Mechanical Characterization of Glass fiber / Nanoparticles – Epoxy Hybrid Polymeric Composites

By

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Dedication

I dedicate this work to my parents, whose unwavering support and confidence in my abilities has made this work much easier

Acknowledgements

All praise belongs to Allah Almighty, the Most Benevolent, the Most Merciful, who has granted me the strength, courage and willpower to complete my work, and to overcome all the impediments that come in my way. I consider myself, highly fortunate to be able to complete this work in the time allotted to me.

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Abstract

Utilization of fiber composites for development of new and modification of already present structures has increased largely in the past few decades. Fiber Reinforced Polymer composites have many qualities like corrosion resistant, longer life time, less weight, specific stiffness and high strength are effortlessly built, and can be custom-made to fulfill execution prerequisites. Fiber Reinforced Polymer composites are ordinarily manufactured utilizing a polymer framework, for example, vinyl ester, polyester or epoxy, and protected with different evaluations of glass, potentially aramid fibers or carbon, for auxiliary applications. Because of its favorable attributes, Fiber Reinforced Polymer composites have been incorporated into new development and modification of structures through its utilization as protection in bridging decks, seismic updates, outside support and concrete. The aim of this research is to provide enhancement in the mechanical strength of FRP composites by addition of Nano particles. Various Nano particles can be utilized in this regard like nanoparticles of Titanium oxide. Nanoparticles of Aluminum Oxide, nanoparticles of Zinc Oxide, nanoparticles of Silicon oxide and many others.

The advantages of Fiber Reinforced Polymer composites can be acknowledged from its physical qualities and their great potential in creating auxiliary frameworks with service time surpassing conventional materials. The composite is light in weight thus it can bring about faster construction and also lowers the costs of developing it. This brings about lessened ecological effects. Fiber Reinforced Polymer composite materials have many attributes like great stiffness & strength. Due to these attributes, the Fiber Reinforced Polymer composites requires less amount of material to accomplish comparative execution as conventional materials. This brings about reduction in production of waste and it also limits the assets utilized. One of the essential

purposes behind addition of the fillers that are inorganic to polymers is to enhance their mechanical execution through improvement in durability of a composite and the quality or the firmness of the composite. Thorough research has been carried out on the impact of particles of Nano sized silica in enhancing various properties of various polymers.

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Chapter 1

Introduction

There have been enormous studies on the Polymer-nano filler-composites in the past few decades. Mostly these are organic polymers matrix incorporated with inorganic nano-particles [1]. These mixed matrix composites have the combined advantages of organic polymers which includes ductility and flexibility, and inorganic nano-particles that provides thermal stability, rigidity and mechanical toughness, yet, the size and volume fraction of the nano-fillers characterizes the major advantage of their use [2]. The decrease in the magnitude of filler from micro to nano, corresponds to unique properties of mixed matrix composites as the small size increases the interfacial area. This increase in interfacial area crafts a substantial volume fraction even if the nano-filler loading is low. Ceramic [5], metal [9], glass [3, 4], rubber [10], thermoplastics [11, 12] and silicate [6-8] particles are strengthening mediators that have been effectively utilized for this purpose. The mechanical response of polymer-nano particle composite with respect to the effect of volume fraction and nano-particle size have also been numerously studied [13-17]. Based on the lengthways fracture propagation on the surface of particles and considering the interspacing between them, a small number of diagnostic and mathematical models have also been proposed. It has also been showed that there is a difference in the fracture occurrence mechanisms between the polymer composites filled with large, micro and nano sized particles. [18-21]. Amongst the many polymer nano-composites, the ones with silica have good mechanical properties, have been utilized in a wide range of applications that include automobile, aerospace and electronics industries and are frequently reported in literature. Over the past decade, research has expanded rapidly to improve the properties of nano-composites with silica. Research is being carried out on novel preparation and characterization techniques for silica induced polymer nano-composites, to enhance their mechanical properties and exploring their new applications.

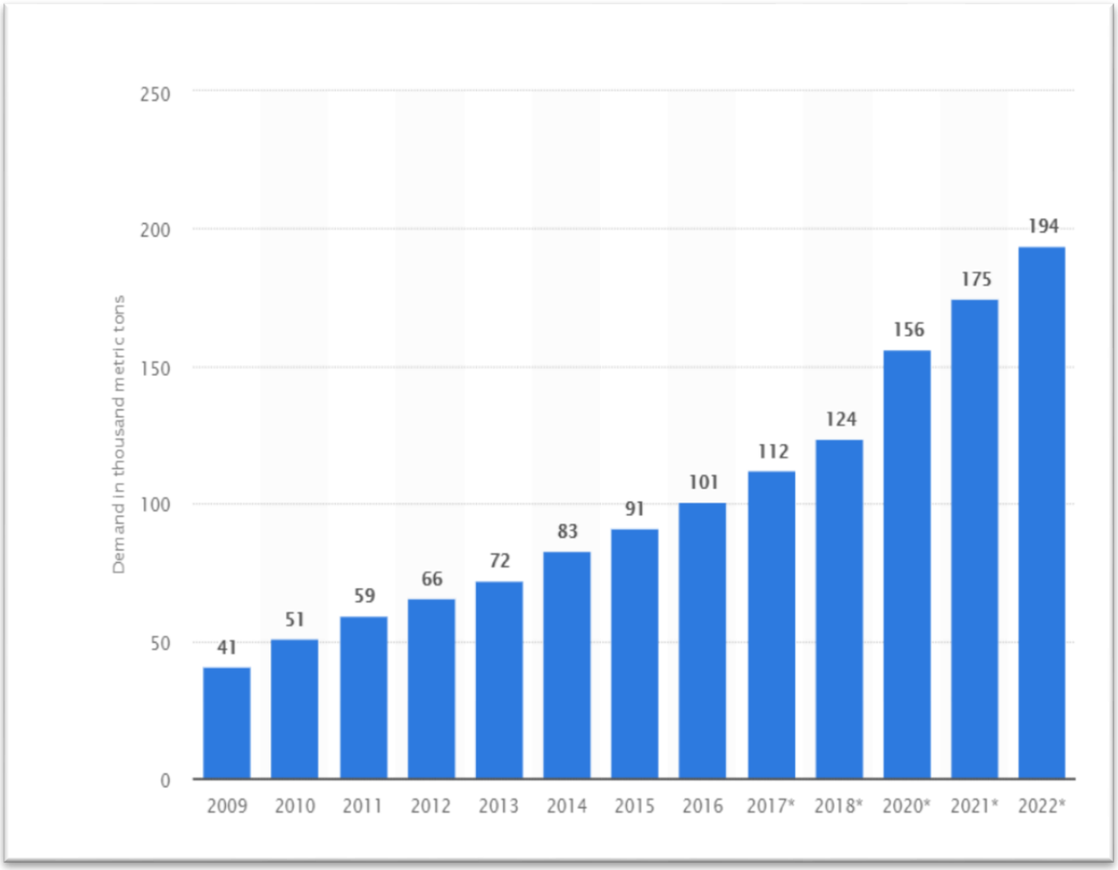

Figure 1-Demand for Glass Fibers

The demand for reinforced fiber plastics from 2009 to 2018 is provided in figure 1. Furthermore, a forecast from 2019 to 2022 is also displayed. As can be seen, a decade back the global demand for reinforced carbon fiber plastics reached 41,000 metric tons.

Comprehensive industrial fabrication of thermoset composite such as polyesters [22], vinyl-esters, phenols and epoxy, for premium applications in engineering is commonly accomplished by curing through autoclave, liquid infusion and filament winding [23]. The aforementioned processes are incompatible to be used in-line with nano-particle modified polymer resins. While nano-fillers in polymer base have been validated as an effective method to improve the realization of composites, film infusion in resins or resin film infusion is the only practicable technique which favors the rheological alteration of the polymer matrix in understanding fiber reinforced hybrid composites [24-25].

In comparison to predictive behavior composites at small loading percentages, the large surface area and aspect ratio of nano-sized particles improve the thermal and mechanical properties of polymer/nano-composites. The shape, size, dispersion quality, volume fraction and the contact between polymer and filler reportedly influence the properties of polymer/nano-filler composite. Nano-fillers such as nano-fibers and nano-tubes of carbon have been extensively studied for their applications in polymer composites [26, 27]. Characteristics of layered silicates, nano-silica and nano-clay and their interaction with polymer matrix are also remarkable. Nano-silica, amongst all aforementioned organic and inorganic fillers holds a distinct place because of its low cost, chemical structure, surface modification simplicity and specific intrinsic properties. These inorganic fillers have shown noteworthy improvements in impact, mechanical and thermal properties [28]. Substantial work has also been done of epoxy nano-composites reinforced with nano-silica [29–34]. Significant consideration has been given to composites reinforced with fiber and mongrelized with nano-fillers. Improvements in tensile strength and magnitude of three phase carbon/epoxy/CNT was reported by Lee et al. [35] with 1 wt.% CNTs modified with silane.

The advantages of Fiber Reinforced Polymer composites can be acknowledged from its physical qualities and their great potential in creating auxiliary frameworks with service time surpassing conventional materials. The composite is light in weight thus it can bring about faster construction and also lowers the costs of developing it. This brings about lessened ecological effects. Fiber Reinforced Polymer composite materials have many attributes like great stiffness & strength. Due to these attributes, the Fiber Reinforced Polymer composites require less amount of material to accomplish comparative execution as conventional materials. This brings about reduction in production of waste and it also limits the assets utilized. One of the essential purposes behind addition of the fillers that are inorganic to polymers is to enhance their mechanical execution through improvement in durability of a composite and the quality or the firmness of the composite. Thorough research has been carried out on the impact of particles of Nano sized silica in enhancing various properties of various polymers. The addition of these nanoparticles enhances the mechanical properties along with the thermal characteristics. For instance, Shao-Yun Fu et al. studied the impacts of size of particle, loading of particle and particle and network adhesion on various mechanical properties of the composites for example sturdiness, rigidity of the composites and the strength of the composites [36]. They did it for a scope of particulate composites. These composites comprised of both Nano and micro sized fillers [37]. Researchers have used particles of Nano sized silica in mix with particles of Nano sized clay, in epoxy systems, and contemplated their impact on various mechanical characteristics of the systems [38]. Large concentration of Nano silica in composites results in improved properties of the specimen [39, 40]. An increase 58% and 19% was found by Jumahat et al. [41, 42] in the compressive strength and modulus respectively in an epoxy lattice. It was achieved by adding Nano silica (13 wt.%). This suggests good nanofiller matrix interactions.

Fibers characteristics define the tensile properties of a polymer or a fiber composite. Qualities of the resin lattice define the pressure and other properties along the thickness. The most generally utilized polymer framework for cutting edge composite materials is epoxy resin. Throughout the years, many endeavors have been made to change epoxy to enhance the lattice ruled composite properties. By including either fillers [43, 44] or elastic particles/rubber [45, 46]. The inclusion of elastic particles/rubber diminishes its strength and also diminishes its modulus. But this inclusion enhances the epoxy's fracture toughness. While the inclusion of fillers enhances the strength of epoxy and enhances the modulus of epoxy. But this inclusion of filler diminishes its fracture toughness. The inclusion of fillers also enhances the epoxy's heat deflection temperature [47]. As epoxy, particles having size in the range of micro and nano size have been investigated as filler to deliver elite composites.

Introduction to Common Nano particles

1.1.1. Silicon oxide nanoparticle (SiO_2)

Silica nano particles usually found in a form of colloidal solution or white color powder. It's one of unique characteristics is greater surface area and non-porous surface which can produce greater contact when fabricated in a polymer composite. An extraordinary position is grasped by nano silica due to its various characteristics for example minimal cost required, simplicity of changes in surface for enhanced network adhesion, its chemical structure and many other natural properties.10 nm sized Nano silica used for enhancement of strength in fiber glass composites. By addition of Nano silica tensile strength of composite increased whereas viscosity of composite marginally decreases. Glass transition temperature remained un affective.

1.1.2. Titanium oxide nanoparticles (TiO_2)

In discussion to properties of Titania nanoparticles large value of (RI) refractive index and UV light absorption have been seen effective for use in composites. these nano particles as a white colour pigment in food colouring, paint, various products for care and as a sunscreen with UV absorber. The photo related activity of TiO_2 has observed to be rely on various selective properties: phase of crystal, good surface area, defined crystal properties, surface morphology, lattice properties, and crystalline phase. Titania nano particles synthesised polymer composites is playing key role in enhancing various properties. Nano composites containing Titania nano particles due to its specific structure gives improved mechanical characterisation.

1.1.3. Aluminum oxide nanoparticles (Al_2O_3)

Adding alumina nano particles to fabricated nano composite improved bending capacities and improved water repellant properties. The A.C conductivity and dielectric constant would be very improved at certain range of frequencies by incorporating alumina nano particles. The more concentration of alumina nano particles, AC conductivity will be high and low dielectric constant were obtained at various range of frequencies. X-ray diffraction as well as tensile measurements were studied.

1.1.4. Zinc oxide nanoparticle(ZnO)

Because of their very peculiar framework and small size ranging from 1nm-100nm, Zinc Oxide Nano sized particles display greatly enhanced biological and physio-chemical characteristics in comparison to Zinc Oxide in bulk. They are a versatile material with great electrical, optical and catalytic attributes. They are reasonable for an expansive scope of uses, for example, sensors for gas, Ultra-Violet shielding, bio-sensing application, semiconductors and photo-degradation of contaminations. The techniques for Zinc Oxide nano particles generation incorporate the macro-emulsion technique, vapor deposition method, sol gel process, hydro thermal synthesis method and precipitation methodology. [48-49].

Some common methods to disperse nano particles in epoxy resin or composites are discussed below.

1.2. Outline of the Thesis

1st Chapter details the introduction to enhance the mechanical strength of FRP composites by addition of Nano particles. Various Nano particles can be utilized in this regard like nanoparticles of Titania. Nanoparticles of Aluminum Oxide, nanoparticles of Zinc Oxide, nanoparticles of Silica and many others.

2nd Chapter includes examples of the research work carried out to enhance the mechanical strength of FRP composites by addition of Nano particles.

3rd Chapter summarizes the experimental techniques used to synthesize some of nano particles, and also the characterization techniques used to study their various physical and chemical properties.

4th Chapter studies the results obtained from different characterization techniques for all the synthesized polymer composites, and these results are then discussed in detail to explain their significance in my work.

5th Chapter gives a concise summary of the entire work and also lists recommendations for future work

Chapter 2

Literature Review

Reinforced fiber composites are becoming favorite and preferable materials in aerospace, marine, automobiles, structural materials, sports materials railways and many more in accordance to their large stiffness and mechanical strength. Generally, the strength of polymer composite is described by the features of fiber, whereas, the compressive features for cross-section are styled by the features of its polymer phase. The most widely employed matrix for polymer composite materials is liquid resin. Large number of tries have been done over the years to alter resin by the addition of rubber or filler particles, so in results the composite tensile strength is increased. By adding fillers and rubber particles are indirectly proportional. The former decreases the fracture toughness while the latter increases it. On the other hand, the same phenomena are inversely observed on the addition of both fillers and rubber particles on the modulus and strength. Addition of fillers also improves the temperature of heat deflection [50]. Recently, micro and Nano sized particles are being considered as fillers for epoxy in order to create better performing composites with improved properties. Silicon Carbide (SiC) whiskers were used by Wang et al. [51] lateral to the hinge of composite layers in whole process to enhance fracture properties. Sherman et al. [52] reformed unifacial carbon/epoxy composite by applying tiny bits of alumina. Mahfuz and his team [53] witnessed a 39 % improvement in flexural strength by instilling 1.5 wt.% nanoparticles of Sic in carbon/epoxy composite. Gojny et al. [54] described the effect of CNTs on the electrical and mechanical properties of glass fiber reinforced plastic (GFRP).

