

CHAPTER 1. INTRODUCTION

Composites are basically made up of two or more components in which one constituent is stiff, short/ long fibers, particulate material called a filler/reinforcement, other constituent, a binder/matrix/resin that holds the filler or constituents in place. The matrix material can be polymeric (e.g. epoxies), metallic or ceramic. When the fillers/constituents and the matrix are combined to form composites, best thing is that they hold their individual identities and structural effects or properties on the final composite material [1]. The resulting composite material will usually consist of the filler and matrix stacked to get the desired unidirectional or bi- directional or tri-directional properties. Polymer composites are playing an important role as construction materials in some various applications. They are widely used now a day in application with marine, sporting goods, defense, electronic industry packaging, electronics, automotive, aerospace, and construction industries, because of advanced properties [2, 3]. They are light weight and have superior mechanical properties over monolithic materials which make them suited for vast applications[4].

Carbon fiber-reinforced polymers are a new class of polymer composites, constituted of multiple layers of fibrous materials, which are extremely strong and light weight [5]. Carbon fibers have high elastic moduli and strength due to which these are used as a reinforced material in various resins for the manufacturing of composites with superior mechanical properties. Carbon fiber reinforcement is now widely been used in some thermoplastics, metals and even with carbon. Carbon fiber are expensive but are common in applications where high strength to weight ratio and high rigidity is desired for example in aerospace, automotive, civil engineering, sports goods and an increasing lot of various other consumer and technical products, where performance of material is more important and cost of materials is not a matter of concern and can be neglected up to some extent.

The only reason limiting the composite use in engineering practices or applications is the lack of reliable method of experiment for the evaluation and calculation of mechanical

properties of reinforced polymer composites, difficulties in the deformation process, numerical techniques and evaluation of the load-carrying ability of reinforced composites, and the requirements for advance and more economical manufacturing methods and processes [6]. The mechanical properties of CFRPs are evaluated by the properties of its constituents, shape of specimen of composites, type of interaction at matrix/fiber interfaces, and processing methods [9, 10]. Some composite parameters are determined from already known properties of constituents.

The conditions of deformation, failure and fracture behaviour of fiber composites have been explained by many researchers. Determining mechanical parameters of composites in terms of characteristics of individual constituents gives wide scope for the design of materials with desired properties [11]. The most commonly used CFRPs are biaxial, tri-axial and Quadra axial type fabric, in which straight, uncrippled are aligned in the elastic properties of the fiber. The present study had been conducted with an aim to investigate the prediction of the mechanical properties of carbon fiber-reinforced epoxy composites using calculative and experimental approach. The theoretical analysis was compared with experimental results for the composites prepared. The results indicate the mechanical properties of composite material made were superior to that of epoxy, when carbon fiber was mixed up to some extent and then decrease in properties was observed.

Orthotropic materials have more complex fracture behavior than isotropic materials. Like, fracture in CFRPs occurs under tensile because of fiber pull-out, fiber bridging, matrix/fiber de-bonding, and matrix cracking. Quantity of the fiber volume, matrix or resin properties and production techniques of the composite affects this behavior. This work aims to examine how the mechanical characteristics of carbon fiber reinforced epoxy composites shows variation when fiber is mixed in varied amount. Mostly the binding polymer used is thermoset resin such as epoxy, but sometimes other thermoset or thermoplastic polymers, like polyester, vinyl ester or nylon, are used to prepare composites. The properties final properties of CFRP goods can also be affected by the type of the binding matrix (the resin).

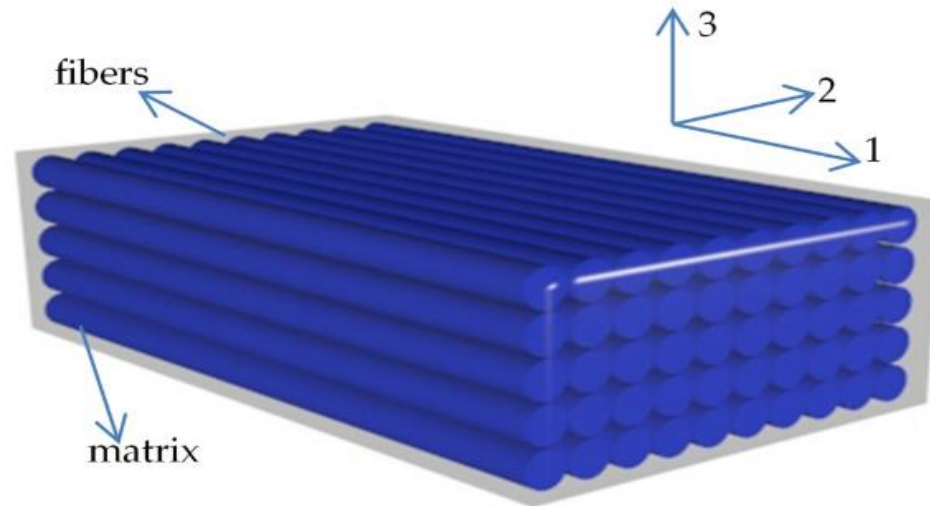


Fig: 1.1A composite material (ref: intechopen.com)

As stated earlier, Carbon fiber is expensive as compared to the other commonly used reinforcement materials, but in certain applications [12] the combination of superior performance characteristics blended with light weight make cost of secondary importance, like in aerospace and rocket applications where cryogenic liquid fuel is used instead of the solid fuel of propellants of launch vehicles and rockets in aerospace applications because of the excellent specific impulse, the ratio of the less calorific energy as compared to volume of the cryogenic liquid fuels results in pressurized, large and heavy tanks when casted of metallic materials. Due to above reasons polymeric composites are now used in parts and components of reusable launch vehicle. Several applications like the cryogenic fuel tanks, cryogenic fuel delivery lines, and parts of the cryogenic side of turbo-pumps have carbon fiber as reinforced material in polymer composites [13]. Even in defense sectors they are also used like in tanks and guns. The barrels of tanks and guns are also made up of carbon fiber composites.

