properties by 5 percentage weight and 6 hours specimen is that the specimen may be cut out from the sheet where clay particles are coagulated giving a large gain in properties for the specimen. Otherwise specimen with 3 percentage weight clay and 6 hours post ultrasonication showed maximum gain in properties except the specimen with 5 percentage weight clay & 6 hours post ultrasonication which may be due to the same reason as explained for gain in tensile strength by the specimen with 3 percentage weight clay & 6 hours post ultrasonication.

5.4 RESULTS OF X-RAY DIFFRACTION OF THE SAMPLES

XRD graphs and corresponding tables of peak list for each specimen are as follows

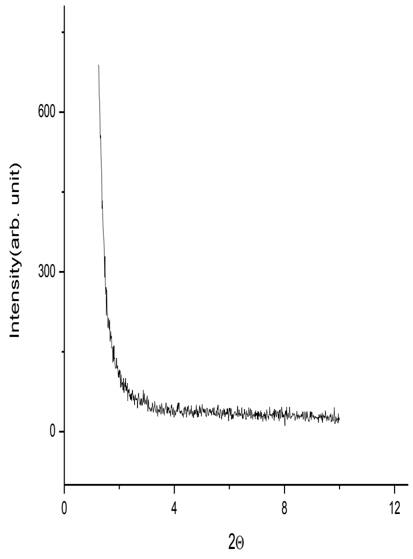


Fig 5.11 XRD graph 2 %wt & 4hrs

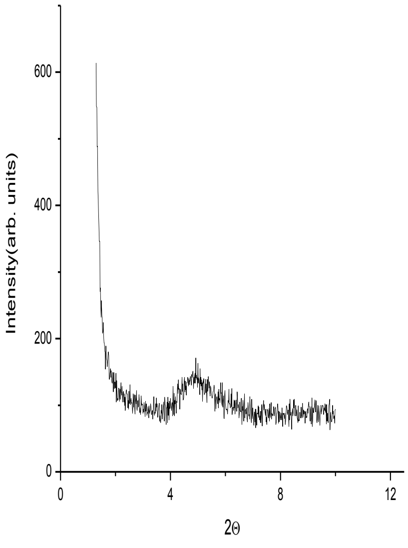


Fig 5.12 XRD graph 2 %wt & 6 hrs

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
0.0710	4516202.00	0.0468	1243.42100(back suface peak)	100.00
0.1541	533311.10	0.0468	574.38150(back suface peak)	11.81

Table 5.3 Peak List of 2 %wt clay & 4 hours post ultrasonication specimen

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
0.0552	6355911.00	0.0384	1599.93700(back suface peak)	100.00
1.1706	180.75	0.1791	75.46833(back suface peak)	0.00
4.8771	17.95	0.8187	18.11920	0.00

Table 5.4 Peak List of 2 %wt clay & 6 hours post ultrasonication specimen

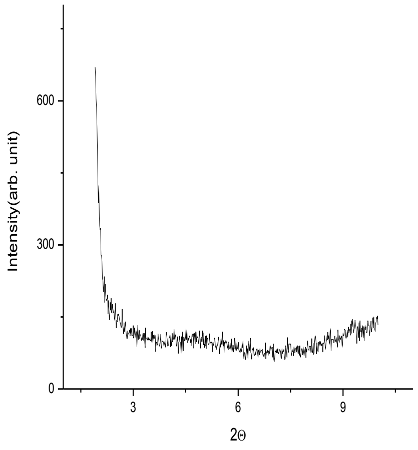


Fig 5.13 XRD graph 3 %wt & 4hrs

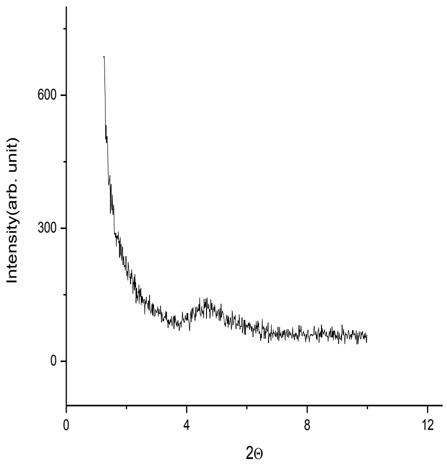


Fig 5.14 XRD graph 3 %wt & 6 hrs

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
0.0501	8886421.00	0.0384	1764.83300(back suface peak)	100.00
0.5449	1028.58	0.0640	162.11670(back suface peak)	0.01

Table 5.5 Peak List of 3 %wt clay & 4 hours post ultrasonication specimen

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
0.0710	3326109.00	0.0384	1243.59900(back suface peak)	100.00
0.1496	344766.20	0.0256	590.66500(back suface peak)	10.37
4.6555	14.08	0.8187	18.98113	0.00

Table 5.6 Peak List of 3 %wt clay & 6 hours post ultrasonication specimen

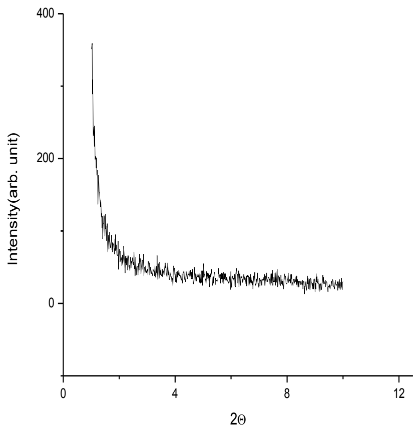


Fig 5.15 XRD graph 5 %wt & 4hrs

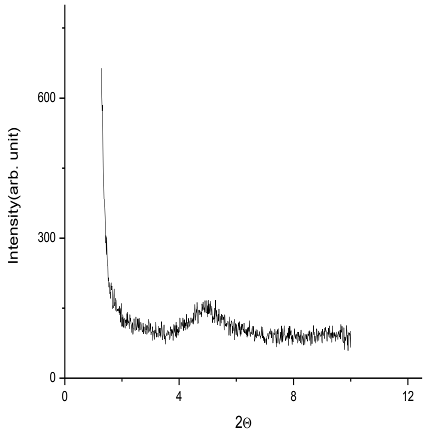


Fig 5.16 XRD graph 5 %wt & 6 hrs

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
0.0613	49597.16	0.0256	1440.77400(back suface peak)	18.94
0.1522	261830.90	0.0512	580.31290(back suface peak)	100.00

Table 5.7 Peak List of 5 %wt clay & 4 hours post ultrasonication specimen

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
0.0550	5957427.00	0.0384	1604.86700(back suface peak)	100.00
0.2589	11097.31	0.0384	341.18690(back suface peak)	0.19
4.9311	18.63	0.6140	17.92094	0.00

Table5.8 Peak List of 5 %wt clay & 6 hours post ultrasonication specimen

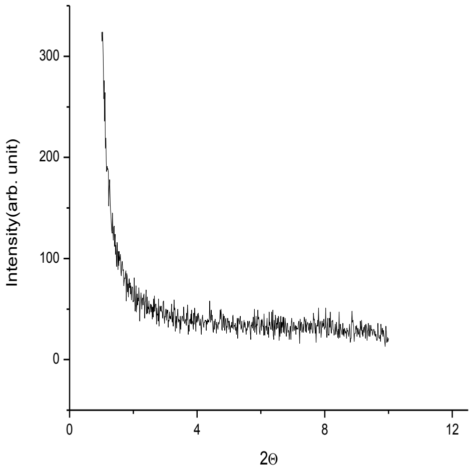


Fig 5.17 XRD graph 0 %wt(EPDM+Glass fibre)