Because of the following surprising characteristics in nano-phase hybrid i.e. reduction in permeability of gas, high resistance against particular solvents, enhanced mechanical stability and improved flammability properties these have gained more acceptability and acquire surprising interest among researcher. Nano-phase hybrid are composed of organic polymer and inorganic filler that is mostly clay mineral of silicate layers [55]. Numerous hybrids of polymer/clay minerals have been synthesized so far by introducing clay in following polymers: Polyamides [56], PI [57], epoxy [58], PU [59], PET [60] and finally PP [61]. These nano-filler should have the following properties to make them compatible for used in polymer based nano composite, i.e. high aspect ratio, more surface area to volume ratio of nano-size particle of clay. These polymer/nano hybrid also acquire low filler volume fraction because of the above mention features. In case of 1 nm thick interface approximately 0.3% of entire volume of polymer can be filled with micro-particle composite and in contrast around 30% total space of polymer can be occupied with nano-size particle composites. Conversely, due to increase specific area ultimately lead to coalescence of nano-composites that decrease their strength as a result of stress concentration. Main parameter for synthesizing polymer/nano-base composite is the incorporation of optimized concentration of clay in a polymeric matrix.

Different groups have been given profound study to the assimilation of nano-filler (clay) into base matrix for strengthening fiber reinforced composites [62]. Xu and Hoa [63] synthesized carbon fiber by adding clay into epoxy as base matrix by employing hot melt lay-up in addition autoclave process. Bozkurt et al. [64] found that the flame resistance of epoxy fiber can be improved by the addition of MMT clay. Karmann et.al [65] enhanced the flexural strength of the glass fiber by making hybrid of layered clay and epoxy as base matrix. Subramanian and Sun [66] synthesized composites by using vacuum assisted wet lay-up method, they stitched unidirectional E-glass fiber and an epoxy vinyl ester resin through above mentioned method. In addition, the compressive strength of composite fiber increases due to presence of nano-particle of clay. Chowdhury et al. examined the incorporation of nano-size particle clay into polymeric base matrix for the improvement of flexural properties as well as thermal resistance of the fiber. Lin et al. investigated the influence of fiber orientation on clay scattering in the layered clay/epoxy hybrid composite. Furthermore, the unidirectional glass fiber was oriented parallel and perpendicular to resin and fabricated by using state of art technology "VARTM" (vacuum assisted resin transfer modeling). This orientation of nano-particle in glass fiber in multi-directions have much influence

on the mechanical properties of polymer/clay composite and further enhancement would be resulted by increase in clay loading. Miyagawa et al. observed the effect of integration of bio-compatible based clay particle into epoxy nano-composite for carbon fiber composite. Results obtained that no increase in flexural strength and modulus observed by introducing of nano-clay in epoxy fibers.

In this study, a uniform homogenized molecular mixture of epoxy resin and nano-size particles of clay was assimilated by using high intensity ultrasonic liquid processor. Furthermore, effect of concentration of nano-clay on the thermal and mechanical characteristics of epoxy were analyzed by conducting the following tests: DMA, TGA and three-point bending test. After finalizing the optimized concentration of clay in epoxy resin, nano-phase carbon/epoxy composite were fabricated by using VARTM. For the assessment of mechanical strength following tests were conducted: flexural test, tensile and fatigue test. And for the assessment of thermal performance TGA and DMA were employed.

2.1. Composite preparation

The main concern in composite preparation is the mixing process and the obtained homogeneous mixing of nano silica in polymer composite. Therefore, prior to the composite preparation, the compatibility between the two components has to be assured to avoid silica agglomeration, using one of the methods described in the previous section.

The simplest method of nano silica composite preparation is homogenous mixing of silica into the polymer composite. i. e., by melt or solution blending. Besides sol-gel method, melt blending and in-situ polymerization are also widely used among the preparation techniques.

2.1.1 Blending

Melt blending is normally used method in composite preparation due to its efficiency and operability. In the process, the polymer and the inorganic filler (i.e., silica) are sheared in the melt at a temperature which is equal or more than the melting point of the composite. Under suitable conditions the material exfoliates and disperses to some extent. This technology is very versatile and can be applied to various polymers. It is also possible to add swelling and capitalizing agents in order to improve the exfoliation and reach a better adhesion between the two major components. Solution blending, on the other hand, is a liquid phase powder processing process that allows a excellent molecular mixing. Solution blending can be achieved by either dissolving only the polymer matrix or dissolving both the matrix and the nanoparticles.

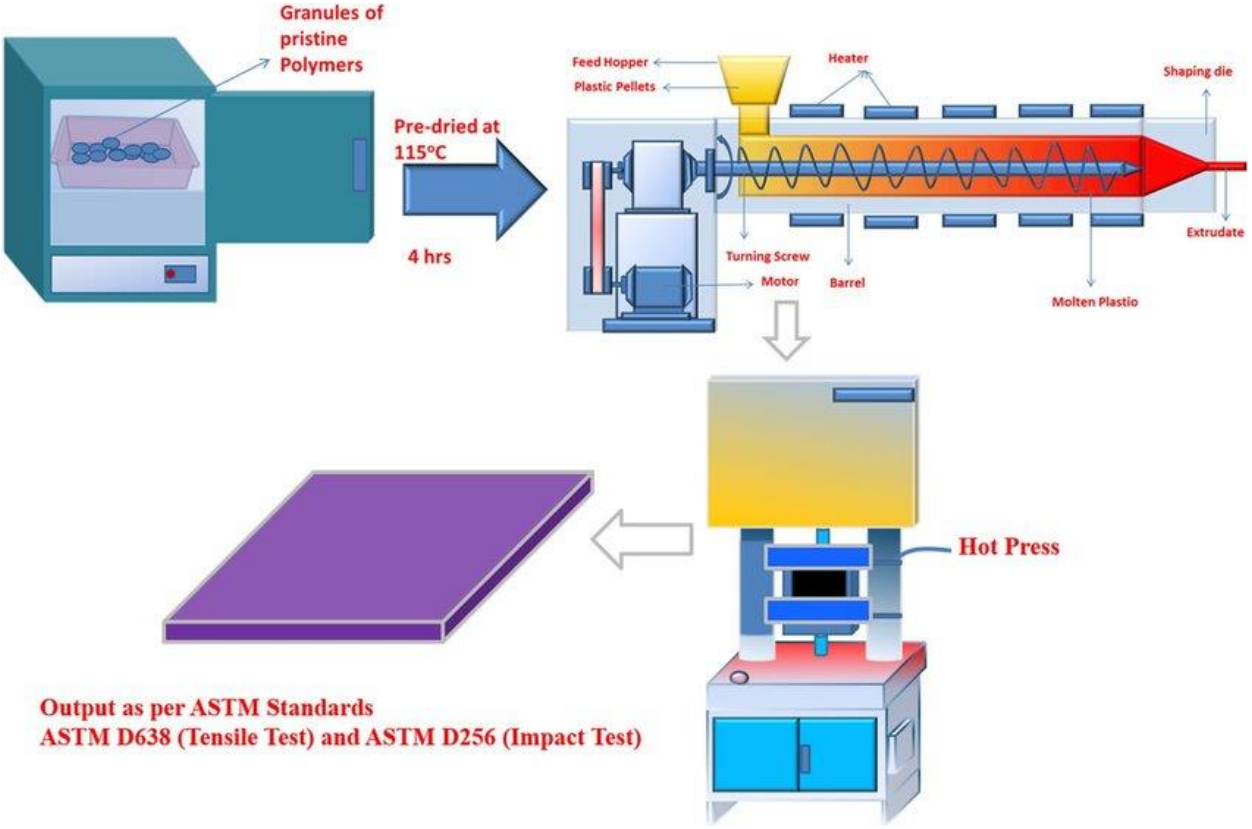

Figure 2-Melt Blending

2.1.2 Sol-gel process

The sol-gel process is a synthesis route consisting of the preparation of a sol, the effective gelation and the solvent removal. Within the past decade’s sol-gel process have been widely used novel organic polymer composites or inorganic polymer nano-composite. In the field of composites, the aim is to carry out the Sol Gel reaction in the presence of polymer molecules have various functional groups that enhance their bonding to the inorganic section.it proves to be an affective increasing strength method that can increase filler particles within a polymer matrix.

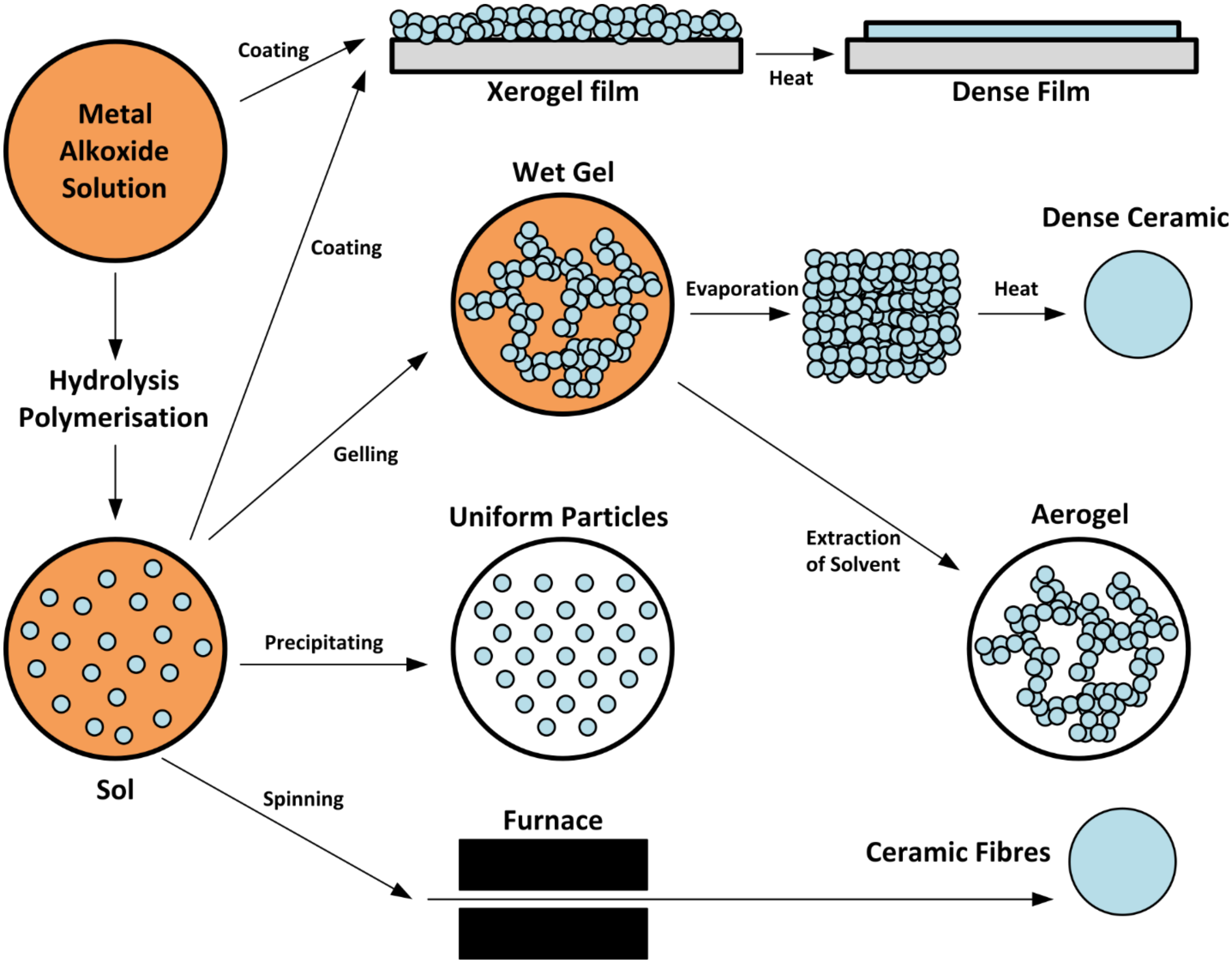

Figure 3-Sol Gel Process

2.1.3 In-situ polymerization

In situ polymerization is a very successful and fast way to build a nano-composite. In this process, the inorganic fillers have initial treatment with specific surface modification elements and then mixed directly to the liquid resin during the polymerization. With the help of solution method, nano particles are introduced to a composite solution by the help of solvents such as THF, chloroform and acetonitrile to integrate the polymer composite and nano particles.

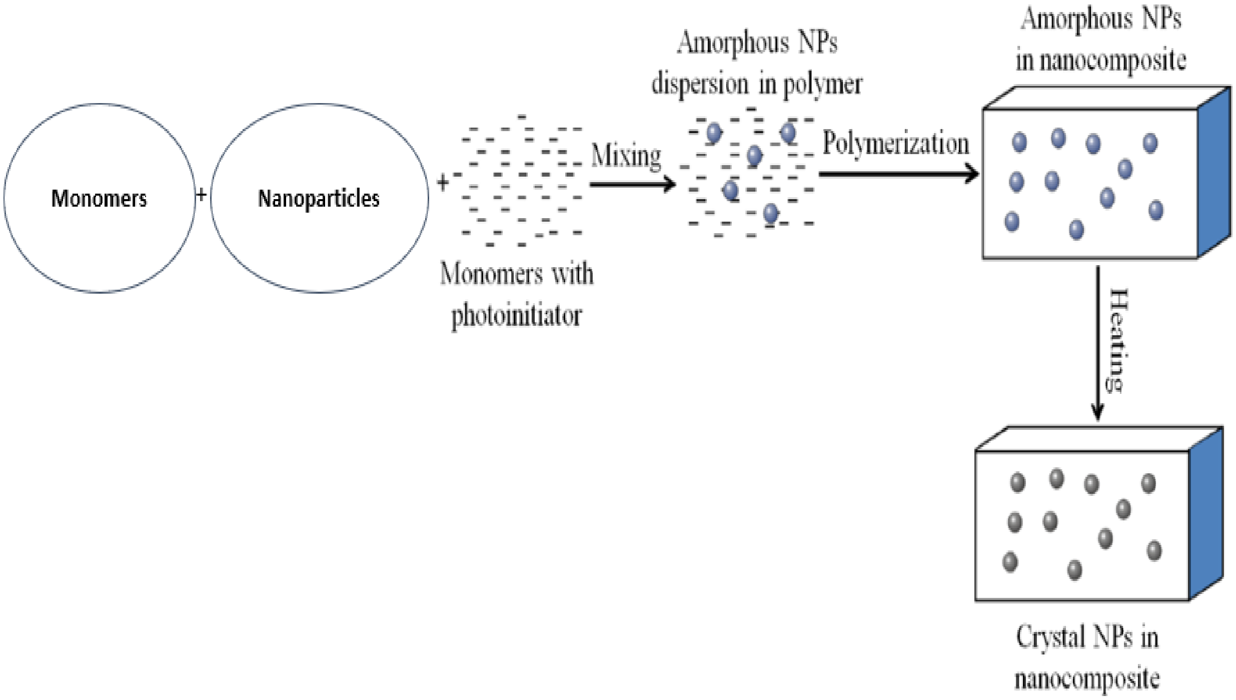

Figure 4-In Situ Polymerization

2.1.4 Resin film infusion process (RFI)

The Fabric is sandwiched between epoxy resin films. This sandwich of the resin film and fabric is then placed atop of a mold plate made of metal. The reason for doing this is to assure that the fabric will absorb the film. This sandwich of resin film and fabric is then cut according to our requirements. These slivers are placed atop of each other to get the thickness required. Vacuum is applied and measured, using a sensor, to the resin film and fabric sandwich. This can be done in a convection oven by vacuum bag method. This is done for the curing of the resin film and fabric sandwich. Then the sandwich is heated to a maximum temperature of 80°C at a heating rate of 2°C and this temperature is held for 30 minutes. The specimen is then heated at 120°C for 60 minutes. This is done to cure the specimen. After this the heating is turned off and we allow the specimen to cool. It is cooled down to 25°C slowly. Then it is demolded [23]. Synthesis of various hybrid composites is possible at different concentrations. Compared to respective control composite specimens, their characteristics have been appraised.