A carbon fiber polymer composite has zero coefficient thermal expansion coefficients, which makes them suitable for the use in such applications. If barrels are to be made from metallic materials then, firing of the bullets or the missiles, creates intense heat inside

barrel, metals have high thermal coefficient and they get expand due to the intense heat generated.

1.2 Objective

To study properties of carbon fiber reinforced polyurethane modified epoxy composite.

To achieve this objective the sub-objectives are as follows:

1. Prepare the samples of polyurethane modified epoxy resin in different ratio.
2. To test the prepared samples for mechanical properties and characterize them.
3. To prepare the composite samples of polyurethane modified Epoxy resin by reinforcing it with Carbon Fiber in different direction.
4. To test the prepared samples for mechanical properties.
5. To compare the samples prepared on the basis of their properties.

CHAPTER 2. Literature Review

Development of composite materials, its design and processing techniques is an important advancement in the material history. The composite material is made by combining two or more than two materials – generally the one having different properties. The constituent materials, combined to give unique properties to the composites. However, inside the composite, constituents remain physically separable; they neither dissolve nor blend into each other. A composite material is a combination of two or more constituent materials which results in better properties of the individual constituent materials. Comparing to metallic alloys, the constituent materials retains its separate chemical, physical, and mechanical properties. The two constituents are material providing reinforcement and the other is a resin or matrix or base material. Composite materials have several advantages like high strength and stiffness, low density compared to bulk materials, resulting in weight reduction in the finished part. The reinforcing material provides improved strength and stiffness. In most of the cases, the reinforcement materials as compared to matrix are hard, strong, and stiff. The reinforcement is mainly a fiber or a particulate. Particulate material has dimensions approximately equal in every direction. They are of several geometry- spherical, platelets, or any other regular or irregular geometry. Particulate composites are much weaker and stiffer than continuous fiber composites, but they are generally of low cost. Composites reinforced with particulate are reinforcement (up to 40-50 vol. %) because of difficulty in processing and brittleness.

Composite materials can be classified as following on two level:

1. Based on matrix/base material

The primary/base phase, which has a continuous character, is called as matrix. Matrix is generally ductile and have less hard phase. It holds the reinforced materials and shares with it. Some inorganic materials, polymers and metals are used as matrix materials in the design of structural applications, with remarkable success. Such material remains elastic till the

failure point and shows decrease in failure strain, when applied with tension and compression. The first level of classification is on the basis of the matrix constituent as shown in fig. 2. The major composite classes include Organic Matrix Composites (OMCs), Metal Matrix Composites (MMCs) and Ceramic Matrix Composites (CMCs). Organic matrix composite contains mainly two class of composites, namely Polymer Matrix Composites (PMCs) and carbon matrix composites also known as the carbon-carbon composites.

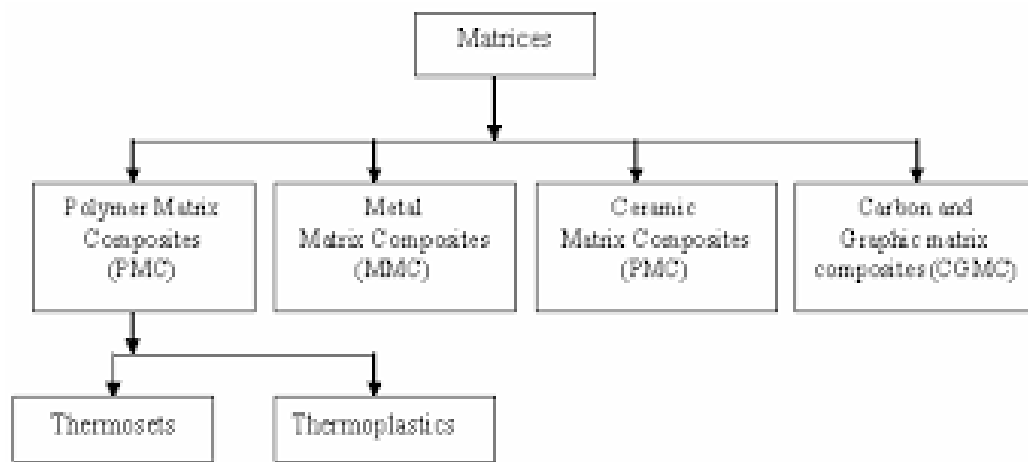


Fig: 2.1 Classification of matrix material

2. Based on the reinforcement material

The second phase/phases are dispersed in the matrix in discontinuous form (as shown in fig 2). This secondary phase is known as dispersed phase. Dispersed phase is generally stronger than the base material; therefore, it is sometimes called as reinforcement phase. Reinforcement materials of the composite materials can be in form of fibers, particle of fabrics or whiskers. Fiber has one very long axis and other axes are either circular in nature or very close to circular shape. Particles do not have preferred orientation and so does their shape. Whiskers have preferred shape and are generally less in diameter as well as in length when compared to fibers [12].