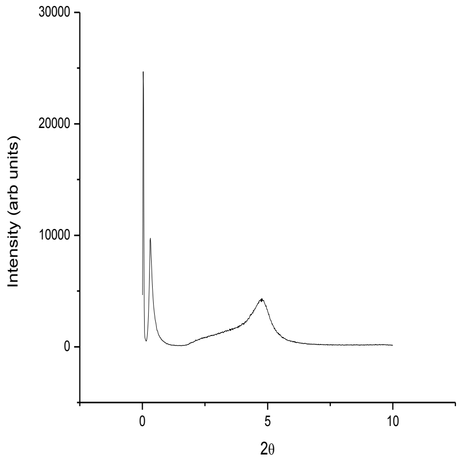


Fig 5.18 XRD graph of clay powder

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
0.0614	49865.73	0.0256	1439.81500(back surface peak)	17.71
0.1500	281594.30	0.0512	588.86030(back surface peak)	100.00

Table 5.9 Peak List of 0 %wt(EPDM+Glass fibre) specimen

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
0.0392	23457.61	0.0384	2251.94000(back surface peak)	100.00
0.3208	7980.16	0.0895	275.42540(back surface peak)	34.02
4.6751	864.23	0.2496	18.88615	3.68
4.8452	1229.13	0.1560	18.26854	5.24

Table 5.10 Peak List of Clay Powder

5.4.1 Discussion of results of X-ray diffraction graphs

Results are concluded by comparing the XRD graphs and tables of nano composite specimens with XRD graphs and tables of EPDM+Glass fibre & clay powder. Before conclusion initial information which can be picked from the results is that peaks with position 2θ from 0° to 1° are back surface peaks and not from the specimen, so these peaks has no significance. Now the conclusion made for each specimen as follows

i. Specimen with 2 percentage weight clay and 4 hours post ultrasonication

Since there is no peak within the range of position 2θ from 2° to 5° , so either there is no inter calation of clay or exfoliation has been achieved. It seems to be the first case that there is no intercalation of clay. The clay particles are coagulated at some point within the specimen and the portion which is cut out for XRD testing may not have any clay particles in it.

ii. Specimen with 2 percentage weight clay and 6 hours post ultrasonication

Here is a peak in range of position 2θ from 2° to 5° at a position 2θ =4.8771° with the d-sapcing of 18.11920 Å , so there is something in the specimen. As there is no peak in EPDM+Glass fibre at lower angle of position 2θ from 2° to 5°, so we are comparing it with only clay powder with a peak at position 2θ = 4.8452° and with a d-spacing of 18.26854 Å, since the d-spacing of the specimen is decreased so it does not seems to be the formation of nano composite as there is no intercalation of clay particles with elastomeric molecular chains and the peak available in the specimen is of some impurity present in the specimen with clay particles.

iii. Specimen with 3 percentage weight clay and 4 hours post ultrasonication

Almost similar case as shown by the specimen with 3 percentage weight clay and 4 hours post ultrasonication and may be the similar reason. Although there is a peak at position 2θ = 1.5867° with a d-spacing of 55.67884 Å, it seems to be some impurities present in the specimen not the clay intercalation.

iv. Specimen with 3 percentage weight clay and 6 hours post ultrasonication

Since there is a peak at position 2θ = 4.6555° with a d-spacing of 18.98113 Å indicating a shift in angle of 2θ = 4.6751° for clay to a lower side and d-spacing is also increased as compared to clay powder resulting in an intercalated structure for the specimen or in other means , a nanocomposite formation take place.

v. Specimen with 5 percentage weight clay and 4 hours post ultrasonication

Similar cases are shown by 4 hours post ultrasonication specimens and this is also one of them showing the similar pattern of graph & may be the similar reason for it that ultrasoniaction time of 4 hours is unable to properly disperse the clay within the EPDM matrix and showing almost the same pattern as shown by EPDM+Glass fibre.

vi. Specimen with 5 percentage weight clay and 6 hours post ultrasonication

With specimen of 5 percentage weight clay and 6 hours post ultrasonication, a peak in the range of position 2 θ from 2° to 5° has come at the position of 2 θ = 4.9311° with a d-spacing of 17.92094 $\mathring{A}$ indicating that again an impurity is present in the specimen with the clay.

5.5 RESULTS OF SOLVENT SWELLING MEASUREMENTS

Weight change of the glass fibre reinforced nano composite specimens as well as glass fibre reinforced EPDM+Glass fibre specimen were recorded with respect to time by using two solvents (toluene and water). The results obtained are described below.

5.5.1 Weight change of specimens when dipped in toluene with respect to time

Visual observation of the specimens before and after the test are shown in the following figures 5.19 & 5.20