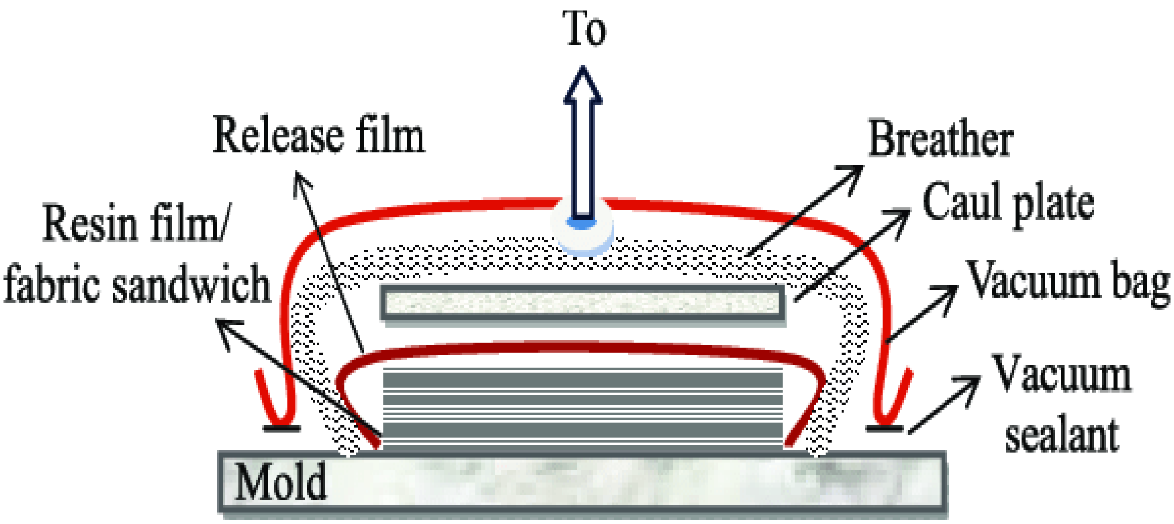

Figure 5-Resin Film Infusion Process

2.1.5 Conclusion

Through a comprehensive literature review of the techniques and study of current industrial trends across the globe, melt processing was deduced to be the most common procedure for polymer nanocomposite development. However, the most attractive process for synthesis of fiber reinforced composite is RFI process which was chosen for the current study that focuses on reinforcement of fiber glass with nanofillers The Conventionally autoclave based procedures are utilized in the aeronautic industry for enhancing structural segments. RFI can possibly supplant autoclave-based procedures as a financially attractive option. RFI process is preferable for specific composite structures. Materials synthesized by Resin Film Infusion process have fantastic auxiliary properties tantamount with autoclave-based procedures. Materials manufactured by Resin Film Infusion process have brilliant drapability along with close to zero content of void. Resin Film Infusion method additionally guarantees the substantial reduction in capital cost. In addition, for huge amount of production this is the main procedure that encourages fabrication of composites with consistently scattered Nano materials. All other regular procedures neglect to accomplish this as scattering remains a noteworthy obstacle. Next chapter describes in detail the experimental methods.

Chapter 3

Experimental Methods

3.1. Materials Used

All the chemical materials utilized for the nano alumina synthesis were bought from Sigma Aldrich. Aluminum-nitrate-nonahydrate {Al $(NO_3)_3 \cdot 9H_2O$}, Urea {$CO(NH_2)_2$}. In the production of zinc oxide nano particles precursors utilized was Zinc-Sulphate heptahydrate (Molecular weight=287.49gram/mol, company named Sigma Aldrich), whereas distilled water is the solvent for process.

Table 1-List of Materials

S. No.	Material Name	model	Manufacturer
1	di-glicidyl ether of bisphenol A	CAS-1675-54-3	Sigma aldrich
2	Silicon di oxide Nano particles	CAS-112945-52-5	Sigma aldrich
3	Titanium di oxide Nano particles	CAS-13463-67-7	Sigma aldrich
4	aluminium di oxide Nano particles	Synthesized	synthesised
5	Zinc di oxide Nano particles	Synthesized	synthesied

3.2. Synthesis of aluminum oxide nano particles

Large number of methods are used for production process of aluminum nano particles. among all these processes the best process is combustion solution process. This process is firstly savior of energy and secondly its environment friendly process in manufacturing of low budget nano-adsorbents. In these days study, combustion solution process comprises little changes that primarily consist of heating action taken place in furnace. The low budget aluminum-nitrate was used as oxidizing agent and urea was taken as a fuel. Mixture of these ingredients was taken in account for the ratio of one to one (1:1). Mixture solution is heated on a hot plate as a pretreatment. After preheating, gel like solution is obtained and dehydration is done up to temperature of 500 degree Celsius. Mixture is than left in hot furnace for about 1 hour in order to get more purity. Fluffy type product is obtained which is placed on mortar and pestle in order to ground. The produced nano-particles of alumina were characterized by XRD and utilized in reinforcement purpose.

3.3. Synthesis of zinc oxide nano particles

Zinc oxide can be synthesized using many different methods including micro emulsion synthesis, spray drying, sol-gel method, pyrolysis, controlled precipitation, RF plasma synthesis, vapor transport process etc. controlled precipitation method was used here for the synthesis of zinc oxide nanoparticles

Nano-particles of zinc synthesized by the help of various methods which contains synthesis of micro-emulsion process, drying process using spray, sol-gel technique, under control precipitation, RF synthetic plasma, vapor transportation process etc. control precipitation process is used here for production of nano-particles of zinc

Hepta-hydrate NaOH mixed dropwise in aqueous solution of zinc-sulphate. Molar ratio was used one ratio two (1:2). Mixing action has been done and continue for almost eighteen hours. Firstly, peracetate are achieved having white color. Than filtration and washing action has been done on precipitates. Washing action has been carried out by distilled water. Drying action is achieved by the help of muffle furnace kept at controlled temperature of 100 degree Celsius. This mixture is then turned into fine powder by grinding. This grounded mixture is subjected to calcination at various temperature.by increasing calcined temperature there will be decrease in yield. Zinc oxide nanoparticles were characterized using XRD and used for reinforcement of fiber.

3.4. Composite fabrication by mixing of polymer matrix with FRP

Composites were fabricated through resin-film infusion process (RFI); [21, 22] methodology involved is as follows. Fig. 5 illustrates the Resin Film Infusion methods schematics.

The Fabric was sandwiched between epoxy resin films. This sandwich of the resin film and fabric was then placed atop of a mold plate made of metal. The reason for doing this was to assure that the fabric will absorb the film. This sandwich of resin film and fabric was then cut according to our requirements. These slivers were placed atop of each other to get the thickness required. Vacuum was applied and measured, using a sensor, to the resin film and fabric sandwich. This was done in a convection oven by vacuum bag method. This was done for the curing of the resin film and fabric sandwich. Then the sandwich was heated to a maximum temperature of 80°C, heating rate of 2 degree Celsius and this temperature was kept for 30 minutes. The specimen was then heated at 120°C for 60 minutes. This was done to cure the specimen. After this the heating was turned off and to allow the specimen to cool. It was cooled down to 25°C slowly. Then it was demolded [23]. Synthesis of various hybrid composites is possible at different concentrations. Compared to respective control composite specimens, their characteristics have been appraised.

3.5. Testing and Characterization

3.5.1 Working principle of FT-IR Spectroscopy

FTIR or Fourier transform infrared spectroscopy is method which is applied to check the functional groups present in sample. Functional groups like silica, phenols are verified in addition carbon bonding with carbon and as well as with hydrogen is also checked by specific infrared rays. This testing also shows the bond shift in reference and fabricated sample. Infrared rays penetrate into sample to get information regarding its chemical properties. different functional groups can be identified by their specific peaks and curves.

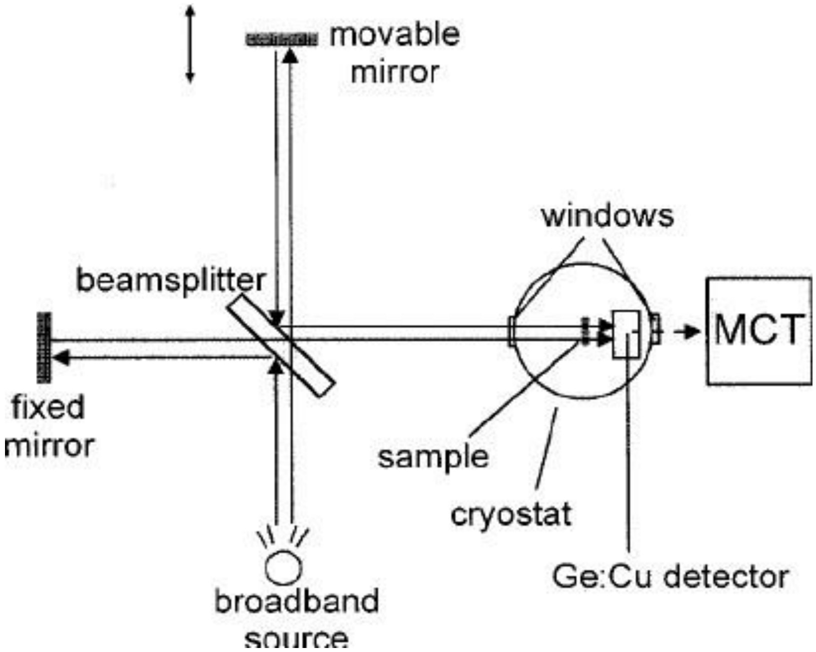

Figure 6- Working principle of FT-IR spectroscopy

3.5.2 Working principle of Scanning electron microscopy

SEM is a type of electron microscope.in this testing beam of electron is used to reveal surface morphology of tested sample. Scanned images are formed by the help of electron beam at different magnifications. This testing also approved the homogenous incorporation of nano particles in fiber glass layers which is extremely important to get better mechanical strength and toughness. Three types of magnification are used in this research which involves 5kx, 10 kx and 20 kx. images are shown in results portion.

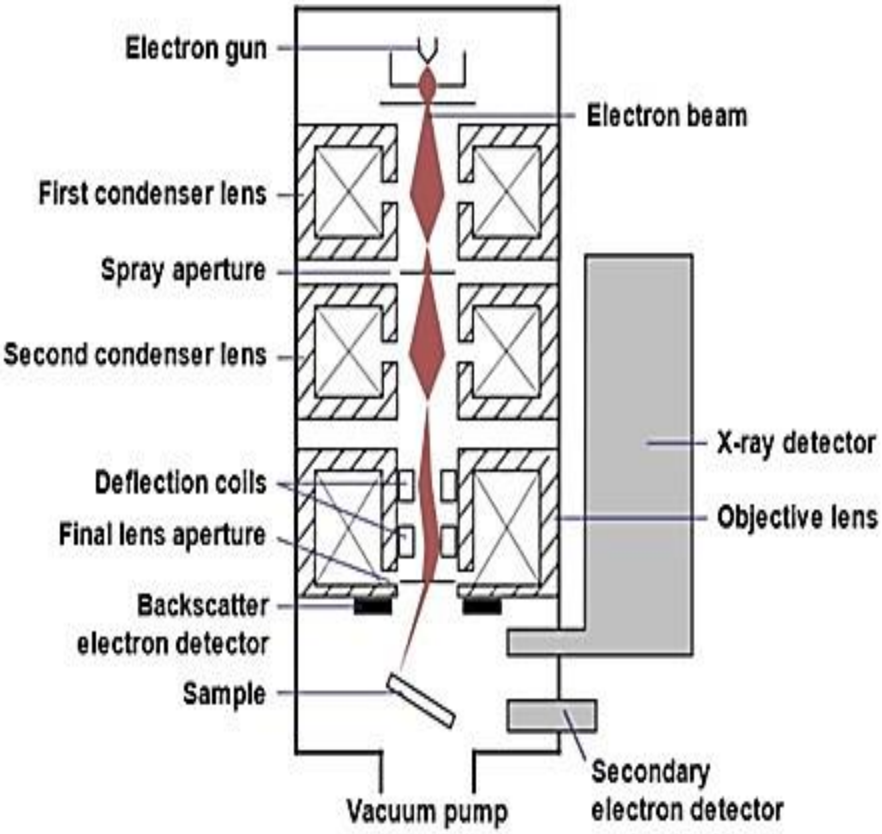

Figure 7- Schematic diagram of Scanning Electron Microscope

Working principle of Tensile Testing Machine

Universal tester or universal testing machine is used to check tensile strength, compressive strength. Stress strain curves are also be generated through this test. its apparatus is connected with computer by which we can select specific parameters to check mechanical strength. this machine consisted two jaws one is upper jaw and other is lower jaw between which sample is fixed.by the help of specific software force is applied on sample and shows results by help of graphs. Sample which is checked for tensile strength is selected according to standard ASTM 3039. Dimensions of samples are selected according to instructions of ASTM 3039. Velocity is kept at 0.1mm/mi. After applying this force tensile testing of reference and fabricated samples are checked.

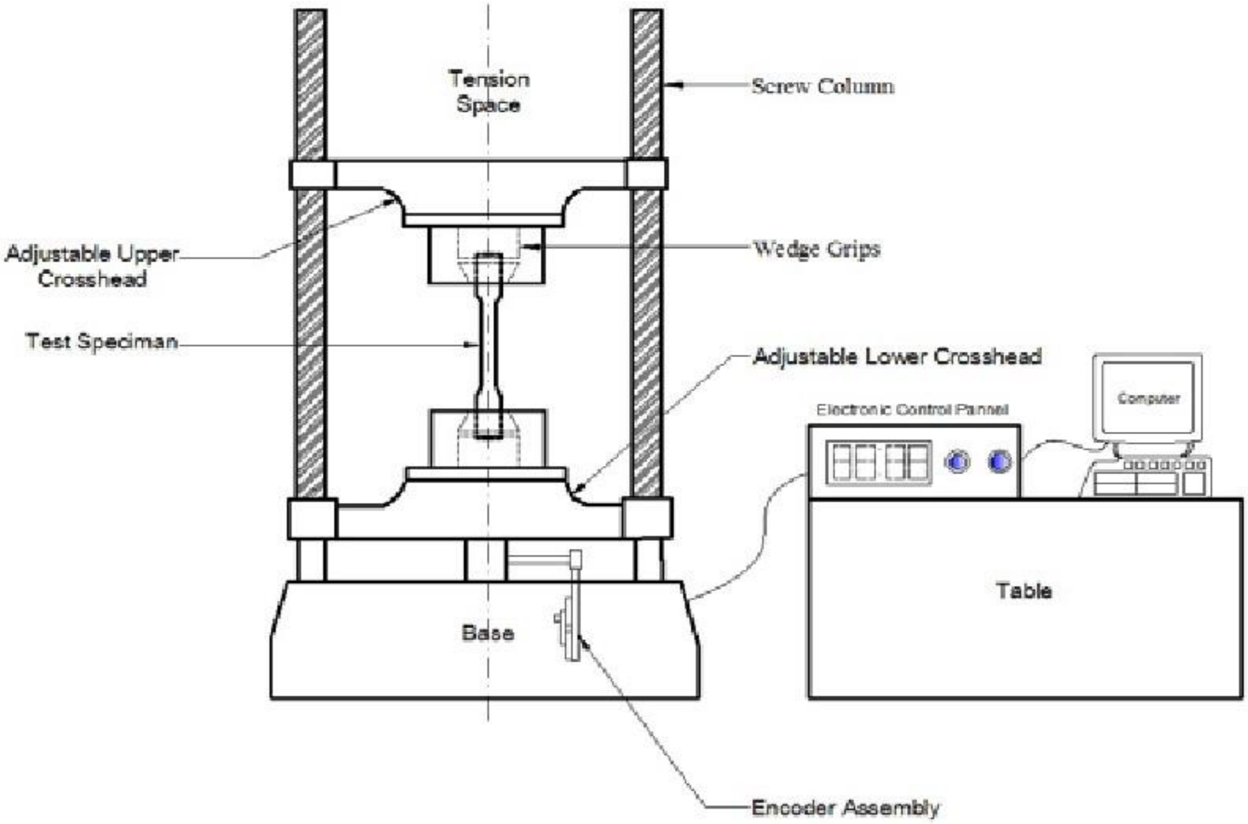

Figure 8- Schematic diagram of Tensile Testing Machine

3.5.3 Working principle of Differential Scanning Calorimetry

It is technique which involves temperature. Heat of various intensities is used to check various functions like glass transition temperature, melting and boiling point of controlled sample and sample to be compared both are examined to verify the difference. temperature of sample is adjusted and its behavior is noted with respect to temprature.in this article behavior of glass transition temperature is studied for reference composite and nano composite.