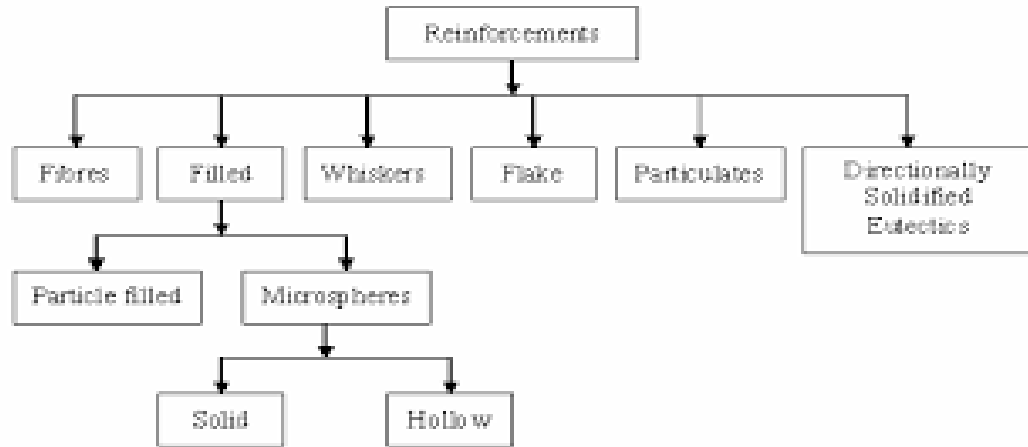


Fig: 2.2Classification of reinforcements

2.1 Polymer matrices Composite

Polymer matrix is weak, and has less stiffness, viscoelastic materials. The strength and stiffness of Polymer matrices composites is because of reinforcing fibers. Mainly two important class of polymers are used as matrix materials; these are thermosets and thermoplastics (shown in fig 2.1). Now a day, thermosets are widely used as a matrix resins for various applications, and still thermosets are making slow rise. Thermosets are more resistance to solvents and anti-corrosive as compared to thermoplastics, but some exceptions are still present. Thermosets mostly undergo into curing process during the fabrication of parts, after that they become rigid and can't be reformed. Whereas, Thermoplastics, can be soften and reformed again and again by application of heat (like wax). There are several varieties of polymers in both classes.

Polymer matrices composites (PMCs) are composed of a various short or continuous fiber bind together in organic polymer matrix. The reinforce material in a Polymer composites provides high strength and high stiffness. The Polymer composites are designed so that the mechanical loads applied on structures in service are supported by the reinforced material. The function of resin is to bind the fibers together and also distribute loads between the fibers.

Polymer matrix composites are classified into two categories: reinforced plastics, and advanced composites. The classification is based on the extent of mechanical properties mainly strength and stiffness, however, there is no clear line separation between the two. Reinforced plastics, which are relatively low in cost, generally consist of polyester resin has low-stiffness glass reinforced fibers. Advanced composites, which have in use recently, nearly, 14 years, primarily in the aerospace applications, has superior strength and stiffness, and are relatively costly. Polymer matrix composites are light weight having superior stiffness and superior strength in the direction of the reinforced material. Due to this combination they are useful in aircraft, automobiles, and other moving structures. Other properties which are desired are anti-corrosion and fatigue resistance as compared to the conventional metals. Because of the high decomposition temperatures of polymer matrix, however, current PMCs are limited to service temperatures below about 600° F (316° C)[13].

At present, polymer composite materials also have applications in the industry of high-grade and staple products, such as the automobile industry, shipbuilding, construction and many more.

1) **The automobile industry-** Composite materials can remarkably reduce fuel consumption, and are anti-corrosion and shows high damping, so their large application of composite materials in the automobile industry. According to a report, the application ratio of automotive steel has shown drop to 14%~15%, and it has been reported that in year 2000, there was one in five cars which was produced using composite materials in the United States of America. Also, to decrease environmental pollution, many countries are aggressively increasing the use of natural gas to replace gasoline as motor fuel, and the cylinders of natural gas use fiber reinforced polymer structure. The working pressure of such cylinder can vary from 20~100MPa, life span of 10~20 years, and these cylinders have been in series and into practical applications. Polymer composite materials are also used in automobile components like glass fiber unsaturated polyester. In the past, they were produced by hand lay-up and spray-up molding, but in recent years, sheet molding compound (SMC), glass fiber mat reinforced thermoplastics (GMT) compression molding and resin transfer molding (RTM) are also used. The method of making SMC is by chopped glass fiber roving or glass fiber mat is impregnated using the mixture like paste

resin, of unsaturated resin system, fillers and other additives, and then wrapped with polyethylene or polypropylene film on both the sides of itself to have the sheet type compound. SMCs are widely used because of continuous production, easy application and low cost. In addition to glass fiber reinforced composite materials; the application of advanced composite materials in the automobile industry is also there. Due to high cost limits the use of advanced composite materials, but the good news is that the present cost of carbon fiber has dropped close to the price that automobile industry can accept.

2) **The shipping industry-** From a long time composite material are used in fishing boats, tugs, yachts, boats and minesweepers. The composite materials are lightweight and can bear high external pressure, development of composite materials submersibles is in progress, which will further enhance the application of composite materials in submarines.

3) **The construction industry-** In the construction industries, composite materials are used in variety of lightweight structural houses, decorative materials, sanitary ware and cooling towers, storage tanks and many more, besides, in present year, they are now being used in the application of the reinforced in concrete and the bridge. Composite materials are used as reinforcement in concrete instead of steel to make new type of concrete, which have attractive prospects, because it can increase the earthquake resistance and diamagnetism of building structure. The glass fiber, carbon fiber and aramid fiber or hybrid fibers for two-dimensional or three-dimensional woven or braiding are also used as reinforcement material. Now a day, such types of concrete has been used in the foundation of bridges and buildings, such as magnetic observatories, high-frequency electrical room and also many other applications, that extends service life of buildings and always improves performance. The application of composite materials in the construction of houses, bridges, tunnels, culverts, subways and also in related structural applications of concrete and also in various infrastructure projects, also in recent years it has become the fastest-growing civil and one of the most promising areas, and it has become keen area of the research and development now a day. Composite materials in many forms are used in the field, such as continuous cable, guard rails, handrails, grating; beams, columns, poles, stakes; laminates, wrapped material, short fibers (reinforced cement), ribs. Now, the mostly used fiber composite materials, is carbon fiber composite materials for infrastructure repairing,

renovating and strengthening, and the application forms are wrapped material (sheet) and laminate. The technology originated in the late 1980s and the early 1990s, was used for the restoration of Osaka earthquake, the Los Angeles earthquake. Thereafter, Japan, the United States and Europe are now promoting this technology; it has been rapidly developed into many application fields such as civil engineering, masonry, concrete work, and so on. The technology is useful in rehabilitation and reconstruction of the “921” earthquake in Taiwan, and further stimulated the Taiwan carbon fiber industry[14].