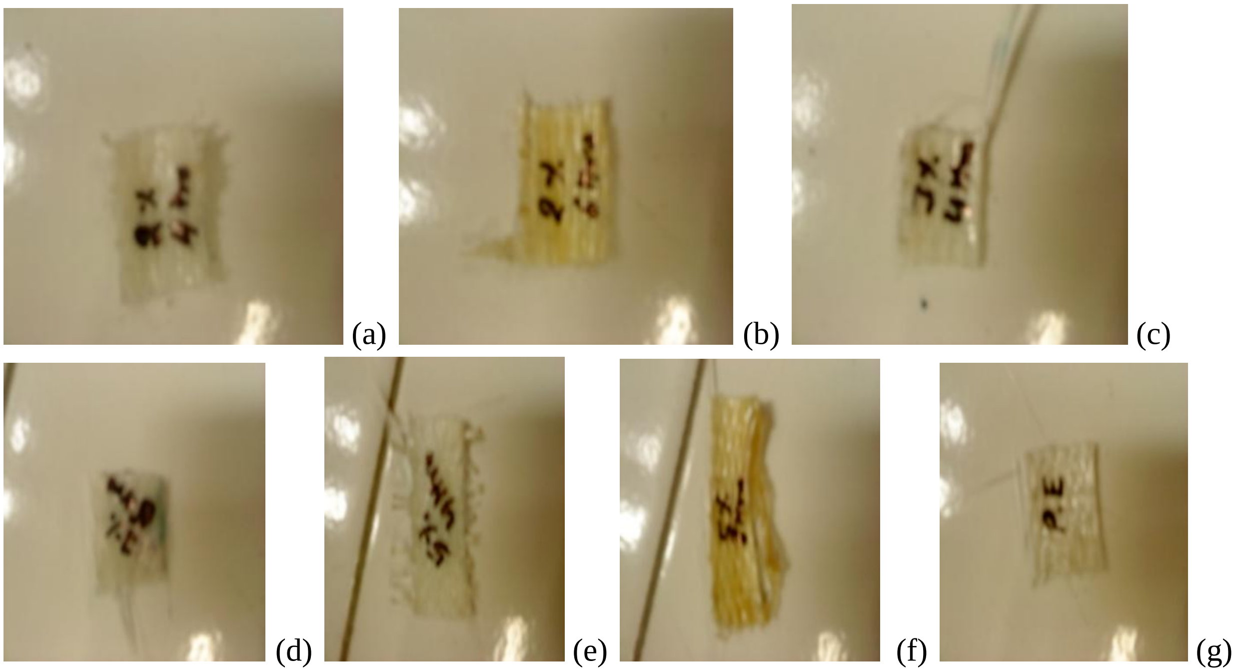


Fig 5.19 Specimen shape before the test

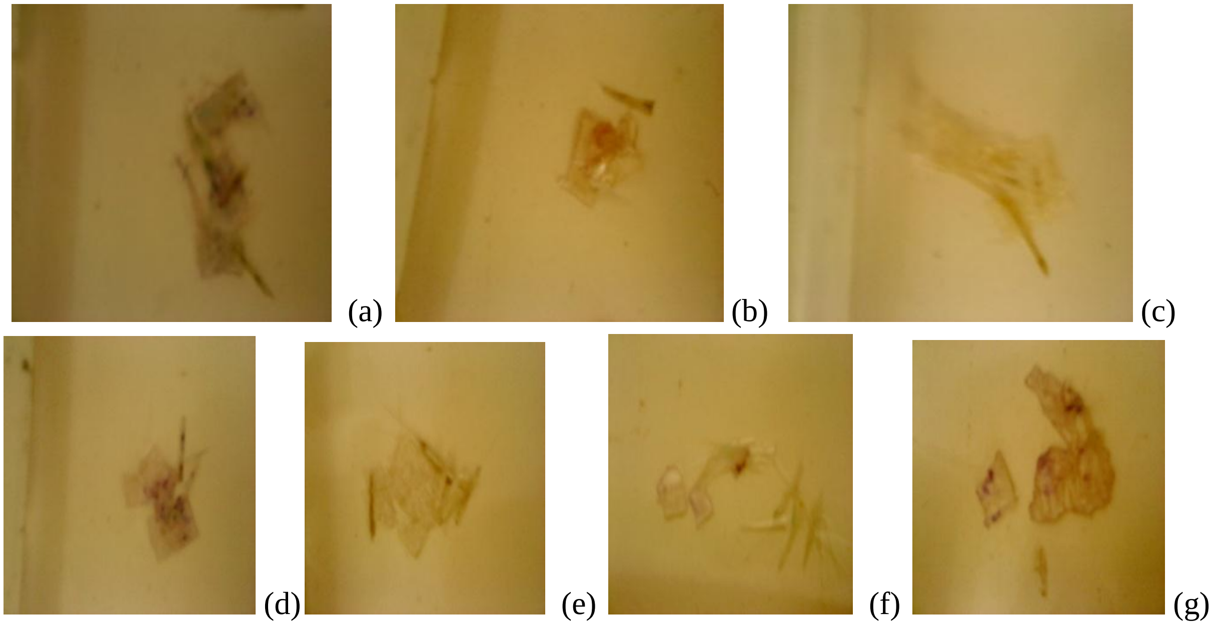

(a) (b) (c) (d) (e) (f) (g)

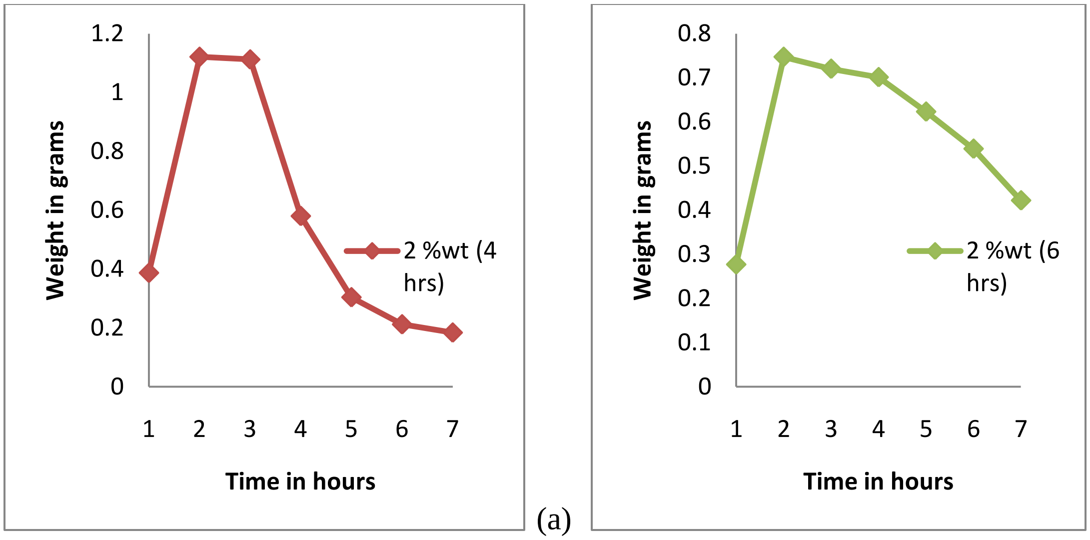
Fig 5.20 Corresponding Specimen Shape after the test

The data obtained about variation in weight of each specimen after every hour when dipped in toluene is shown in table 5.11

Specimen type/ Time in hours	Initial value	After 1 hr	After 2 hr	After 3 hr	After 4 hr	After 5 hr	After 6 hr
0%wt(EPDM+ Glass fibre)	0.318	1.088	1.035	1.022	0.927	0.876	0.792
2 %wt & 4 hrs	0.387	1.121	1.112	0.580	0.304	0.212	0.184
2 %wt & 6 hrs	0.277	0.747	0.720	0.701	0.623	0.539	0.422
3 %wt & 4 hrs	0.310	0.423	0.936	0.890	0.910	0.737	0.528
3 %wt & 6 hrs	0.248	0.840	0.813	0.798	0.829	0.731	0.564
5 %wt & 4 hrs	0.488	1.294	1.256	1.217	1.212	0.905	0.768
5 %wt & 6 hrs	0.440	1.220	1.176	0.779	0.597	0.424	0.351

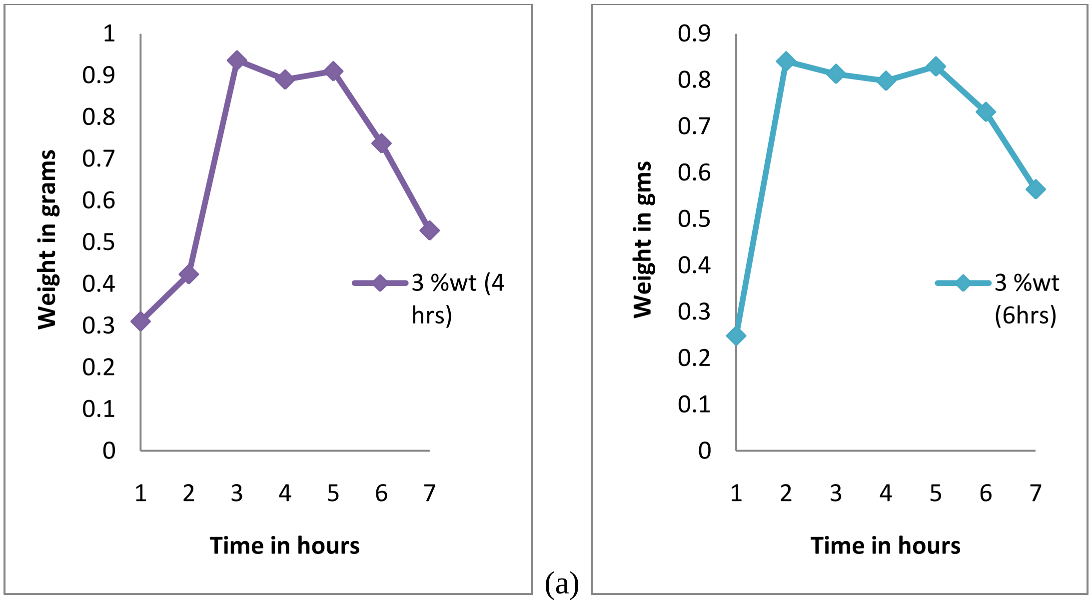
Table 5.11 Values of weights of different glass fibre reinforced specimens after each hour when dipped in toluene

Graphical representation of weight change of individual specimen with respect to time are shown in figures 5.21, 5.22, 5.23, 5.24.