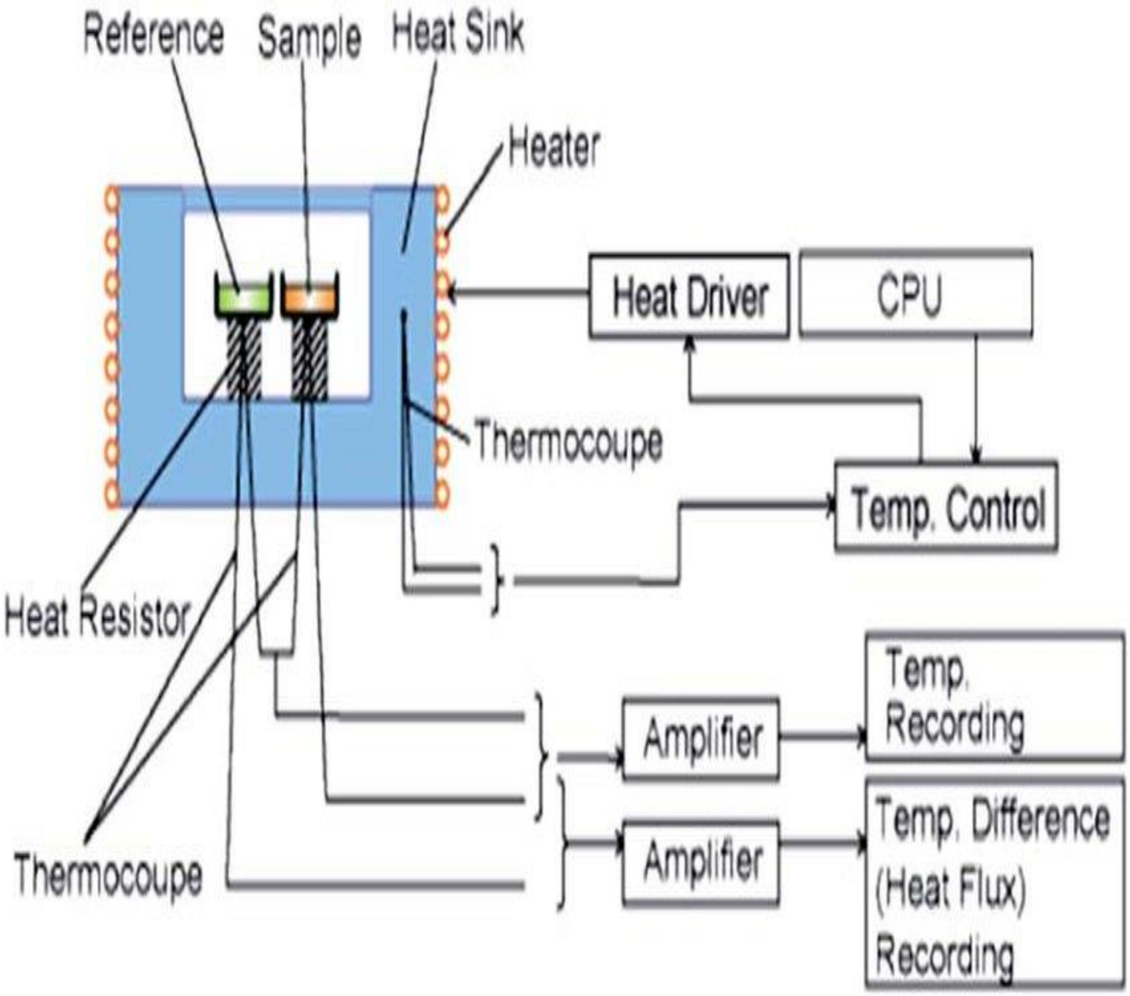

Figure 9-Schematic diagram of Differential scanning calorimeter

3.5.4 Working principle of X-Ray Diffraction

X-Ray diffraction is a very common technique using now a days to determine the structural properties of crystals. Space or gaps between atoms and different layers of atoms can be also determined by diffraction of X-Rays. A tube which contains cathode ray usually named as cathode ray tube is used to generate **x-**Rays, such generated **x-**Rays are then filtered which make it monochromatic. A component of device known as collimator is used to focus the radiation on a given sample. Phenomenon of interreference is done by interaction of these **X-**Rays with the sample. After diffraction these **X-**Rays are collected and then results of these **x-**Rays after diffraction process gives lot of info. about sample.

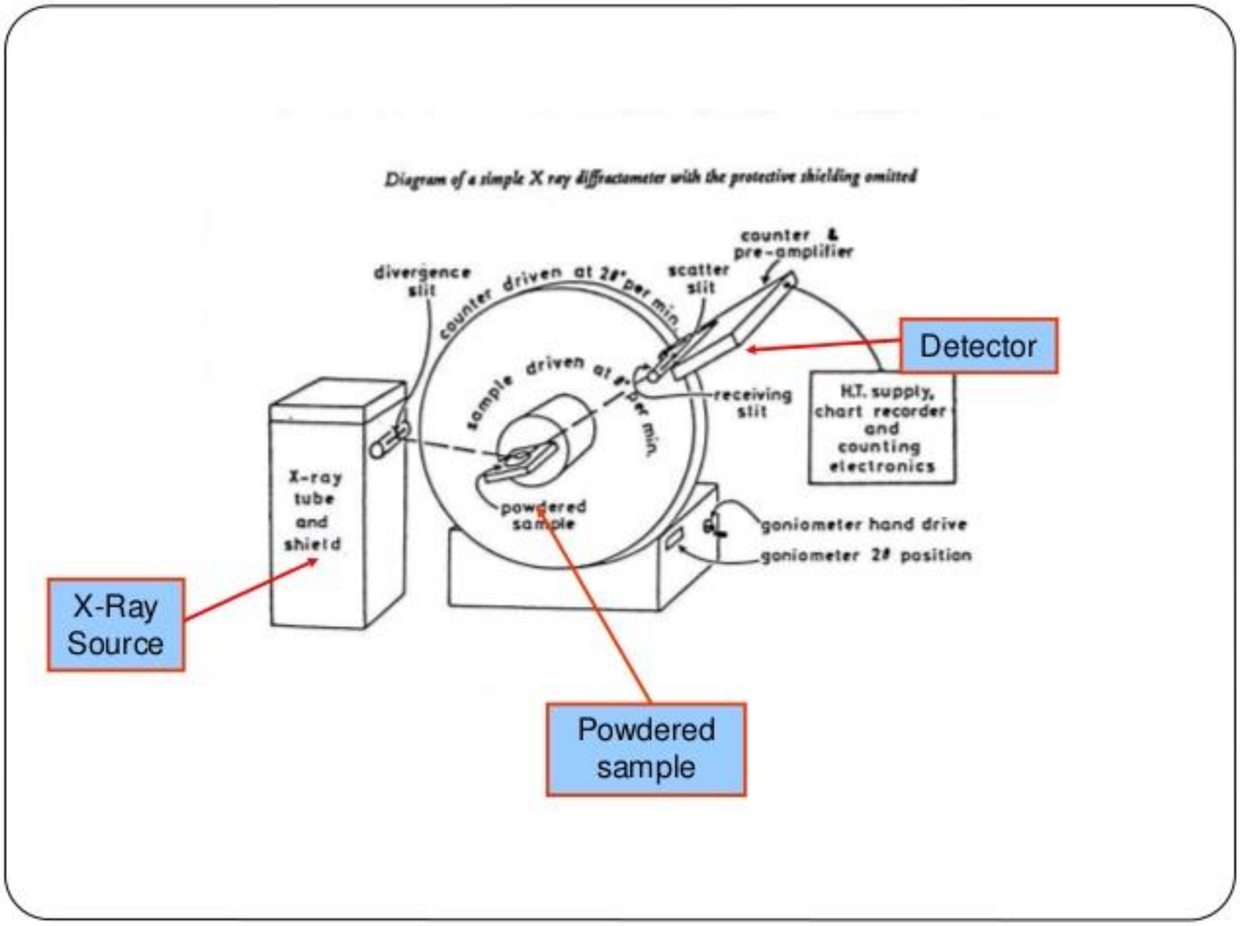

Figure 10-Schematic diagram for X- Ray diffraction

Chapter 4

Results and Discussion

4.1. Characterization techniques

Various characterization techniques are used to check the nano composites for physical and chemical properties. Techniques used for characterization are as follows:

- Fourier Transform Infrared Spectroscopy is technique which is involve to check the functional groups present in sample
- Scanning electron microscope is a type of microscope.in this testing beam of electrons are used to reveal surface morphology of tested sample.
- Differential scanning calorimetry is technique which involves temperature. Heat of various intensities is used to check various functions like glass transition temperature, melting and boiling point of controlled sample
- Universal tester or universal testing machine is used to check tensile strength, compressive strength
- X-Ray diffraction is technique in which constructive and destructive interference are done by X-Rays in sample in order to identify elements.