2.2 Epoxy Resin

Epoxy resin is the widely used thermoset resin in polymer matrix composite. Epoxy resin is itself a family of thermoset of plastics that do not give off reaction products while they cure and also has low cure shrinkage. They have desirable properties such as excellent adhesion, highly chemical and environment resistant, excellent chemical properties, and high insulating property. The epoxy resins are obtained by reacting epichlorohydrin with bisphenol. Resin with varying properties can be obtained by varying proportions of the reactants, as the proportion of epichlorohydrin is reduced; there is increase in molecular weight of the base material. Curing agent/hardener polymerizes the process, resulting in the very dense cross- linked network of polymer.

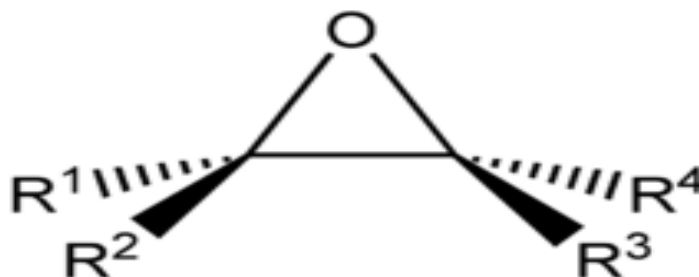


Fig: 2.3 Structure of epoxy resin

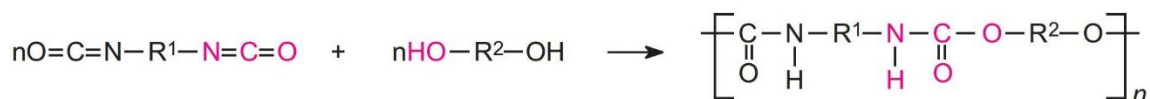
The word epoxies come from the molecules that have the epoxide ring. An epoxide ring is an oxirane structure that consists of three-member ring with one oxygen and two carbon atoms. Epoxies consists of one or more than one epoxide ring cured by reaction with amines, acids, amides, alcohols, phenols, acid anhydrides or mercaptans. Epoxy resin is

used widely in structural adhesives. The desired properties of epoxy are high strength and modulus, less volatile, excellent adhesion, low shrinkage, excellent chemical resistance, and easy processing. The major drawbacks of epoxy are brittleness and the degradation in presence of moisture, manufacturing techniques are autoclave molding, filament winding, press molding, vacuum bag molding, resin transfer molding, and pultrusion. Curing process has a range varying from room temperature to approximately 350°F (180°C). Generally curing ranges between 250°F and 350°F (120° and 180°C). Generally, properties like tensile modulus, glass transition temperature, thermal stability, chemical resistance shows improvement with increase in cross-linking, but brittleness is also increased.

2.3 Polyurethane

Polyurethanes are versatile elastomer and have wide applications worldwide. The mechanical properties of polyurethane can be isolated and manipulated through creative chemistry which gives a number of unique opportunities to solve problems related with performance characteristics. The polyurethanes are the family of polymers which are different from other polymers in that there is no urethane monomer and the polymer is almost invariably created during the manufacture of a particular object.

Polyurethanes are made by the exothermic reactions between alcohols having two or more reactive hydroxyl (-OH) groups per molecule (diols, triols, polyols) and isocyanates that have more than one reactive isocyanate group (-NCO) per molecule (diisocyanates, polyisocyanates). The reaction between a diisocyanate and a diol is as below:



The group formed by the reaction between the two molecules is known as the 'urethane linkage'. It's an important part of the polyurethane molecule.

The importance of polyurethane is its vast range of hardness and with the advantages listed below:

- 1. WideRange of Hardness-** The classification of hardness for polyurethane depends on the pre-polymer's molecular structure can be manufactured from 20 SHORE A to 85 SHORE D.
- 2. High Load Bearing Capacity-** Polyurethanes have high load bearing in both tension and compression. Polyurethane may undergo change in shape under an applied load but will return to its original shape once the applied load is removed with little compression set in the material when designed properly for application.
- 3. Flexibility-** Polyurethanes performs well when used in high flex fatigue applications. Flexural properties can be isolated allowing for very good elongation and recovery properties.
- 4. Abrasion & Impact Resistance-** For applications of severe wear prove challenging, polyurethanes are ideal solutions even at low temperatures.
- 5. Tear Resistance-** Polyurethanes have high tear resistance along with high tensile properties.
- 6. Resistance to Water, Oil & Grease-** Polyurethane material properties will remain stable (with minimal swelling) in water / oil / grease. Polyether compounds will last many years in subsea applications.
- 7. Electrical Properties-** Polyurethanes exhibit excellent electrical insulating properties.
- 8. Wide Resiliency Range-** Resilience is generally a function of hardness. For shock-absorbing elastomer applications, compounds with less rebound are usually used i.e. resilience ranging between 10-40%. In the applications of high frequency vibrations or in where quick recovery is desired, compounds in the 40-65% resilience are employed. In general, toughness is enhanced by high resilience.
- 9. Strong Bonding Properties-** Polyurethane bonds to a wide range of materials during the manufacturing process. These materials include other polymers, metals, and wood. This property makes polyurethane an ideal material for wheels, rollers, and inserts.
- 10. Performance in Harsh Environments-** Polyurethane is very resistant to temperature extremes, meaning harsh environmental conditions and many chemicals will not cause material degradation.

- 11. Mold, Mildew & Fungus Resistance-** Most polyether-based polyurethanes do not support fungal / mould / mildew growth and are therefore highly suitable for tropical environments and FDA applications. Special additives can also be added to reduce this in polyester materials as well.
- 12. Colour Ranges-** Varying colour pigments can be added to polyurethane in the manufacturing process. Ultraviolet shielding can be incorporated into the pigment to provide better colour stability in outdoor applications.
- 13. Economical Manufacturing Process-** Polyurethane is often used to manufacture one-off parts, prototypes or high volume, repeat production runs. Size ranges vary from a couple grams to 2000lb parts.
- 14. Short Production Lead Times-** Compared to other thermoplastic materials polyurethane has a relatively short lead time with significantly more economical tooling costs.