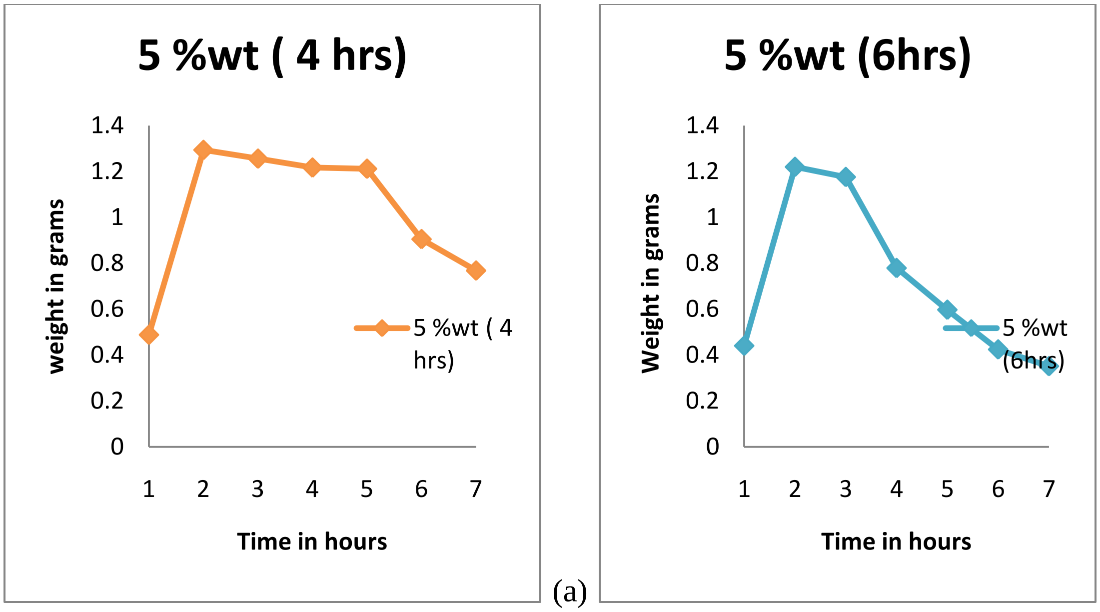
(a) (b)

Fig 5.21 Weight gain with time for the specimen (a) 2 %wt & 4 hrs (b) 2 %wt & 6 hrs



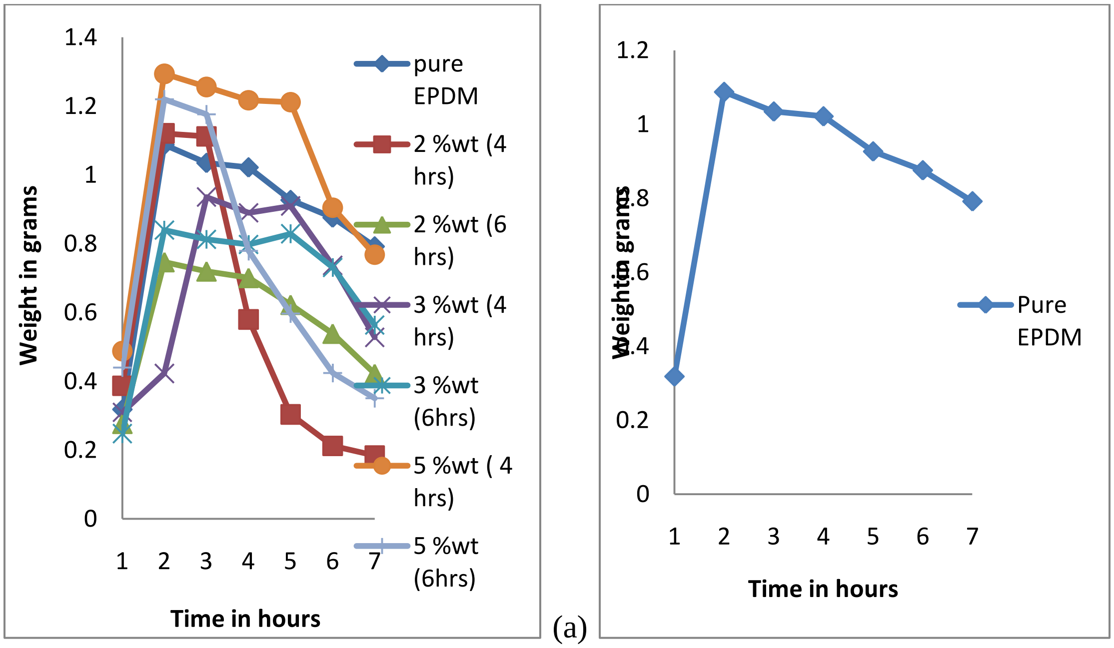
(a) (b)

Fig 5.22 Weight gain with time for the specimen (a) 3 %wt & 4 hrs (b) 3 %wt & 6 hrs



(a) (b)

Fig 5.23 Weight gain with time for the specimen (a) 5 %wt & 4 hrs (b) 5 %wt & 6 hrs



(a) (b)

Fig 5.24 Weight gain with time (a) Comparison of all specimen (b) 0 %wt(EPDM+ Glass fibre)

5.5.1(a) Discussion of results obtained from the study of specimen swelling behavior in toluene

Almost similar patterns are shown by the fibre reinforced EPDM nano composites as that of pristine EPDM. All nano composites as well as pristine EPDM showed a large gain in weight for the very first hour, after that for next two or three hours they showed saturation with a little bit decrease in weights. It may be due to swollen mass of EPDM start losing glass fibres from it.

Then at the end hour study i.e. four to six hours, there is a sudden decrement in weight and the rate of decrease is higher in case of nano composites as compared to pristine EPDM. Another important conclusion is that solvent uptake at the first stage is lower in case of 2 %wt and 3 %wt clay specimens as compared to pristine EPDM specimens, while in case of 5 %wt clay specimen the solvent uptake is more for the first stage as compared to pristine EPDM. Mechanism behind it is not very clear, it may be due to improper dispersion of clay particles at higher weight percentage of clay.