4.1.1. X-Ray Diffraction

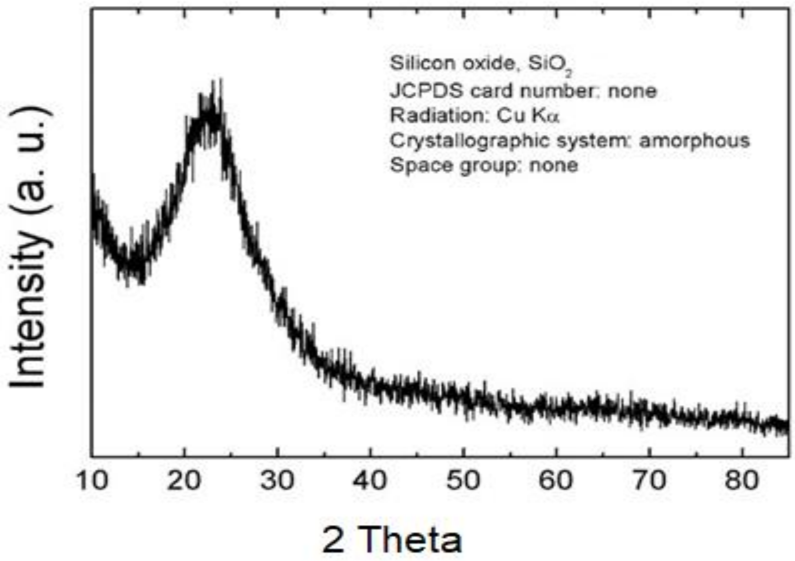

Figure 11-XRD of silicon oxide nanoparticle

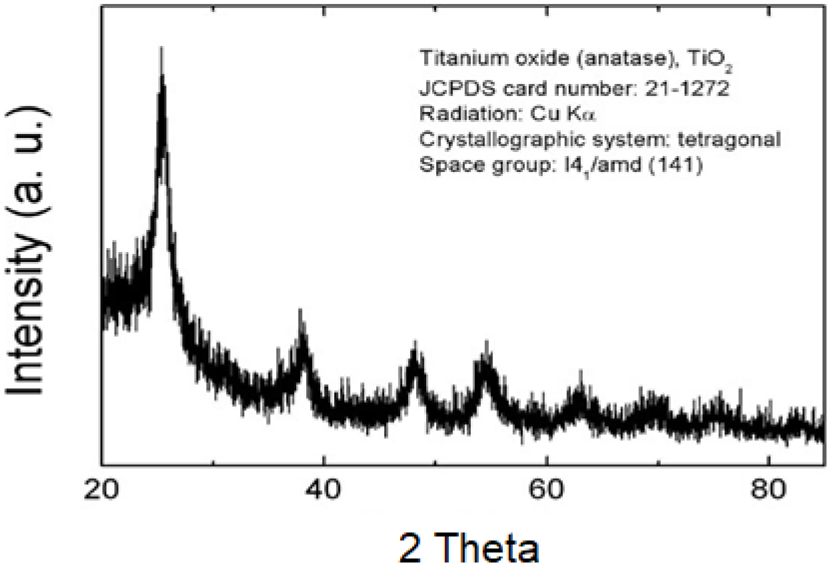

Figure 12-XRD of titanium oxide nanoparticles

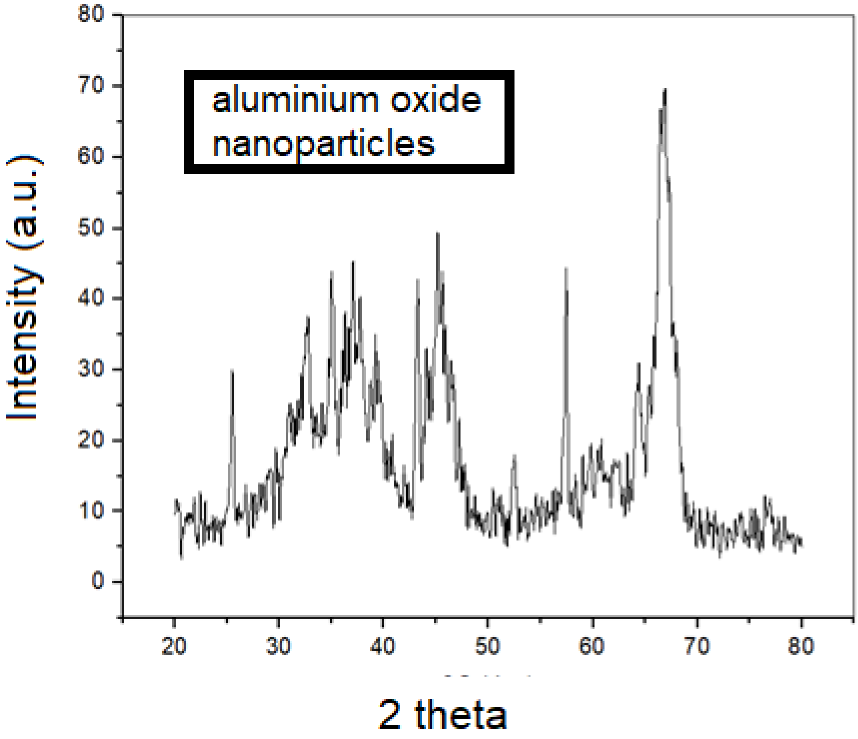

Figure 13-XRD of Aluminum oxide Nanoparticles

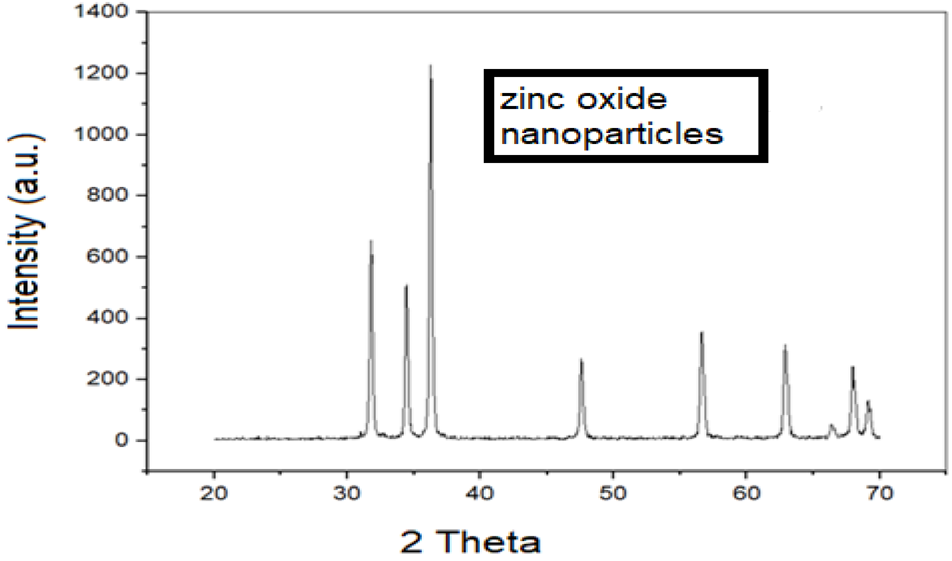

Figure 14-XRD of Zinc oxide Nanoparticles

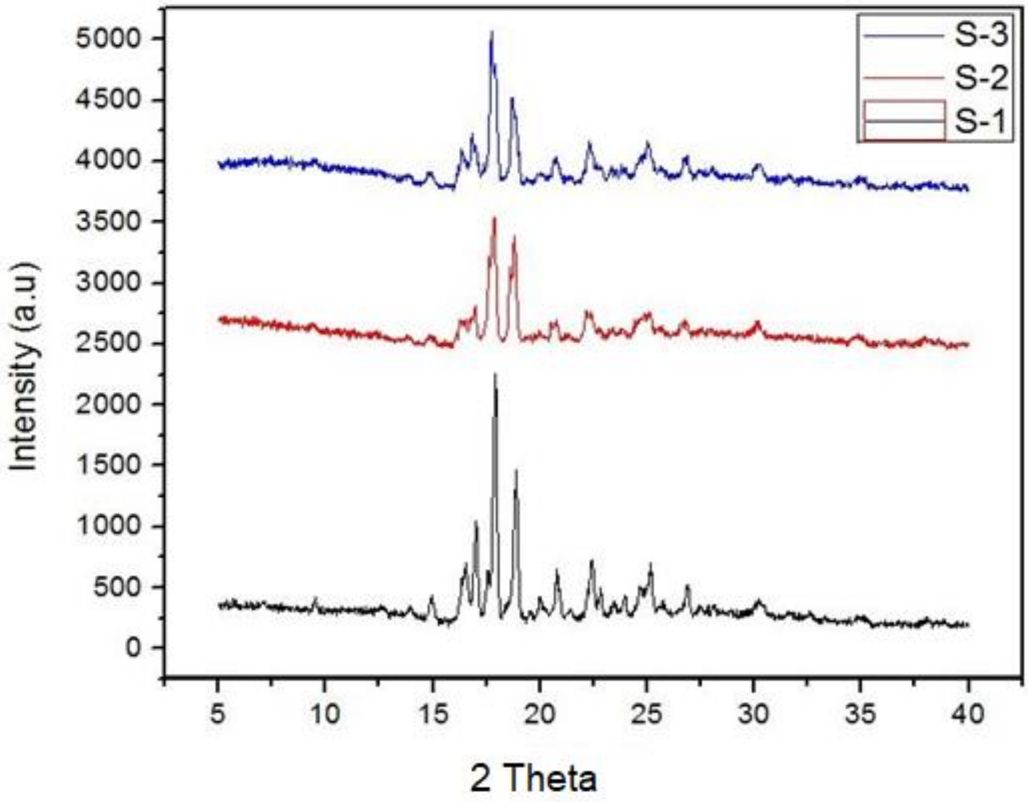

Figure 15-Stacked XRD

4.1.1.1 Alumina Nanoparticles

The phase analysis using X-ray diffraction in fig 13 showed the peaks at 2θ angles around 25.7°, 35.1°, 37.9°, 43.5°, 52.6°, and 66.5° which correspond to the alpha phase of Al2O3 nanoparticles (Fig. 13). The results were in good agreement with the published research.

4.1.1.2 Zinc Nanoparticles

The XRD of sample with zinc nanoparticles having 2θ values with reflection planes at 31.72° (100), 34.39° (002), 36.23° (101) and 47.44° (102) corresponds to the literature available as shown in fig 14. So, all diffraction peaks fit well with hexagonal wurtzite structure of ZnO, which proves that ZnO was successfully synthesized.

4.1.1.3 Nanocomposites

The nanocomposites diffractograms of S-1 indicating filler less sample, S-2 silica fiber glass nanocomposite and S-3 Titania fiberglass nanocomposite as shown in fig15. Titania peak in S-3 at 26-degree 2theta was observed, whereas silica nanoparticles peak was seen in S-2 sample at 22-degree 2theta which was confirmation of their embeddedness.

4.1.2. Tensile Testing Machine

Tensile strength of reference sample, sample containing nano particles of zinc, aluminum, Titania and silica are mentioned in table 2. Sample containing silica and Titania nanoparticles have greater strength than reference sample whereas sample containing silica and Titania nanoparticles has less than reference sample.

Sample containing nanoparticles are taken at three different concentrations 1mg, 3mg and 5mg. from table 2 it can be clearly observed that sample with 1mg concentration of silica and Titania nanoparticles gives higher tensile strength of 29.17 MPa and 27.12 MPa respectively. Whereas tensile strength of reference sample is 25,97 MPa.

Table 2-Tensile Strength of Nanocomposites

Specimen	**GFRP with silica Nano particles Tensile strength (MP)**	**GFRP with Titania Nano particles Tensile strength (MP)**	**GFRP with nano Alumina Nano particles Tensile strength (MP)**	**GFRP with zinc oxide Nano particles Tensile strength (MP)**
Control sample	25.97	25.97	25.97	25.97
1 mg	29.17	27.12	8.68	8.24
3 mg	21.28	17.8	6.31	5.5
5 mg	7.75	7.22	3.00	2.89

Four different nanofillers were chosen for testing the tensile strength, namely Titania Nanoparticles, silica nanoparticles, Alumina Nanoparticles and Zinc Nanoparticles. As evident from the results Titania Nanoparticles enhanced the mechanical strength 3times more than Alumina nanoparticles and 4times more than zinc nanoparticles. On the other hand, the incorporation of silica nanoparticles resulted in the increase of strength of the fibers, which amounted to 3.5 times higher increase as compared to the alumina nano-particles and the increase was the same for zinc oxide nano-particles. This phenomenon has been extensively studied in many different research studies and many experimental evidences and theories could be put forward to explain this phenomenon. This increase in tensile strength can be explained by the fact that Titania nanoparticles is thought to have exhibited much better filler-matrix interactions, leading to more uniform transition of load into the filler phase from the glass fiber matrix, during external loading. For aforementioned reason the underperforming nanofillers were not further pursued for characterization techniques.

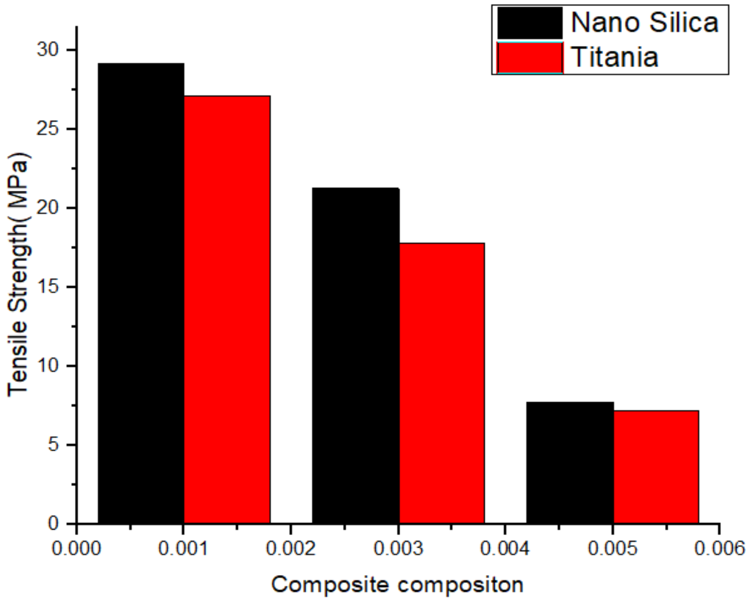

Figure 16-Comparison FRP composites with Nano silica & Nano Titania

Tensile strength of nano composite is decreasing with increasing in concentration of nano particle. In both cases of incorporating nano silica and nano Titania highest tensile strength is observed in sample containing lowest amount of nano particles. This, in turn, can be explained by the weakening of bonds between the polymer chains and the matrix as a whole, on addition of more filler particles. In the bar graph on the next page, it can be seen that there is a slight increase in the strength of the fibers for an equal amount of the addition of both nano-silica and nano-Titania, which is an extension of the fact that both of these fillers have good synergy with the polymer phase.

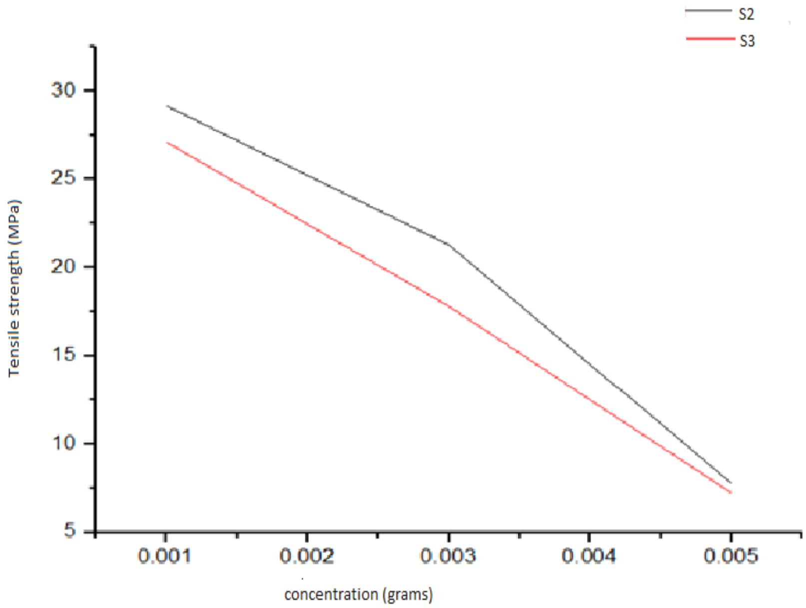

Figure 17-Comparison of samples with silica and Titania nano particles

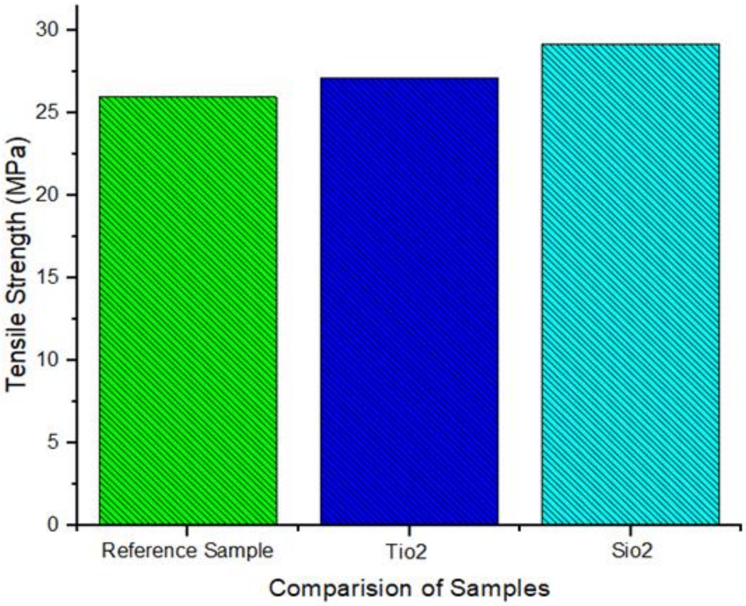

Figure 18-Comparison of reference sample and sample containing nano silica and nano Titania

This block diagram is basically conclusion of tensile strength measured by universal testing machine.29.17 Three different colors green, dark blue and sky-blue are used to show tensile strength of samples. Green, dark blue and sky-blue colors are used for reference sample, sample containing nano Titania and sample containing nano silica respectively. Green block for reference sample is showing lowest tensile strength 25.97 Mpa. Dark blue color is representing sample containing nano Titania its best sample containing 1mg of nano particles gives intermediate strength of about 27.12 MPa. Sky blue color is for sample containing nano silica showing highest strength with 1mg incorporation of nano particle is about 29.17 Mpa

Results reaffirm that when adding silica in a controlled and fixed amount to all the different polymers, the strength of all the fibers slightly decreases. This decrease in strength can be put into explanation by the fact that the polymeric matrix does not quite form a proper homogeneous phase with the polymeric phase, as explained above.

4.2. Differential scanning calorimetry analysis

Differential scanning calorimetry here can easily be used to find out the glass transition temperature of all the samples, both with and without the presence of nano-particles. The glass transition temperature of all samples, including both the unmodified and modified polymer phases, can be seen in the graph below

4.2.1. Graph for composite without Nano particle

The graph in the figure below shows the temperature profile for the polymer according to the analysis carried out by Differential Scanning Calorimetry (DSC). The graph shows a sharp bend at approximately 30 C, which is the evidence of the glass transition temperature being on that particular point which is further highlighted by the arrow in the Figure.