2.4 Polyurethane modified epoxy

Epoxy resins are widely used as a base material in composite material because of excellent heat, moisture, and chemical resistant and also the good dynamic mechanical property. It can't be used as applications in structures because it is highly brittle, high value of coefficient of thermalexpansion and when sharp cracks are present it shows low toughness. Various methods and ways have been proposed to improve the toughness of the epoxy resin network. Most successful method is to incorporate other resin which have better toughness and compatible too[15].So, thermoplastic PU pre-polymer was incorporated to enhance the toughness of the epoxy resin.

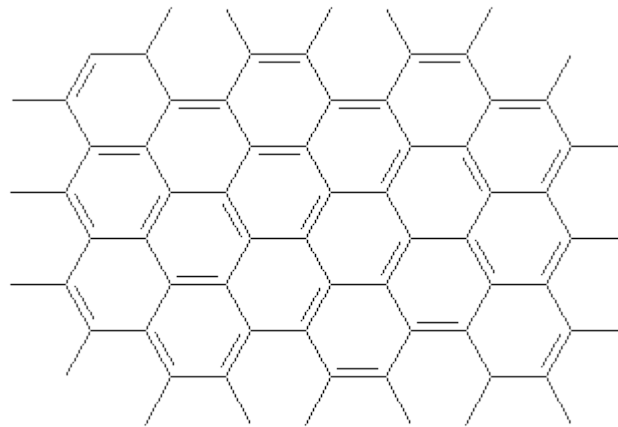
In previous work of Xiao and Gao, in 1994, study was done on the thermoplastic blend of polyurethane/epoxy, which contains excellent elasticity, wear resistance, and toughness [16].Ho and Ang studied the applications of thermoplastic polyurethane-modified epoxy resins in electronics encapsulation, and the result indicated that Epoxy Resin of incorporated PU prepolymer to improve the toughness and reduced the stress of cured Epoxy resin [17].

The primary requirement for thermoplastic PU modified matrix is that, PU should properly react with the resin chemically. It will increase the molecular weight which results in separation of phase and also ensures the strong chemical bonding across PU and epoxy

matrix interface. To avoid the loss in thermal properties, pre polymer in form of powder [16, 17] has been used as the second phase to toughen the highly cross-linked density epoxy.

2.5 Carbon Fibers

Carbon fiber is a polymer in graphite form. Graphite as well known that is the pure form of carbon. In graphite structure atoms of carbon arranged in the big sheets of hexagonal aromatic rings. The sheets look like chicken wire.



a section of a sheet of graphite

Fig: 2.4A section of graphite

Carbon fibre is graphite which has sheets which are long and thin. It may be assumed as ribbon of graphite. Bunch of these ribbons prefer to pack together to form fibres, hence the name carbon fibres. These fibres aren't used by themselves. Instead, they're used to reinforce the plastic materials like epoxy resins and other thermosetting materials to give superior properties to the polymer material. We call these reinforced materials composites because they contain more than a component. Carbon fiber reinforced polymer composites are very strong. They're often stronger than steel, but a whole lot lighter. Because of this, they are now used to replace conventional metals in many uses, from parts of airplanes and the space shuttle to tennis rackets and golf clubs. Carbon fiber is often made from another

polymer (see below), called polyacrylonitrile, with the intense heating process. Carbon fiber is also made from other starting materials (such as pitch).

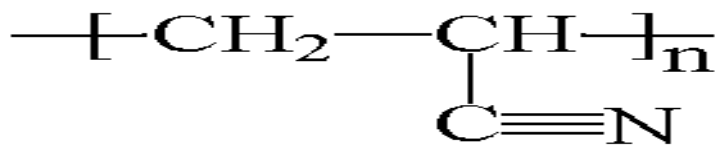


Fig: 2.5 Structure of Polyacrylonitrile

The use of carbon fibers as reinforcement material is being in practice since the 1980s for both vapor-grown and polyacrylonitrile (PAN)-based [18] Carbon fiber, among other fiber types. Having control over the fiber properties by manipulation of process parameters was of keen interest during earlier studies. Brief literature reviews explaining the mechanical properties of Carbon fiber-reinforced polymer composites have been previously published [19-22]. These reviews can be helpful in the development in the background of Carbon fiber reinforced composites. Carbon fiber can be classified as linear, sp²-based (one double bond, two single bond) discontinuous filaments, where the aspect ratio is greater than 100. An alternate route to the production of carbon fiber is through electro spinning [23] in this a fine tip needle syringe is used in this sol-gel process. High voltage is applied to the droplet at the tip of the needle, which causes the solution to spurt out from the needle to a target. Carbon fibers are known for their excellent properties, they have high strength and stiffness-to-weight ratio, high stiffness, long fatigue life, low density, highly corrosion resistance, and environmental stability. They are mainly used to form the polymer composite materials. They are bound in the polymer resin material to give desired properties. Carbon fiber can be in form of continuous fiber or can be chopped in to small pieces and can be used to make the polymer composites.

In present study, toughening of epoxy network using polyurethane as a modifier has been attempted. Afterwards, to further enhance the strength, carbon fibers were added in longitudinal, transverse and random direction with matrix before curing. The effects of carbon fiber and their different percentage in PU/epoxy matrix and neat epoxy samples on the basis of mechanical properties.

2.6 Triethylenetetramine (TETA)

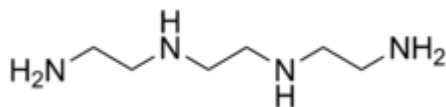


Fig: 2.6 Structure of triethylenetetramine (pic: Wikipedia)

Triethylenetetramine, abbreviated as TETA or trien, sometimes also called trientine (INN), it is an organic compound with the chemical formula $[\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2]_2$. It is an oily liquid which is colorless but, like most amines, have slightly yellowish color due to the impurities result of air-oxidation. They are soluble in polar solvents. The branched isomer tris(2-aminoethyl)amine and piperazine derivatives sometimes are there in commercial samples of TETA. TETA is prepared by heating the mixture of ethylenediamine or ethanolamine/ammonia over an oxide catalyst. This process results in variety of amines, which are further separated by the process of distillation and sublimation.