5.5.2 Weight change of specimens when dipped in water with respect to time

Visual observation of the specimens before and after the test are shown in the following figures 5.25 (a) & (b)

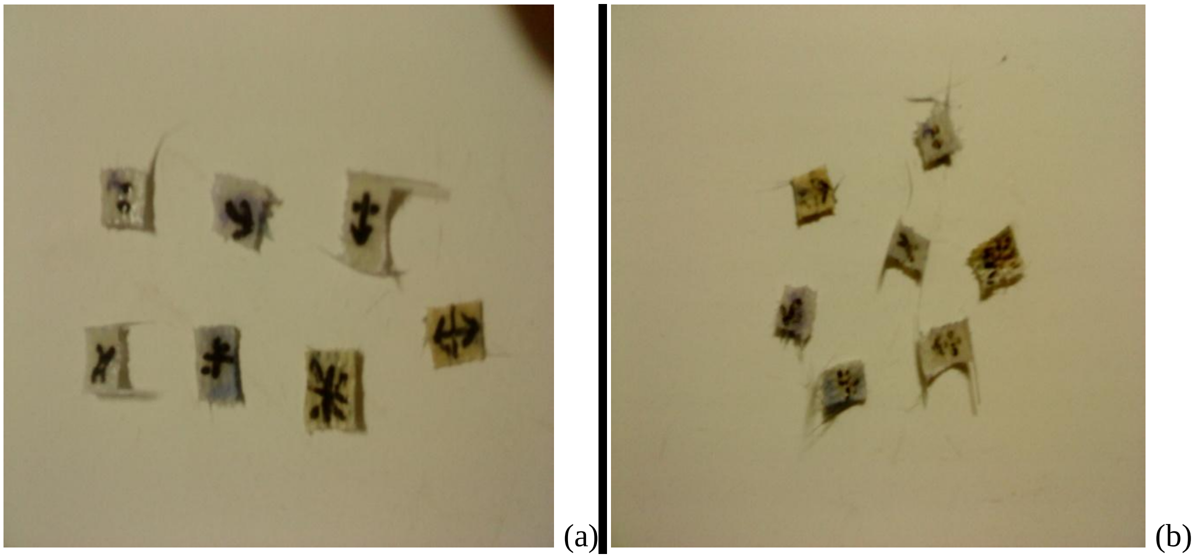


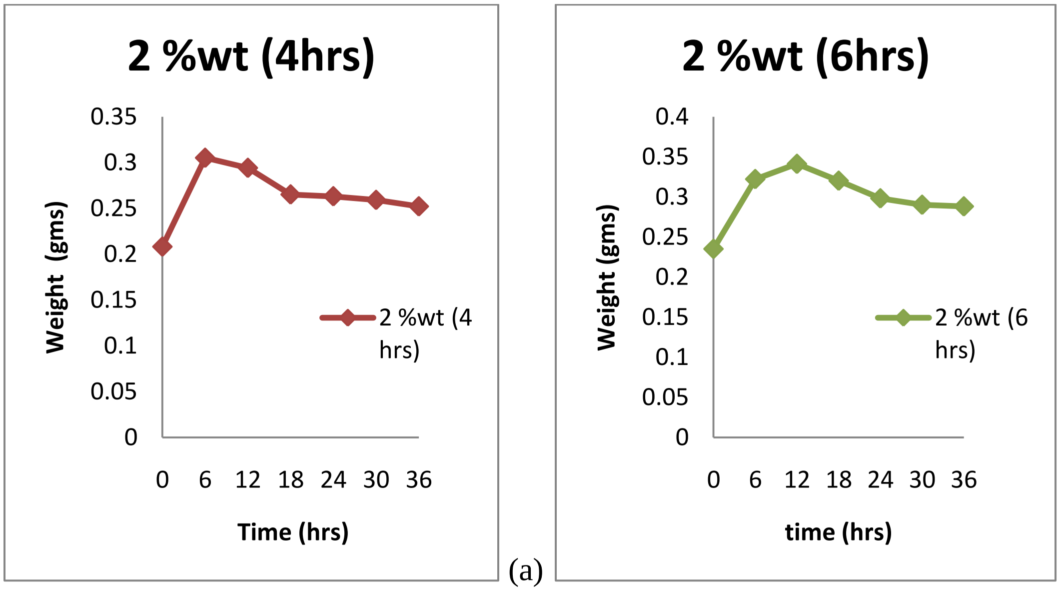
Fig 5.25 Specimen shape (a) before the test (b) after the test

The data obtained about variation in weight of each specimen after every hour when dipped in water is shown in table 5.12

Specimen type/ Time in hours	Initial value	After 6 hr	After 12 hr	After 18 hr	After 2 4 hr	After 30 hr	After 36 hr
0%wt(EPDM+ Glass fibre)	0.239	0.285	0.299	0.306	0.309	0.313	0.312
2 %wt & 4 hrs	0.208	0.305	0.294	0.265	0.263	0.259	0.252
2 %wt & 6 hrs	0.235	0.322	0.341	0.320	0.298	0.290	0.288
3 %wt & 4 hrs	0.189	0.271	0.257	0.232	0.229	0.225	0.222
3 %wt & 6 hrs	0.155	0.253	0.296	0.257	0.253	0.249	0.242
5 %wt & 4 hrs	0.288	0.405	0.398	0.384	0.377	0.355	0.346
5 %wt & 6 hrs	0.175	0.208	0.244	0.240	0.234	0.224	0.219

Table 5.12 Values of weights of different glass fibre rienforced specimens after every six hours when dipped in water

Graphical representation of weight change of individual specimen with respect to time are shown in following figures



(a) (b)

Fig 5.26 Weight gain with time for the specimen (a) 2 %wt & 4 hrs (b) 2 %wt & 6 hrs

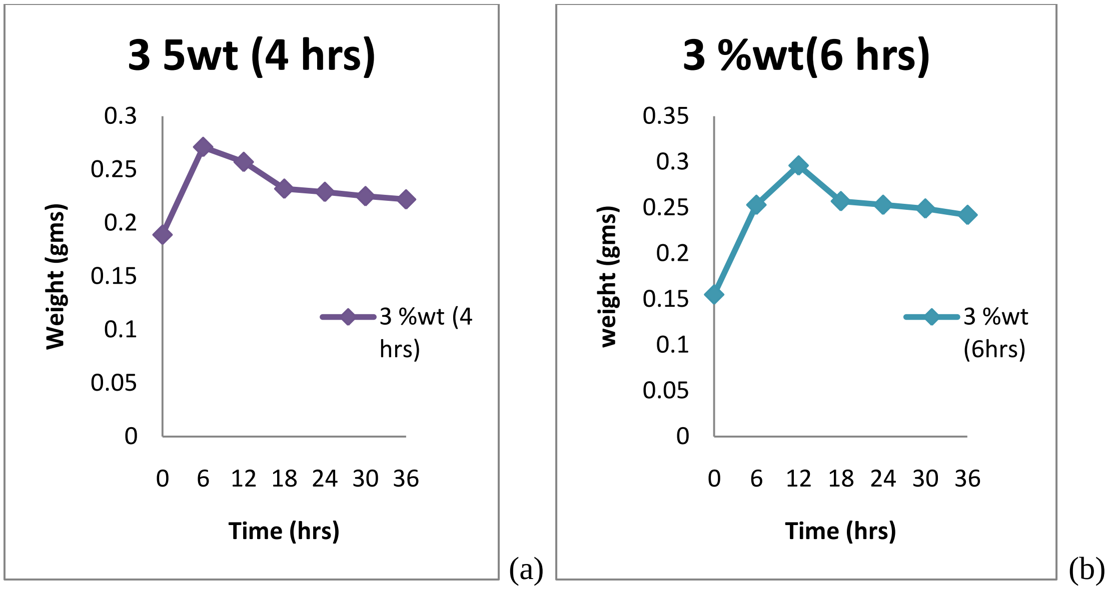


Fig 5.27 Weight gain with time for the specimen (a) 3 %wt & 4 hrs (b) 3 %wt & 6 hrs