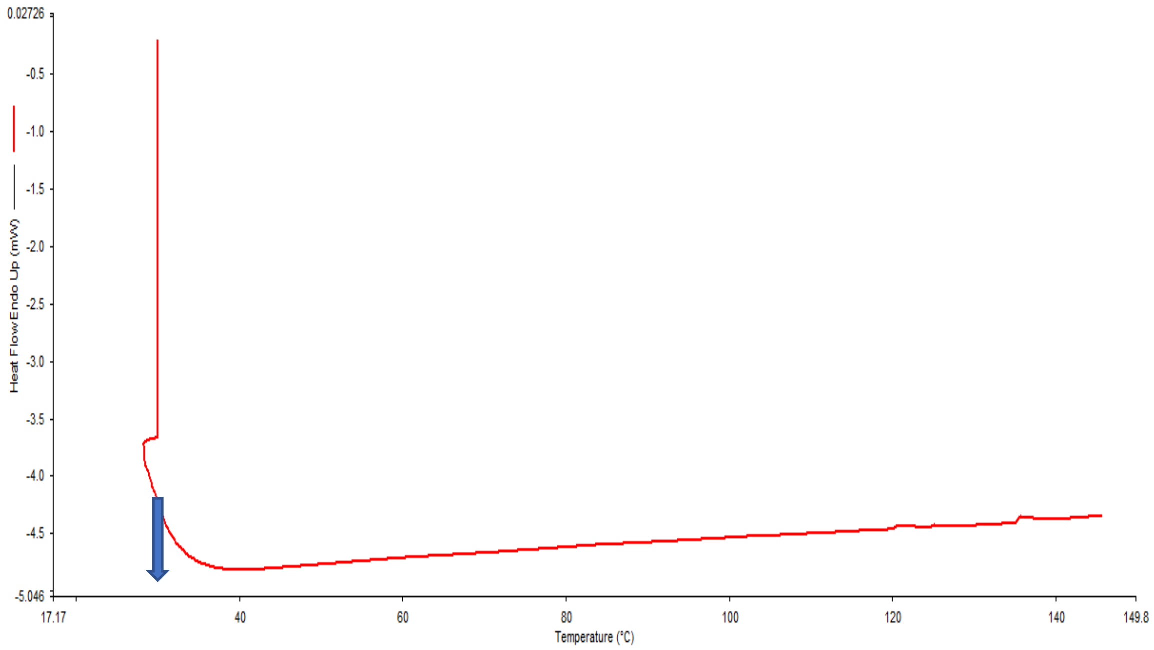

Figure 19-Graph of reference sample for glass transition temperature

4.2.2. Graph for composite with nano silica

In the light of results fabricated sample containing nano silica exhibits increased glass transition temperature than reference sample. These observations clearly exhibit major contribution to the enhanced thermal conductivity which arose due to the structural modification associated within the polymer, caused by Nano silica. Tg was increased up to 42 degree from 30 degree with the addition of SiO_2 and this is thought to be due to ionic conductivity that still increases due the incorporation of silica nano particles. Increase in Glass Transition Temperature (Tg) shows that the transition or change of phase of the composites from amorphous to crystalline, is made difficult due to the incorporation of small amounts of nano-silica, which is one of the main reasons behind the enhanced tensile strength of the said composites on addition of silica.

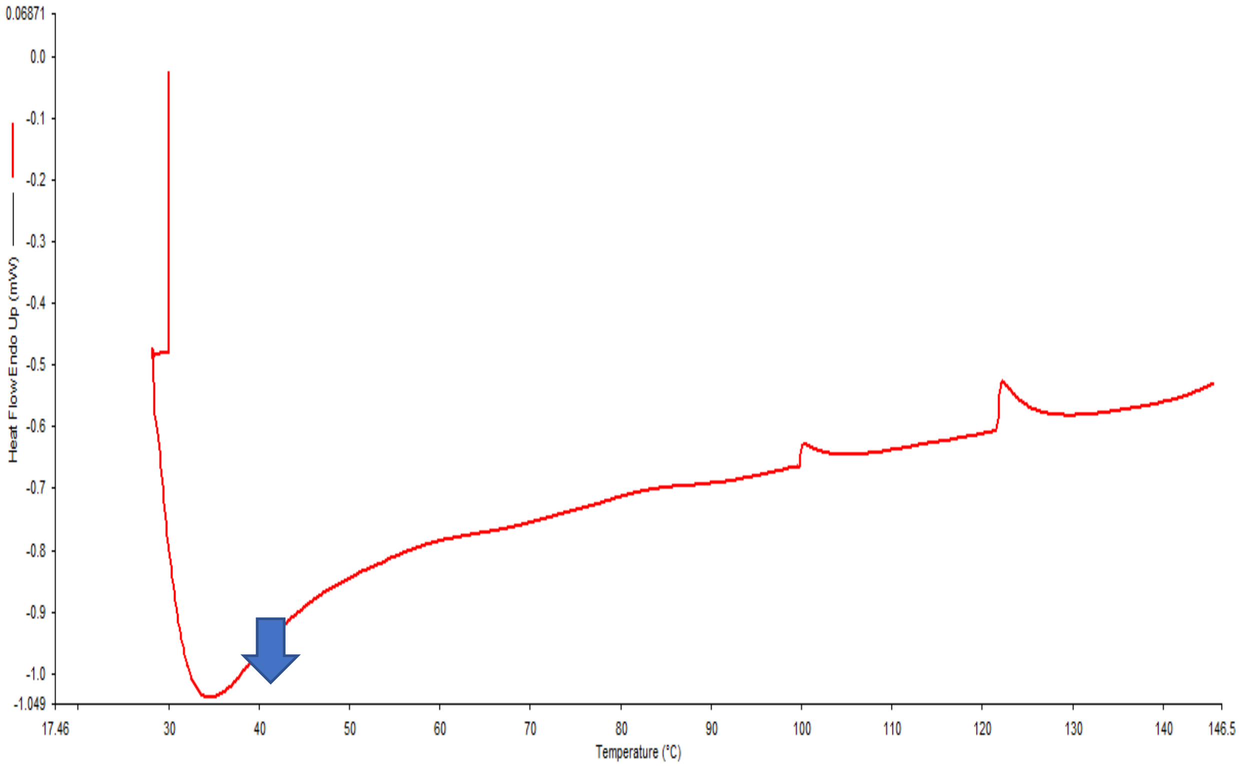

Figure 20-Graph of sample with nano silica for glass transition temperature

4.2.3. Graph for composite with nano Titania

In composites containing Titania nanoparticles glass transition temperature is increased as compared to reference sample, but its value is less than sample containing nano silica. Tg of nano-Titania composite increases to 40 degree Celsius from 30 degree Celsius, and this can be explained again, by the fact that the incorporation of filler makes the transition in phase more difficult and thus requires a higher temperature. The results of this particular analysis are shown in graph and in the subsequent table below.

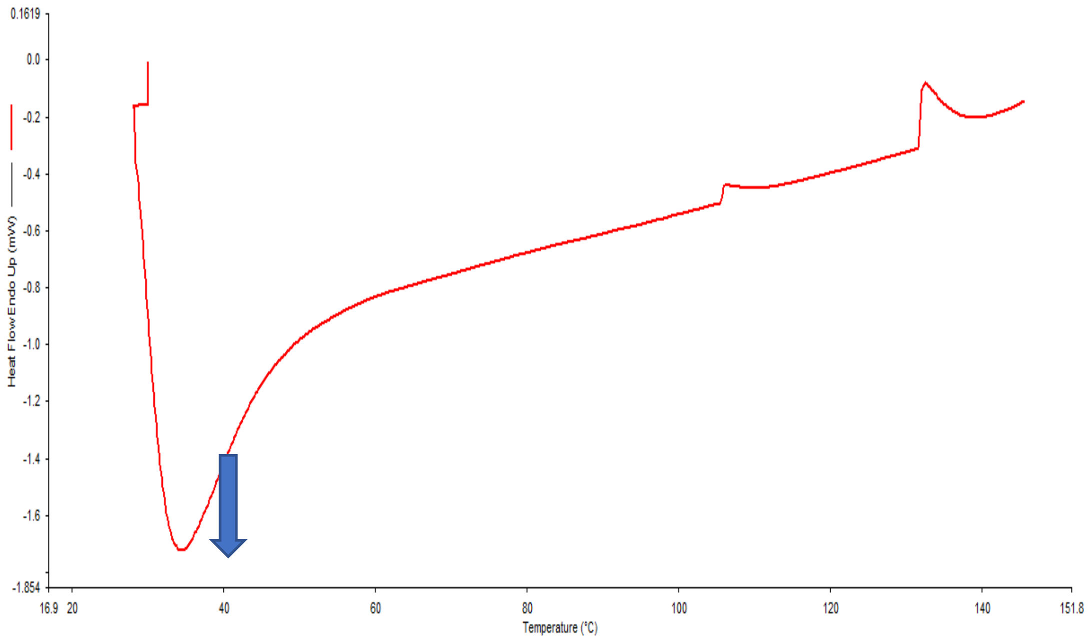

Figure 21-Graph of sample with nano Titania for glass transition temperature

Table 3- Glass transition temperature

Sample	**Glass transition temperature**
Control sample	32 degree centigrade
Sample with nano silica	42 degree centigrade
Sample with nano Titania	40 degree centigrade

4.3. FT-IR Spectroscopy

The functional groups contained within all the samples are explained as in the following figures, which are detailed out using Fourier Transform Infra-Red (FT-IR) spectroscopy.

4.3.1. Fiber glass composite without Nano particle (S1)

FTIR analysis of reference sample which mainly comprises fiber glass sheet and di-glycidyl ether of bisphenol A was carried out. The peaks at 1730 and 1450 cm^{-1} are due to the bending vibration of carbonyl and the stretching vibration peak of C-H in composites. Moreover, $–CH_3$ and $–CH_2$ absorbance peaks for the polymer around 2890 to 3150 cm−1 are observed. Peak at 3400 cm^{-1}, which is bell-shaped is due to presence of O-H bond.

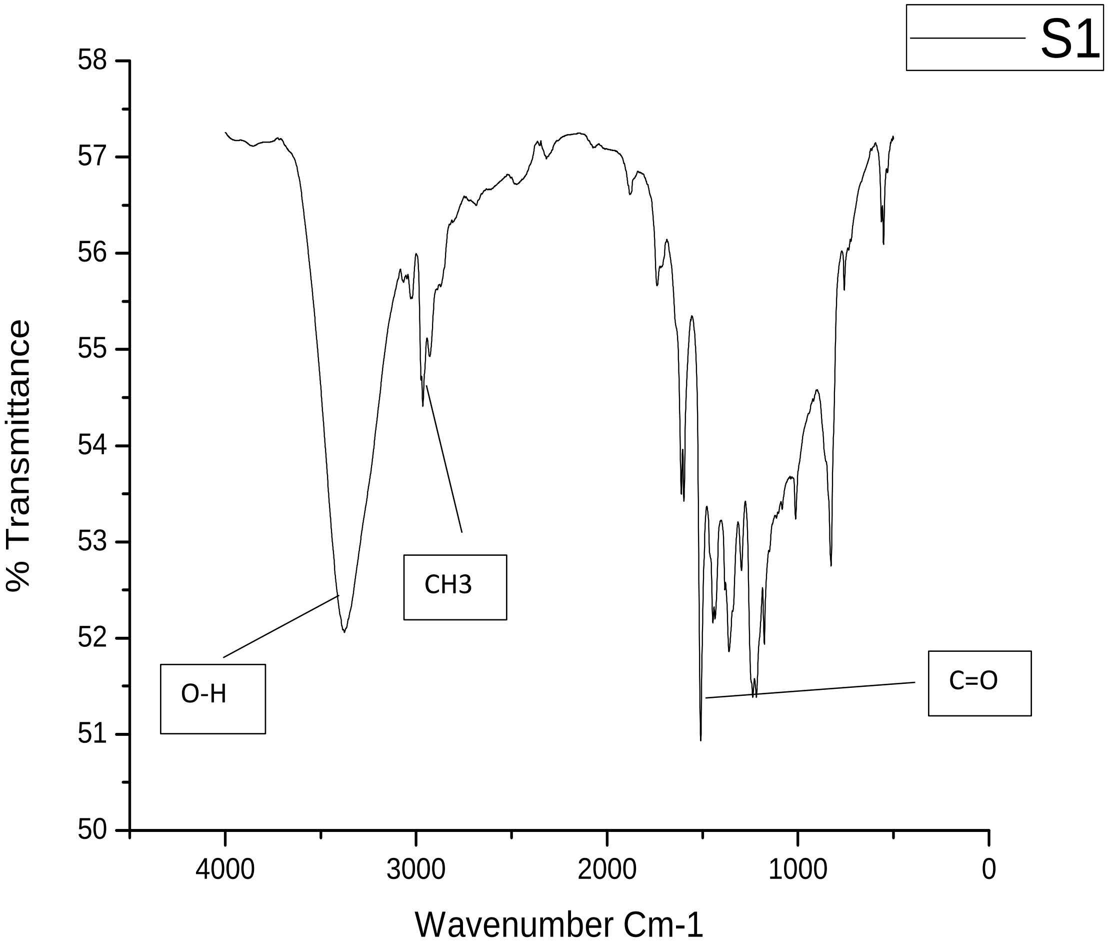

Figure 22- FTIR analysis of reference sample

4.3.2. Fiber glass composite without Nano silica (S2)

FTIR peaks clearly show the presence of di-glycidyl ether of bisphenol A and nano silica particles. If we compare graph of fabricated sample with reference sample, it clearly shows that there is no peak shift in O-H, C=O, C-H bending vibrations and C-O stretching vibrations. All these peaks are still at their respective wavenumber positions with respect to reference sample. C-H aromatic peak is also present near 3000 cm^{-1}. Si-O-SI is located at 1000 cm^{-1}. As there is no shifting of peaks from the reference sample, in the sample including fillers, it shows that the effect of the addition of fillers is purely physical, and there are no chemical linkages.

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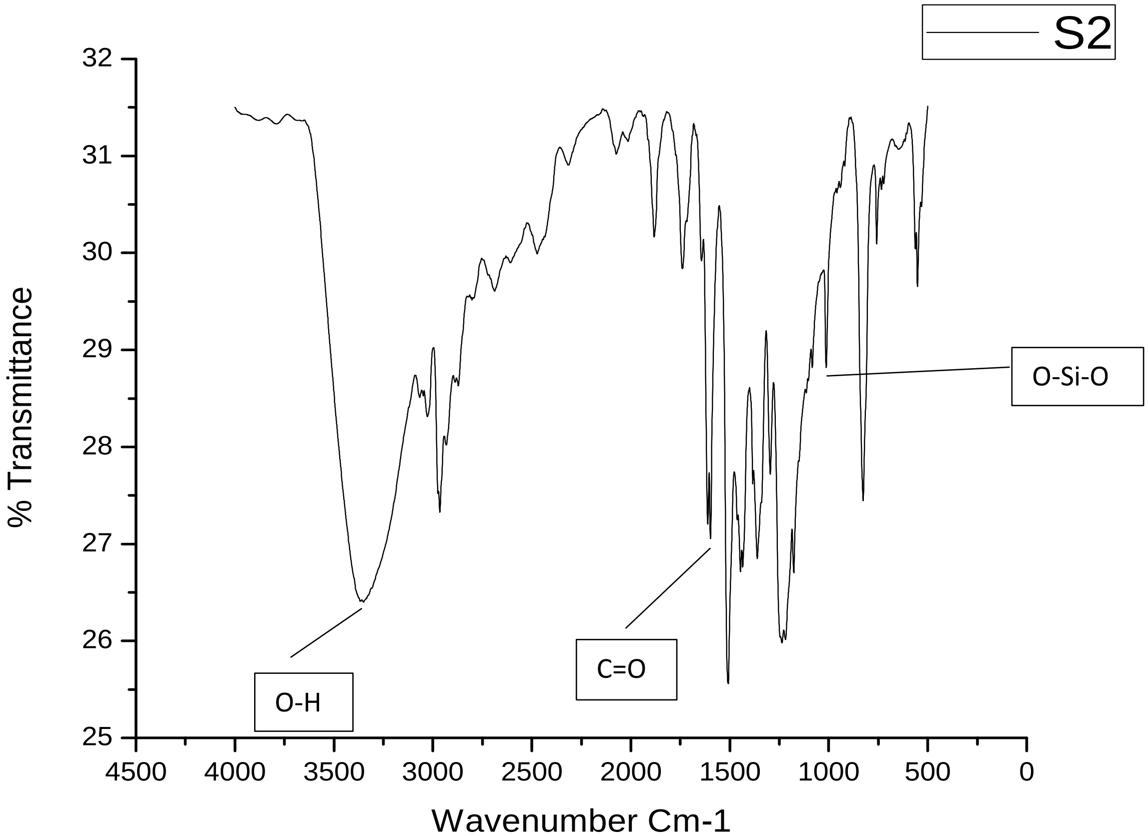

Figure 23-FTIR analysis of sample containing nano silica

4.3.3. Fiber glass composite without Nano Titania (S3)

FT-IR spectra of the TiO_2 samples at various concentrations of NaOH at room temperature were noted from range 4000 to 400 cm^{-1}. The spectra of composite containing nano Titania (Figure) shows four different peaks between 1100 cm^{-1} and 1590 cm^{-1} due to presence of C-O bond bending. The peak at 1150 cm^{-1} is due to C-O-C symmetric bending and the peaks at 1320 cm^{-1} and 1440 cm^{-1} observed for CH_2 asymmetric bending and CH_2 asymmetric stretching. Peak of Titania bond is clearly visible at 826 cm^{-1}.