CHAPTER 3. EXPERIMENTAL

3.1 Materials

3.1.1 Raw materials/Chemicals

In the present study, following raw materials/chemicals are employed:

- 1) Methylene diphenyldiisocyanate(MDI)
- 2) Polyethylene glycol 4000
- 3) Bisphenol A(4,4-isopropylidenediphenol)
- 4) N,N-Dimethylformamide
- 5) Epoxy resin Araldite LY 5052
- 6) Mixture of polyamine hardener Aradur 5052
- 7) Carbon Fiber
- 8) Standard silicone mold was for preparation of specimen

3.1.2 Specification and Sources of Raw Materials/Chemicals

Specification and sources of raw materials/chemicals used in the studies are given in Table

3.1

Table 3.1 Specifications and Sources of Raw Materials/Chemicals

| Sr. No. | Chemicals | Source | Specification |
|---------|-----------|--------|---------------|
|---------|-----------|--------|---------------|

| | | | |
|---|---|---|--------------------------|
| 1 | Methylene diphenyldiisocyanate(MDI) | Polytek Urethane Private Limited | Industrial Grade |
| 2 | Polyethylene glycol 4000 | Thomas Baker chemicals Pvt. Ltd. Mumbai | Laboratory Reagent Grade |
| 3 | Bisphenol A(4,4-isopropylidenediphenol) | Sisco Research Laboratories Pvt. Ltd. Mumbai, | Laboratory Reagent Grade |
| 4 | N,N-Dimethylformamide | Sisco Research Laboratories Pvt. Ltd. Mumbai | Laboratory Reagent Grade |
| 5 | Epoxy resin Araldite LY 5052 | Huntsman Corporation United States, | Industrial Grade |
| 6 | Polyamine hardener Aradur 5052 | Huntsman Corporation United States, | Industrial Grade |
| 7 | Silicone Rubber RTV | Aditya Genuine Products | Industrial Grade |

Table 3.2 Properties of carbon fiber

| Properties | Carbon fiber |
|--|-----------------------|
| Tensile strength (GPa) | ≥ 3500 |
| Density (g/cm ³) | 1.65-1.75 |
| Carbon content (%) | ≥ 98 |
| Electrical resistivity (Ω /cm) | 1.5×10^{-33} |
| Coefficient of linear expansion (/°C) | -0.1×10^{-6} |
| Draw ratio | 1-50:1 |

3.1.3 Purification of Raw materials/Chemicals

The consistency and accuracy in the results highly depends on the quality and purity of reactants employed. The percentage purity of the chemicals used during experimental work is given in Table 3.3. All the chemicals were used as received without doing any further treatment.

Table 3.3. Percentage Purity of the Chemicals

| Sr. No. | Chemicals | Percentage Purity |
|----------------|--|--------------------------|
| 1 | Methylene diphenyldiisocyanate(MDI) | 99% |
| 2 | Polyethylene glycol 4000 | Approx. 99.9 % |
| 3 | BisphenolA(4,4- isopropylidenediphenol) | 97% |
| 4 | N,N-Dimethylformamide | 99% |
| 5 | Epoxy resin Araldite LY 5052 | 99% |
| 6 | Polyamine hardener Aradur 5052 | 99 % |

3.2 Methodology

The systematic methodology highlighting how the progress of proposed work towards achieving desired objectives was proceeded, involves the following steps:

- Selection of raw materials
- Synthesis of Polyurethane prepolymer
 - ◆ Characterization of PU prepolymer

- Mixing of prepolymer to epoxy resin at different ratio
 - ◆ Testing to pick best ratio
- Reinforcing it with carbon fibre and prepared composite
- Characterization and testing of composites

3.3 Experimental work

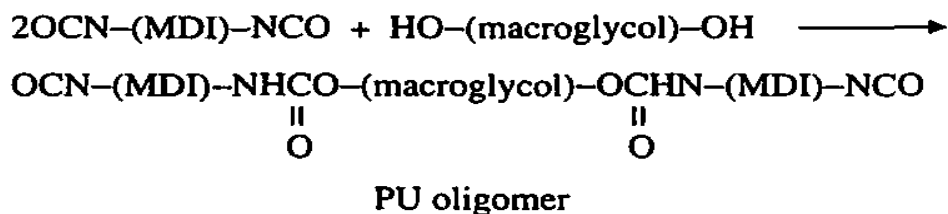
3.3.1 Synthesis of PU modified Epoxy

In this project PEG 4000 and MDI were used for preparation of prepolymer then added with Bisphenol A to prepare PU modified Epoxy resin. N, N-dimethyl formaldehyde used a solvent. Hydroxyl terminated polyurethane prepolymer was prepared by reacting 4 equivalent of MDI against the 1 equivalent of Polyethylene glycol 4000 in dimethyl formamide (DMF) The reaction occurred completely under inert atmosphere at 80°C for 2 hours. Subsequently, this oligomer was further reacted with 4 equivalents of Bisphenol-A at 80°C for 1 hour. The product obtained was dried by heating it at 90°C for 48 hours.