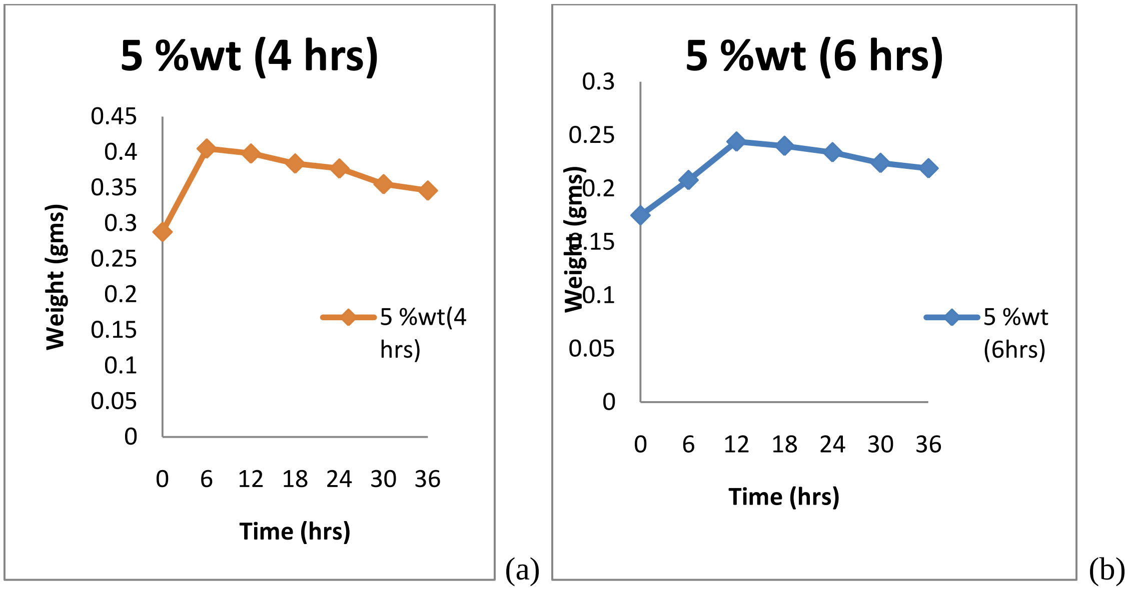
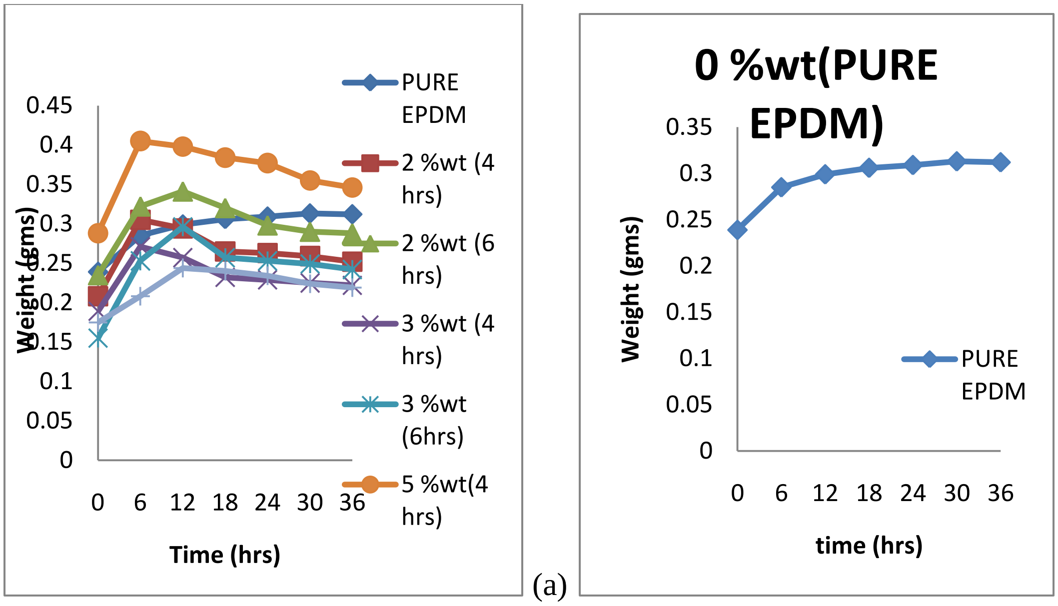


Fig 5.28 Weight gain with time for the specimen (a) 5 %wt & 4 hrs (b) 5 %wt & 6 hrs



(a) (b)

Fig 5.29 Weight gain with time (a) Comparison of all specimen (b) 0 %(EPDM + Glass fibre)

5.5.2(a) Discussion of results obtained from the study of specimens swelling behavior in water

It has been observed that all the specimens show a rapid increase in weight for the very first reading but after that nanocomposite specimens behave in a different manner from the EPDM+Glass fibre specimen. EPDM+Glass fibre specimen show a continuous increase in weight till the last reading is taken but the rate of increase is very very slow as compared to first reading, while nano composite specimen show a continuous decrease after first or in some cases after second reading. The reason for this kind of behavior may be that water uptake of EPDM+Glass fibre require more time for the saturations as compared to EPDM + glass fibre clay nano composite. The reason for decrease in weight of the nano composites may be due to the loss of glass fibre from the base matrix after the saturation takes place.

In water swelling measurements, we also observed the post ultrasonication effect as nanocomposite specimens with 4 hours post ultrasonication show the different patterns from the specimens with 6 hrs post ultrasonication. On the graphical representation, the 4 hours post ultrasonication specimens shows the similar patterns while 6 hours post ultrasonication specimens shows the similar patterns but different one from the 4 hours post ultrasonictaion specimens.

5.6. DETAILS OF SEM IMAGES OF ALL SPECIMEN WITH RESPECT TO CLAY PERCENTAGE

The SEM images as shown in figures for the EPDM/Clay nano composite specimen taken at 100x magnification, 23kV and 100µm from their cut cross sections.