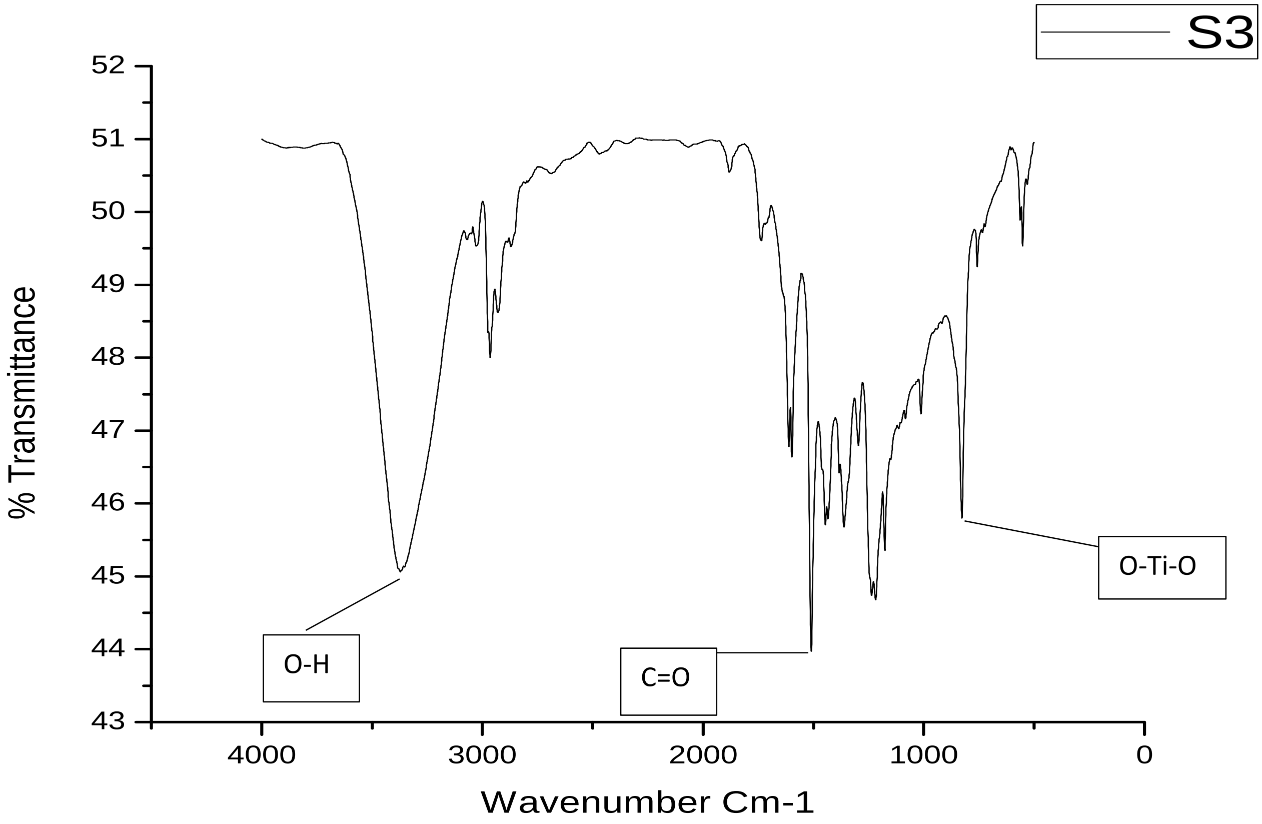

Figure 24-FTIR analysis of sample containing nano Titania

4.4. Scanning electron microscopy

Scanning Electron Microscopy analysis of reference sample and sample with nano particles are discussed below, and the micrographs of all these samples have been analyzed and thoroughly explained.

4.4.1. Composite without Nano particle

SEM images of reference samples at different resolution are given below. Amount of solvent can be seen at surface of fibers which is not completely infused. In fig 25 Selected area in SEM image is showing that solvent is not completely infused in glass fibers. The micrographs show the smooth surface of the glass polymer fibers, which are evidence of the fact that there is good and proper fabrication of the films of the polymer. Moreover, similar results can be seen for different magnifications of the polymer films.

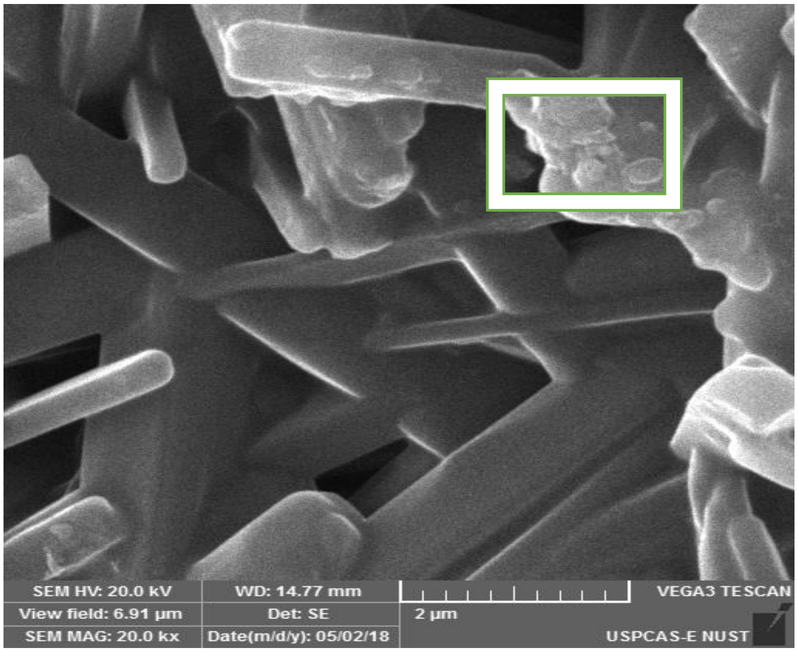

Figure 25-SEM image of reference sample at 20 kx

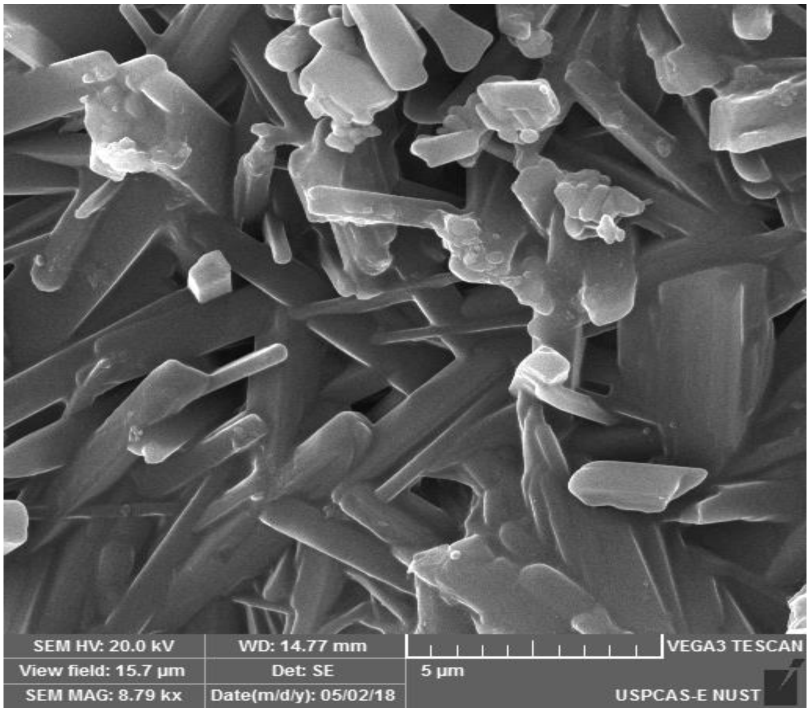

Figure 26-SEM image of reference sample at 8.79 kx

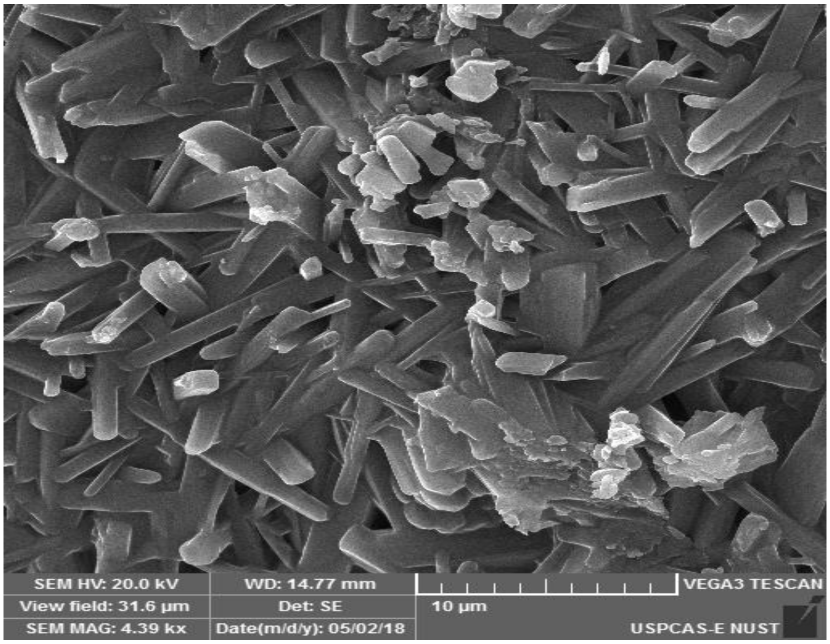

Figure 27-SEM image of reference sample at 4.39 kx

4.4.2. FRP composite with Nano silica

SEM imaging in composite-morphology characterization is an analysis of the fracture surface of a composite filled with a very low amount of silica fillers, i.e. less than 1% by volume. Due to the small amount of silica fillers it is not possible to observe isolated particles or an arrangement of particles. This proves that the lower loading of silica is dissolved into the polymer phase and forms one continuous phase as shown in fig 28 with selected area. The information on the particle inclusion can be revealed with an analysis of the properties of fracture surfaces.

If we compare SEM images taken of nano silica composite with reference sample it would be easily observed that sample with silica shows far more better mixing of bisphenol A and glass fibers as compared to reference sample without nano silica.

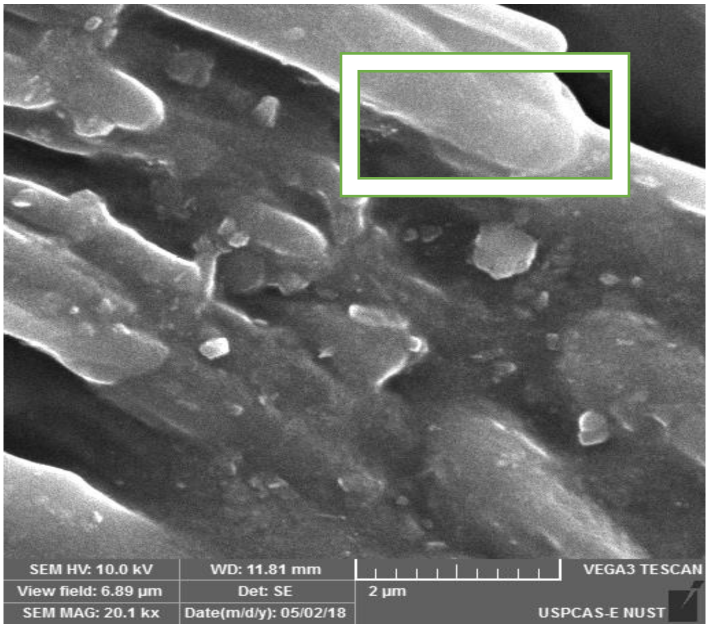

Figure 28-SEM image of sample with nano silica at 20 kx

This complete infusion of solvent in glass fibers is therefore a main reason of the composite being enforced and the mechanical strength being improved. This can again be proven and this point is further strengthened by the consistent surface imaging in all micrographs at different magnifications

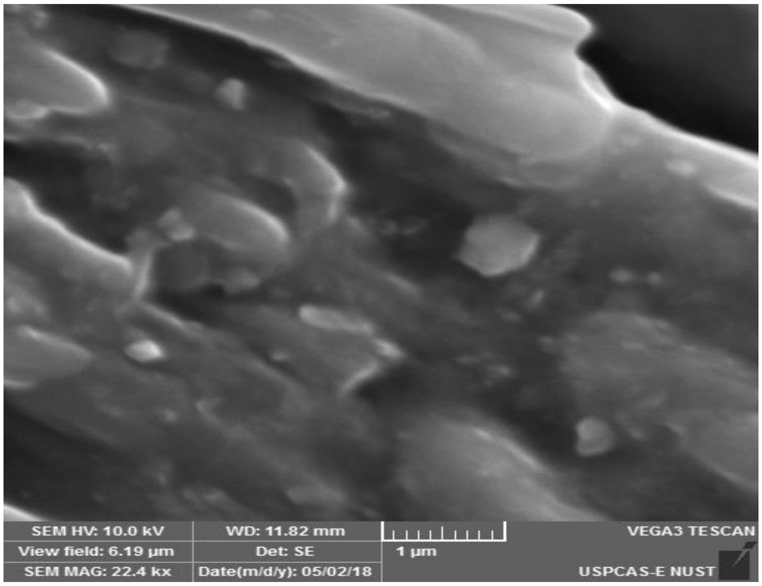

Figure 29-SEM image of sample with nano silica at 22.4 kx

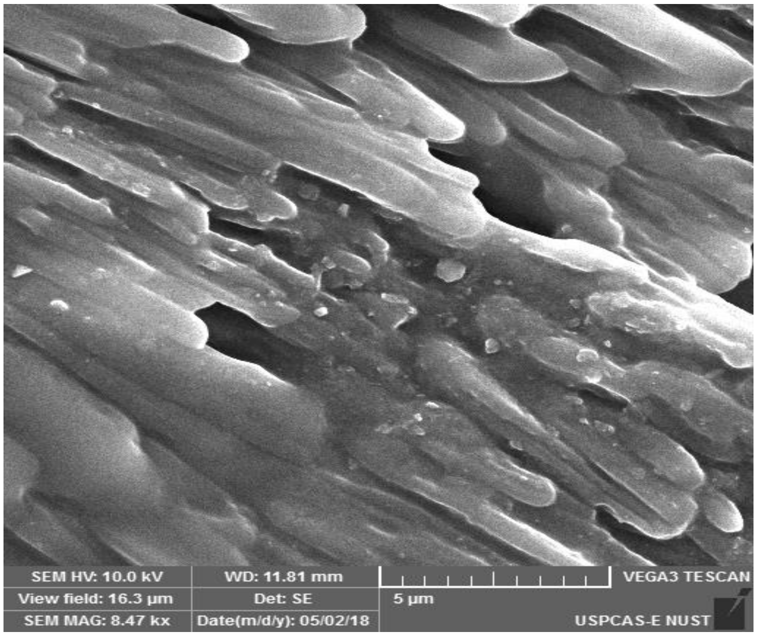

Figure 30-SEM image of sample with nano silica at 8.47 kx

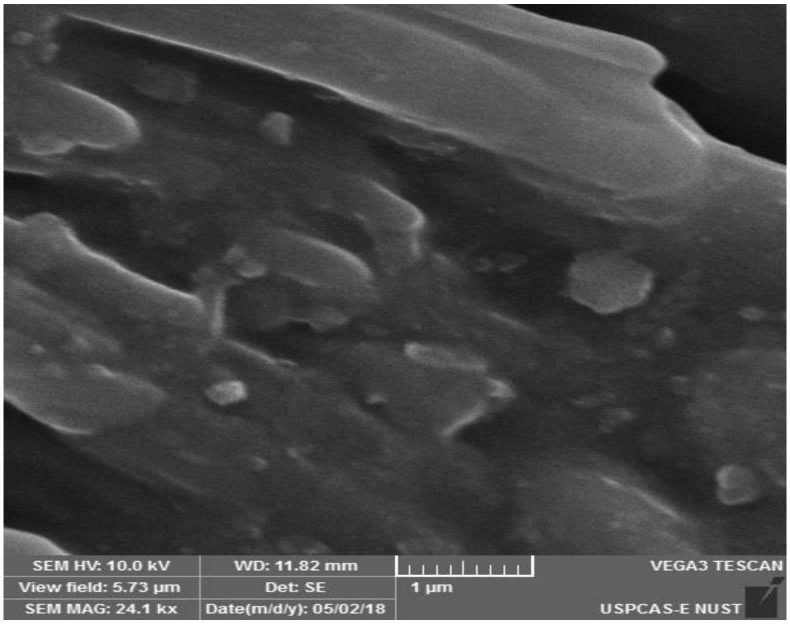

Figure 31-SEM image of sample with nano silica at 24.1 kx

4.4.2. FRP composite with Nano Titania

SEM images of composites with nano-Titania are shown below.