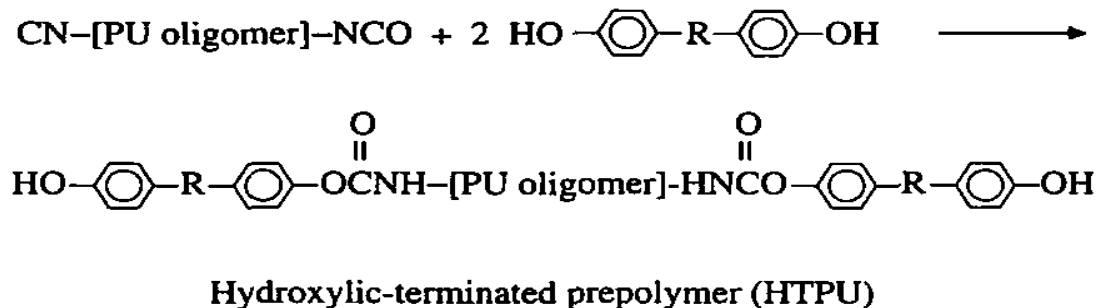


Fig: 3.1Experimental setup

step 1.



step 2.



3.3.2 Preparation of samples

For preparation of the samples, the PU pre-polymer was first dissolved in the epoxy resin Araldite LY 5052 at 120°C and pre-reacted for 30 mins. In stoichiometric ratio of the hardener Aradur 5052 was added and mixed with mechanical stirring. The half of this mixture was poured in the moulds and then carbon fibers (0.131 gm) were laid and remaining mixture was added in mould. The resin composites were cured at 120°C for 3 hours.



Fig: 3.2 Prepared Samples of Different Formulations

3.3.3 Characterization

3.3.3.1 Infrared spectroscopy

Infrared spectroscopy is very important technique for the characterization of polymers. One of the great advantages of infrared spectroscopy is that virtually any sample in any state can be examined. Fourier transforms infrared radiation (FITR) spectrometer calculates the transmission percentage of infrared. Here FT-IR spectrophotometer Nicolet 380 (shown in fig: 8) was used to get the IR spectra of prepared sample. For FTIR analysis of the sample, prepared PU modified epoxy resin first dried in oven and collected in powder form. In order to prepare pellet little quantity of potassium bromide (KBr) was segregated with

powder sample and after that pressing of mixture was done. Analysis of that pellet was done using FITR by keeping the pellet in sample holder.



Fig: 3.3 Nicolet 380 FT-IR Spectrometer

3.3.3.2 Thermal Analysis

Thermo-gravimetric analysis determines the amount and rate at which the change in mass of the specimen as a function of temperature or time in a controlled atmosphere. The measurements are helpful in determining the thermal and/or oxidative stabilities of materials as well as their compositional properties. The process was carried out in N_2 gas atmosphere. Thermogravimetric analysis can be utilized to determine the thermal stability of acrylic copolymer. If no weight change was observed in the polymeric sample in desired range of temperature then polymer will be considered as thermally stable. Thermogravimetric analysis (TGA) of PU modified epoxy and PU modified epoxy with carbon fiber was done on a Perkin-Elmer instrument (shown in fig: 9) from 25 to 900°C at a heating rate of 10°C/min by taking 1mg of powder sample.



Fig: 3.4 Perkin-Elmer TGA 4000 analyzer

3.3.4 Mechanical test

3.3.4.1 Tensile test

The tensile strength was measured by the equation,

$$\text{Ultimate tensile strength} = P_{\max}/A$$

Where, ' P_{\max} ' is the maximum tensile load, ' A ' is original cross-sectional area.

The tensile property of the composites having carbon fiber as reinforcing material, such as strength and elastic or young's modulus, were tested following standard ASTM D 638 using UNIVERSAL TESTING M/c SERIES:9036 STS UTM. Capacity ranging from 50 Kgf to 5000kg. Samples of dimensions as shown in figure was prepared and while performing test the applied load to failure at a speed rate of 10 mm/min. The load cell used was 1500 N and the loading span was 150 mm. For each composite panel, three samples were tested and resulted value was reported.