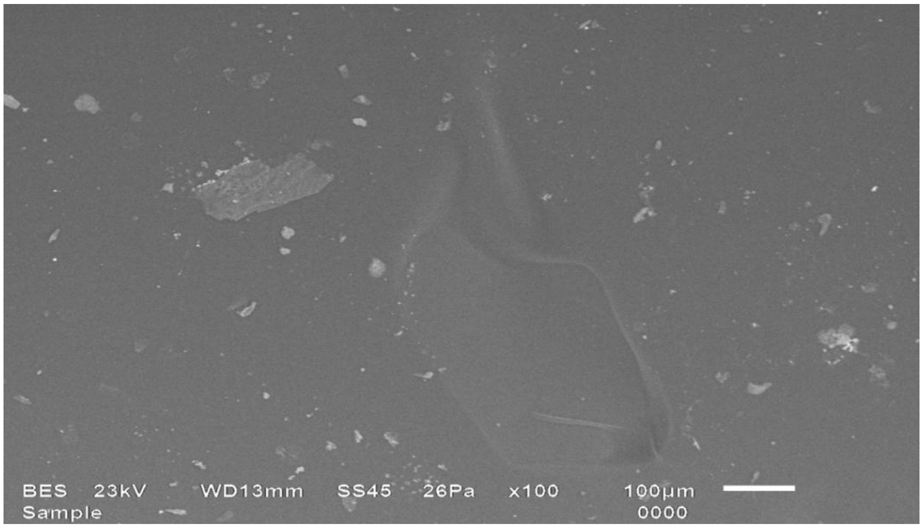


Fig 5.30 SEM Image of specimen with 2 %wt clay & 4 hrs post ultrasonication

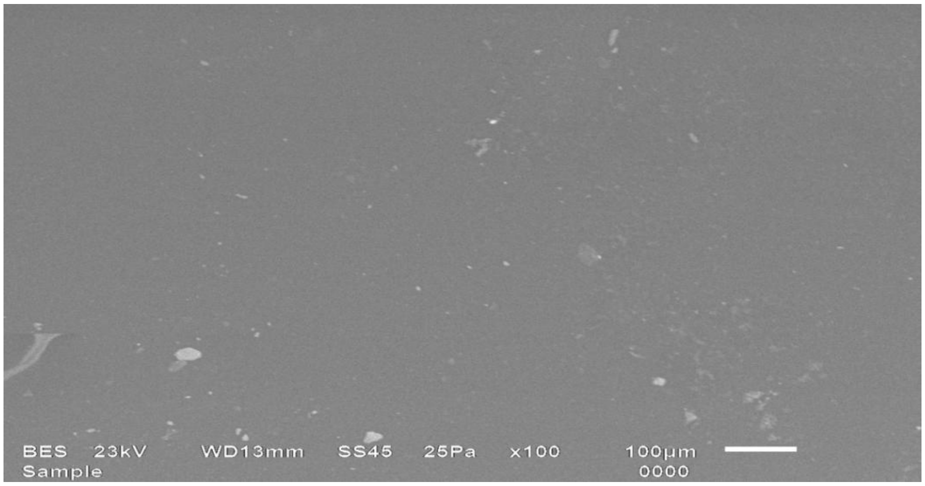


Fig 5.31 SEM Image of specimen with 2 %wt clay & 6 hrs post ultrasonication

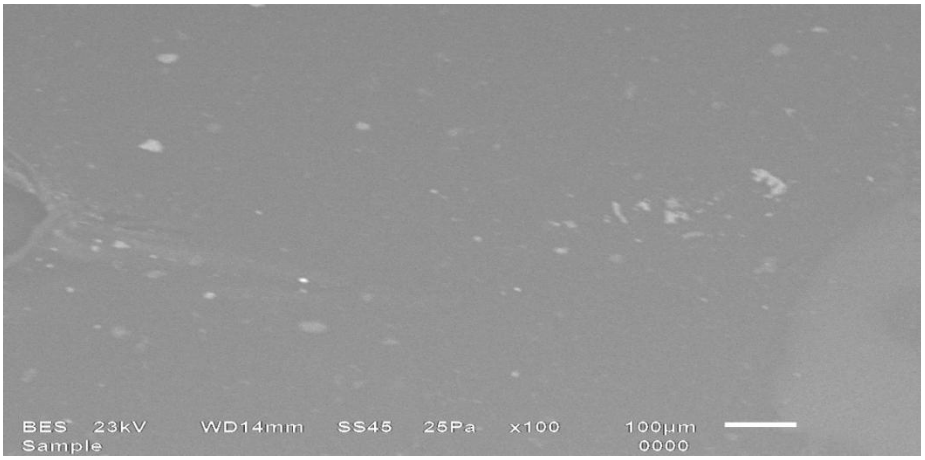


Fig 5.32 SEM Image of specimen with 3 %wt clay & 4 hrs post ultrasonication

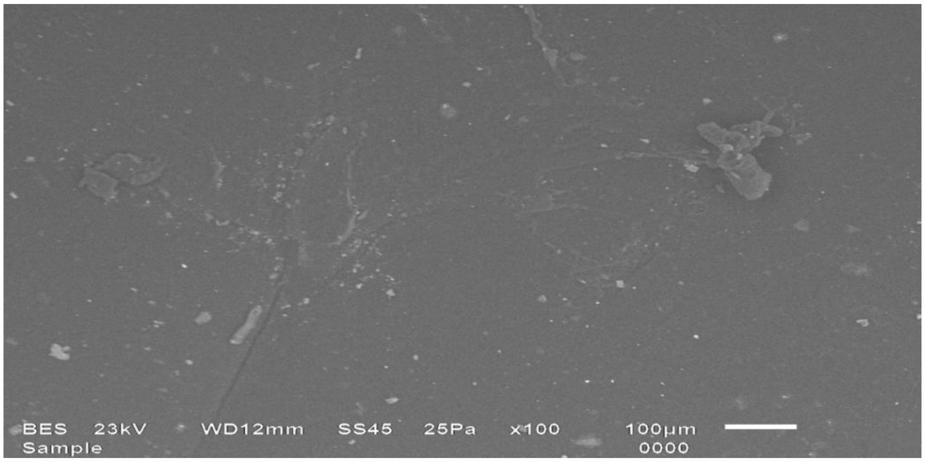


Fig 5.33 SEM Image of specimen with 3 %wt clay & 6 hrs post ultrasonication

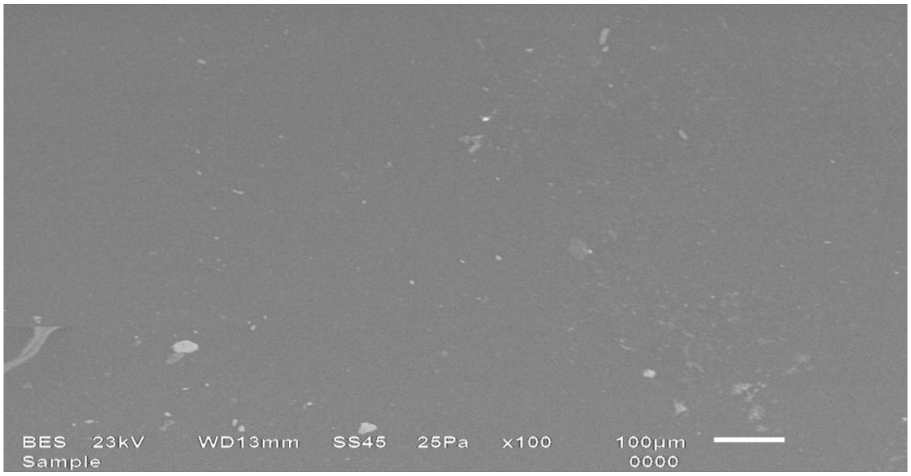


Fig 5.34 SEM Image of specimen with 5 %wt clay & 4 hrs post ultrasonication

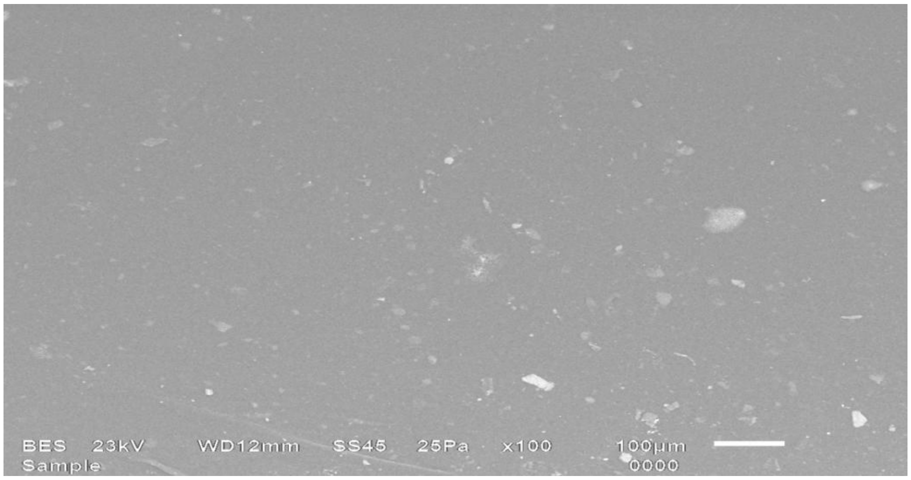


Fig 5.35 SEM Image of specimen with 5 %wt clay & 6 hrs post ultrasonication

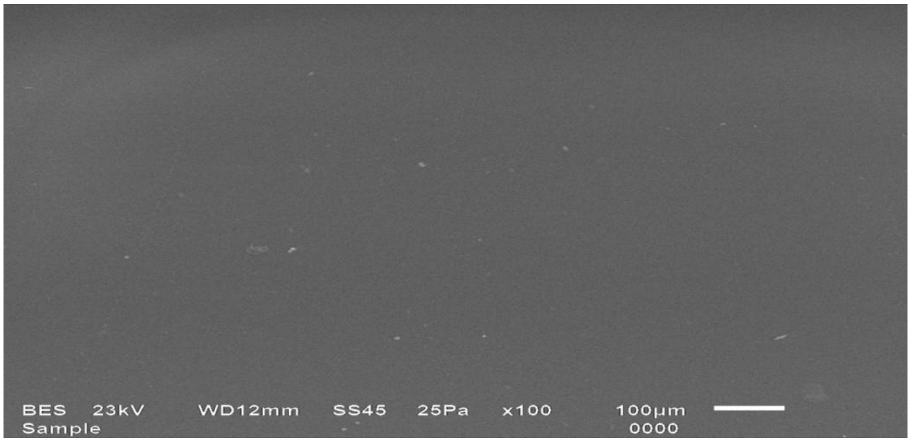


Fig 5.36 SEM Image of specimen with 0 %wt clay (pure EPDM)

5.6.1 Discussion of SEM results

SEM images of the specimens shows that clay particles are uniformly intercalated but there are visibilities of white spots somewhere within the images of few samples at micrometer level. It may be due to the reason of coagulation of many clay particles together instead of combining with the elastomer properly. Overall uniform intercalation can be concluded from the SEM observations of the samples which indicate that nano composite formation take place of the elastomer with clay.

No conclusion can be drawn about ultrasonication from the SEM results of the specimen. SEM images of 4 hours post ultrasonication and 6 hours post ultrasonication look similar to each other at a particular loading level of clay. While effect of clay percentage can be seen from the SEM results as with five percentage weight of clay, the particles are more visible at micro level instead of three percentage weight and two percentage weight clay specimens indicating that with the increasing percentage of clay nano composite formation becomes difficult.

5.7 RESULTS OF TGA ANALYSIS

Graphical representation of TGA analysis between percentage changes in weight with temperature is shown in figure 5.37

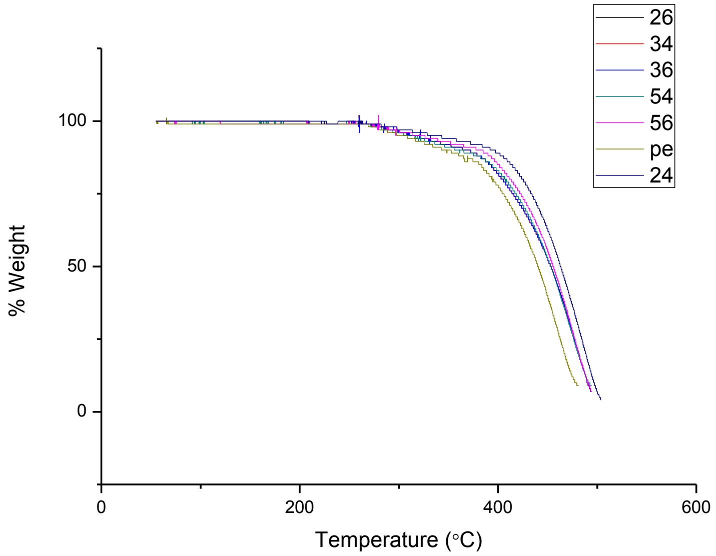


Fig. 5.37 TGA analysis graph between %weight of the specimens and temperature

In this graph weight percentage weight change of every specimen is shown with different colour. Here the color lines shown by the numbers 24, 26, 34, 36, 54, 56 and pe are coded as ’24’ indicates two percentage weight clay and four hours post ultrasonication. Similarly ‘26’ indicates two percentage weight clay and six hours post ultrasonication and so on. Here ‘pe’ indicates the EPDM+Glass fibre specimen.

5.7.1 Discussion of results of TGA analysis

TGA analysis of the specimens show that the percentage decrease in weight starts at higher temperature for nanocoposite specimens as compared to EPDM+Glass fibre specimen indicating that thermal stability has been increased with the addition of nano fillers. It can also be judged that increase is more in six hours post ultrasonication specimens as compared to four hour post ultrasonication specimens.

6.1 CONCLUSION :

The main points which can be concluded from the present work study are as given below