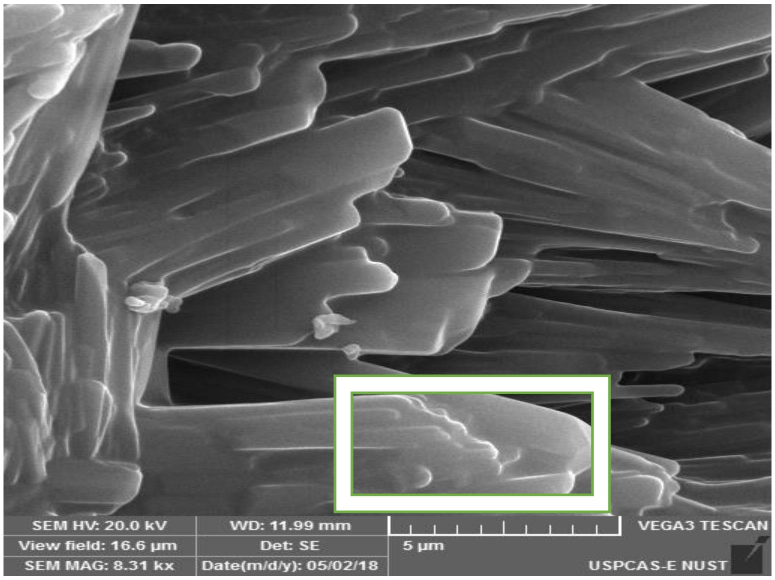

Figure 32-SEM image of sample with nano Titania at 8.31 kx

These images also show a uniform structure and surface properties of the samples containing small amounts of nano-Titania. The smooth and proper structure of the composites as shown by the images, is evidence of better mixing and incorporation of di-glycidyl ether of bisphenol A in fiber glass sheet which is ultimately the reason of enforcement than that of control sample, as was in the case of nano-silica. In fig 32 selected area is showing better infusion of solvent and nano particle in fibers.

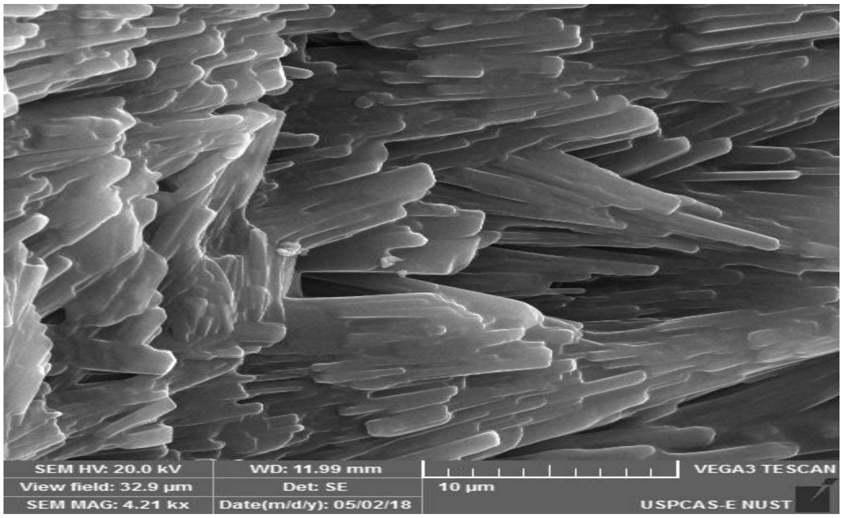

Figure 33-SEM image of sample with nano Titania at 4.21 kx

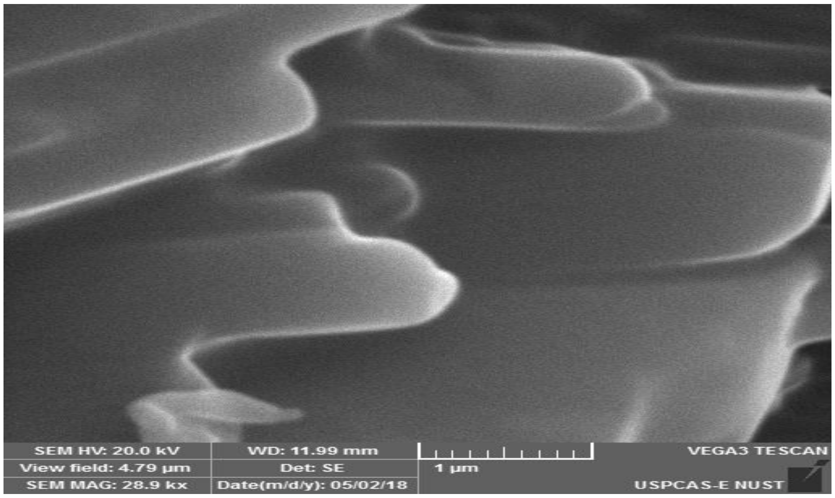

Figure 34-SEM image of sample with nano Titania at 28.9 kx

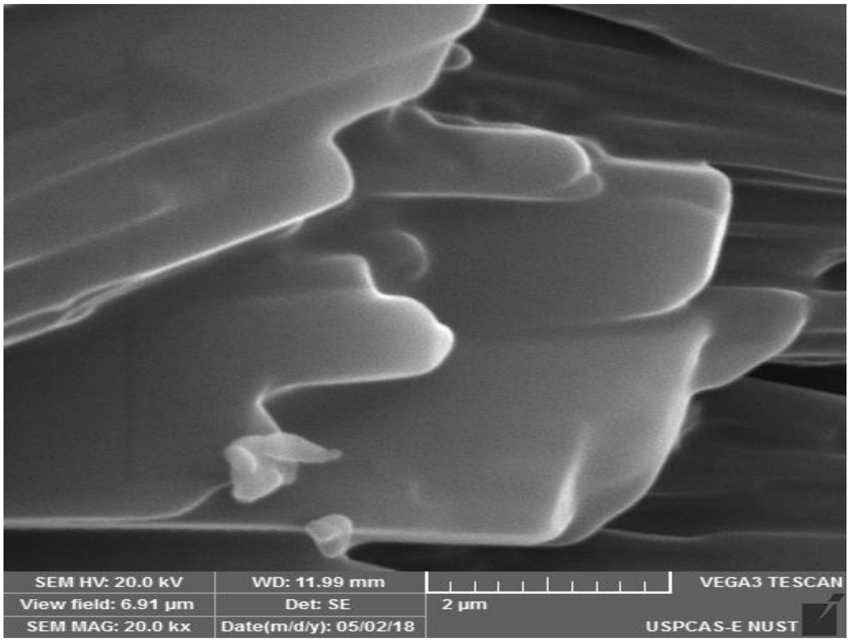

Figure 35-SEM image of sample with nano Titania at 8.3 kx

4.5. Optical Profilometry of pure and composite samples

The profilometry technique has been applied on the pure and composite samples to collect the information about the roughness of surface. The figure 36 to 38 are showing the trend of roughness in samples.

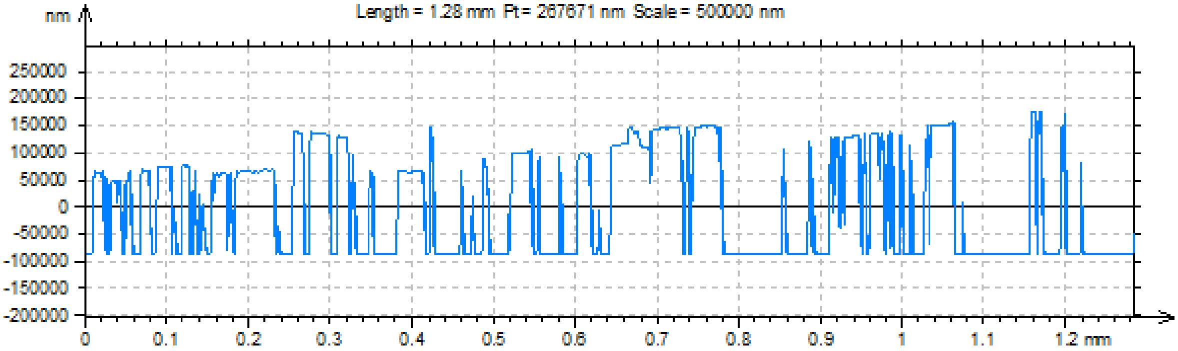

Figure 36Profilometry mapping of reference sample

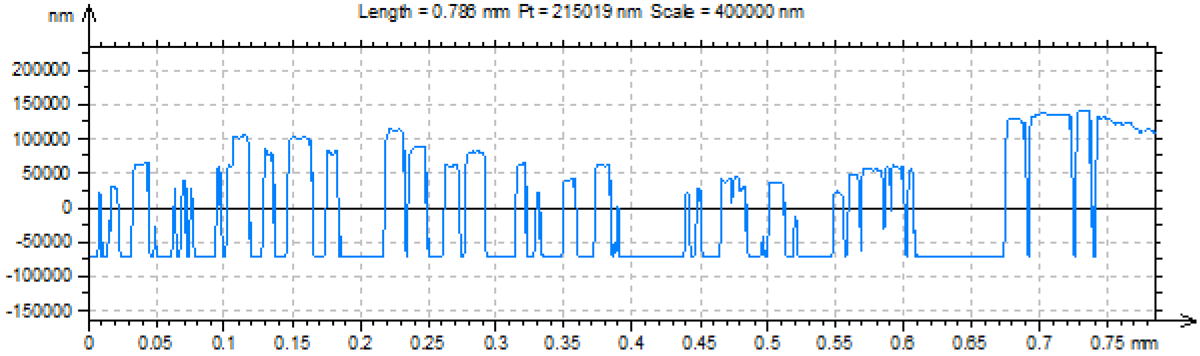

Figure 37 Profilometry mapping of SiO_2 composite

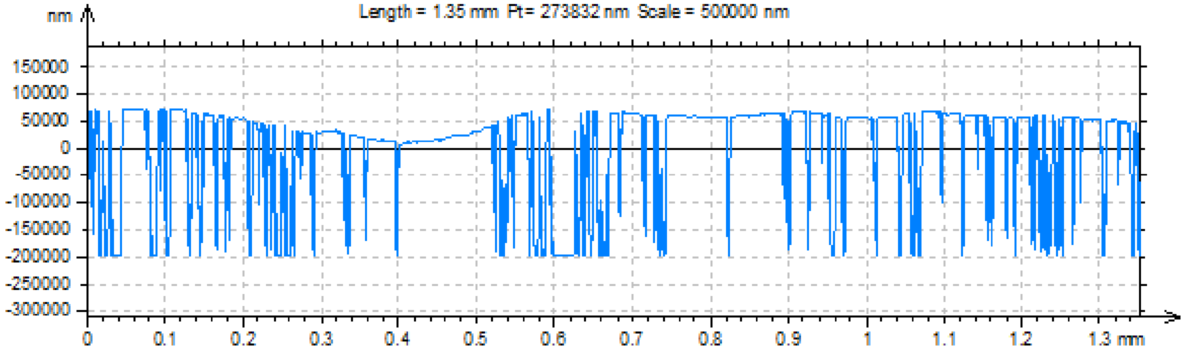

Figure 38 Profilometry mapping of TiO_2 composite

In these figures variations of signals can be seen which are recorded to give two main values to calculate the roughness results. These values are Ra (roughness value) and Rq (root mean square value). These values are given in the form of table below.

Table 4 Roughness values of samples

Calculated parameters	**Reference sample**	**SiO_2 based composite**	**TiO_2 based composites**
Ra(nm)	75285	57997	59320
Rq(nm)	81832	62074	79040

According to this Table 5, the roughness values of reference samples are more as compared to composite samples. The reason behind this is fibrous nature of glass fiber. As SEM analysis has shown that these fibers are irregular with rough surface. The roughness is due to empty spaces. However, addition of nano particles make the surface smooth. These nano particles actually compatible with glass fiber and fill the empty and rough spaces and resulted in smoothness.

If we compare both composites, then it can be observed that SiO_2 nano particles are more compatible with glass fiber and filled more spaces as compared to TiO_2 nano particles. This difference become high when large surfaces are taken in considerations.

Chapter 5

Conclusion

Main objective of the research was to focus on enhancing the tensile strength of BPA using nanofillers, nanocomposites of oxides including Zinc, Silica, Alumina and Titania with BPA were synthesized. Tensile strength testing is the most significant characterization technique for this research showed quite evident results in favor of Nano silica, depicting its superior reinforcement abilities over Titanium oxide nano particles, zinc oxide nanoparticles and aluminum oxide nanoparticles. Tensile strength with Titania nano particles containing sample is also greater than reference sample but when we compare it with sample containing nano silica than Titania containing sample has lower strength. Furthermore, it was also observed that with increased loading of Nano silica beyond 1wt%, tensile strength saw a decreasing trend, at higher loadings nanoparticles are not uniformly distribute in composite, hence the reason for their inefficiency at greater wt.%. Highest tensile strength of 29. MPa was observed for 1wt% Nano silica composite. Sample containing nano Titania and reference sample have tensile strength of 27 and 25 MPa respectively.

In case of thermodynamic behavior glass transition temperature are compared. Improvement in glass transition temperature of samples containing nano particles is observed. Tg of BPA was increased to $42^{o}C$ from $30^{o}C$ (reference sample). Increase in glass transition temperature is an indication that polymer nanocomposite is more stable than reference sample and it is difficult to change from amorphous to crystalline state when heated and this will correlate the improvement in mechanical properties. Glass transition temperature of sample containing Titania is intermediate between reference sample and sample containing silica.

Comparison of fabricated nanocomposite with some other composites is shown in table 4.

Table5 Comparison of tensile strength of manufactured Nano composite with other composites

Sample	**Tensile strength Mpa**
PVC (control sample)	15
PVC + 60 % vol. fractions of SiO2	19
PVC + 60 % vol. fractions of SiO2	21
MEK (control sample)	40
MEK with 1.25 wt.% of nanoparticles of SiO_2	41
MEK with 5 wt.% of nanoparticles of SiO2	38
BPA (control sample)	25.97
BPA with 1 wt. % of nanoparticle of SiO2	29.17
BPA with 3 wt. % of nanoparticles of SiO2	21.28

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