1. Tenslie properties get improved by the addition of nano clay particles to the elastomer and by the reinforcement of glass fibres. But the increment was not up to the extent which was expected as given by Zheng et al. for EPDM/ clay nano composites without fibre reinforcement. Poor physical bonding between glass fibre and elastomer may be a reason for it.

2. Flexural properties also get improved by the addition of nano fillers to EPDM rubber. Large gain in all the flexural properties are shown by the glass fibre reinforced EPDM/clay nano composites as compared to glass fibre reinforced EPDM+Glass fibre. The values of flexural properties has changed to almost double of the values which are shown by the neat EPDM. Although there is not so much physical significance of flexural properties of an elastomer as it can be bend very easily taking almost negligible load. Yet we will conclude that flexural properties get improved by the addititon of clay particles to the neat EPDM.

3. Solvent swelling measurements shows that chemical stability of nano composites are improved by the addition of nano particles to the EPDM+Glass fibre as weight gain is less for nanocomposite specimen after 6 hours immersion in toluene as compared to EPDM+Glass fibre specimen similarly for water, nano composite specimen show less weight gain after 36 hours as compared to EPDM+Glass fibre specimen indicating that hydrolytic stability has improved

4. Thermo gravimetric analysis of nano composite specimen and EPDM+Glass fibre specimen give a clear indication that thermal stability of nanocomposites has been improved as compared to neat EPDM specimen. Highest thermal stability in all the specimens is shown by sample with 2 weight percentage and treated for six hours post ultrasonication specimen.

5. Results of X-Ray diffraction of nanocomposite specimens showed that only 3 weight percentage clay and 6 hours post ultasonication specimens get properly intercalated by the nano fillers. It shows that this composition is actually a nano composite.

6. Scanning electron microscopy show a proper dispersion of the nano fillers with 2 weight percentage and 3 weight percentage of clay but show aggregation of clay particles with 5 percentage weight clay. Although XRD results have proved that nano level intercalation is just achieved with 3 percentage weight clay and 6 hours post ultrasonication yet from micro level observation of SEM it seems to be that clay is uniformly distributed all over the EPDM matrix for the cases of 2 percentage weight and 3 percentage weight clay addition.

6.2 FUTURE SCOPE OF THE WORK:

The work which can be preceded in this area for future studies as given below

I. Behavior of glass fibre reinforced EPDM/clay nanocomposite can be checked with curing aspects by using suitable curing agent.
II. Glass fibre can be replaced with carbon fibres or jute fibres for the future study .
III. Comparative study for glass fibre reinforced EPDM/clay nanocomposite and carbon fibre reinforced EPDM/clay nanocomposites can be done.
IV. Bio-degradability aspects of the nanocomposite can be checked if jute fibre is used for the reinforcement.
V. Higher amount of clay percentage can also be incorporated to check the behavior of fibre reinforced elastomeric nanocomposite .

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