Fig: 3.5 Samples for tensile test

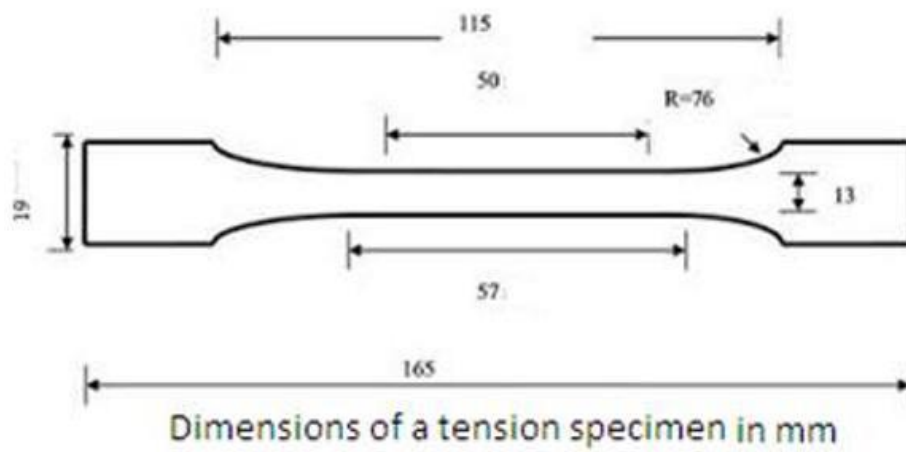


Fig: 3.6 Specimen of tensile testing



Fig: 3.7Startest universal testing machine

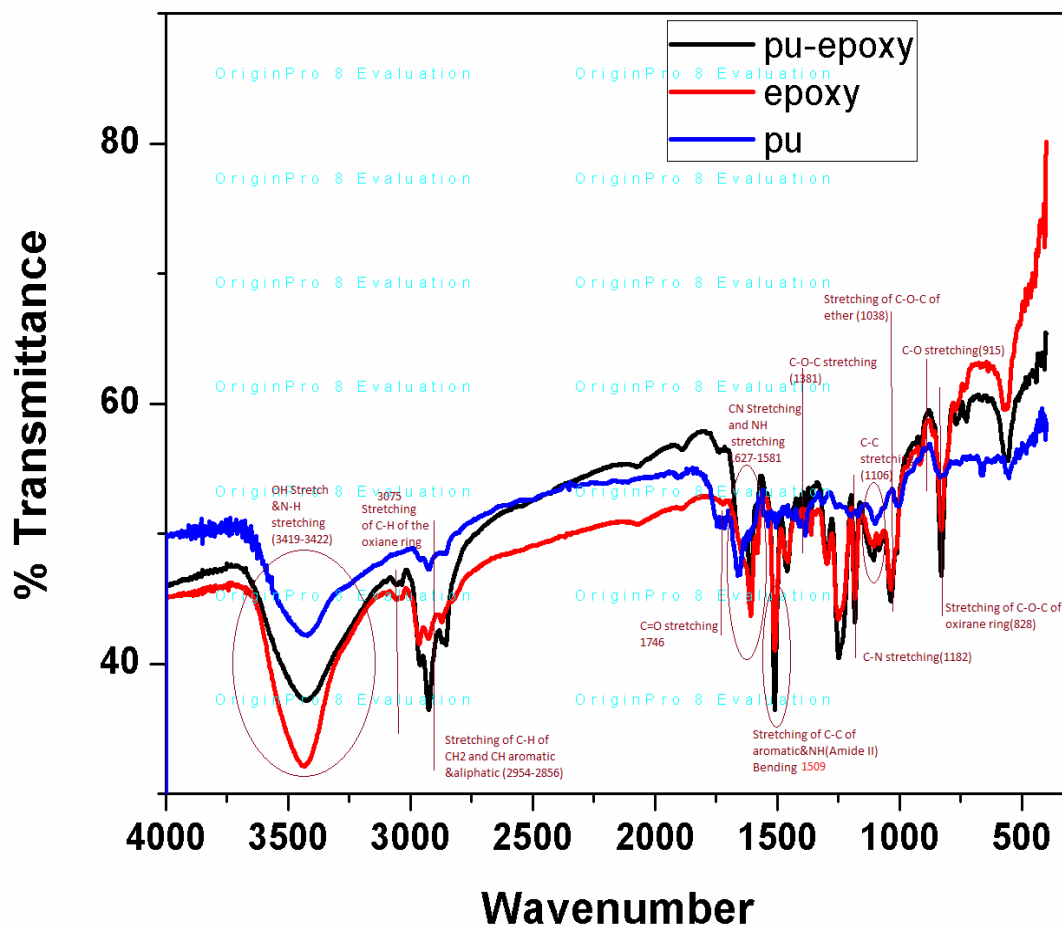
3.3.4.2 Compression Test

The compressive strength was measured by the equation; $\text{Compressive strength} = P_{\max}/A$
 Where, ' P_{\max} ' is the maximum compressive load, ' A ' is original cross-sectional area of specimen.

Compression test is a common method of test that is used to establish the compressive force or crush resistance on a material and the ability of the material to withstand the highest value of the compressive force applied. Compression tests are used to evaluate the behaviour of specimen under a compression load. The maximum compressive stress, which a material can sustain under a load (constant or progressive) is determined. Compression testing is often done to a break (rupture) the sample to a limit. When the test is performed to a break, break detection can be defined depending on the type of material being tested. When the test is performed to a limit, either a load limit or deflection limit is used.

CHAPTER 4. RESULTS AND DISCUSSION

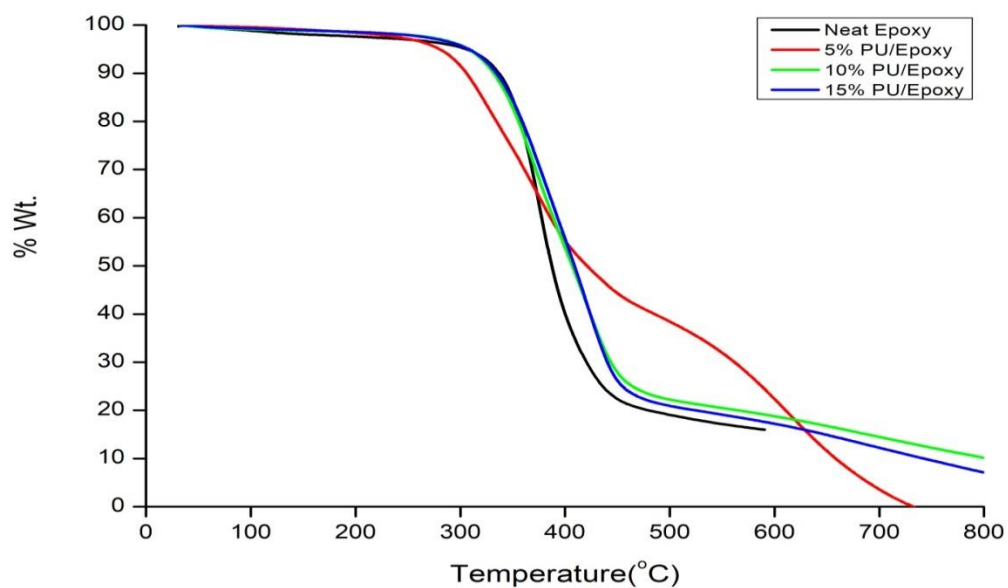
4.1 FTIR



Graph 1

| Range(cm^{-1}) | Observation |
|---------------------------|---|
| 3422 | OH Stretch&N-H stretching |
| 3075 | Stretching of C-H of the oxiane ring |
| 2954-2856 | Asymmetric Stretching of C-H of CH_2 and C-H aromatic &aliphatic |
| 1746-1731 | C=O stretching |
| 1627-1581 | C-N Stretching and N-H stretching, Stretching C=C of aromatic rings |
| 1509 | Stretching of C-C of aromatic&NH(Amide II) Bending |
| 1381 | C-O-C stretching |
| 1182 | C-N stretching |
| 1106 | C-C stretching |
| 1038 | Stretching of C-O-C of ether |
| 915 | C-O stretching |
| 828 | Stretching of C-O-C of oxirane ring |

4.2 Thermogravimetric test



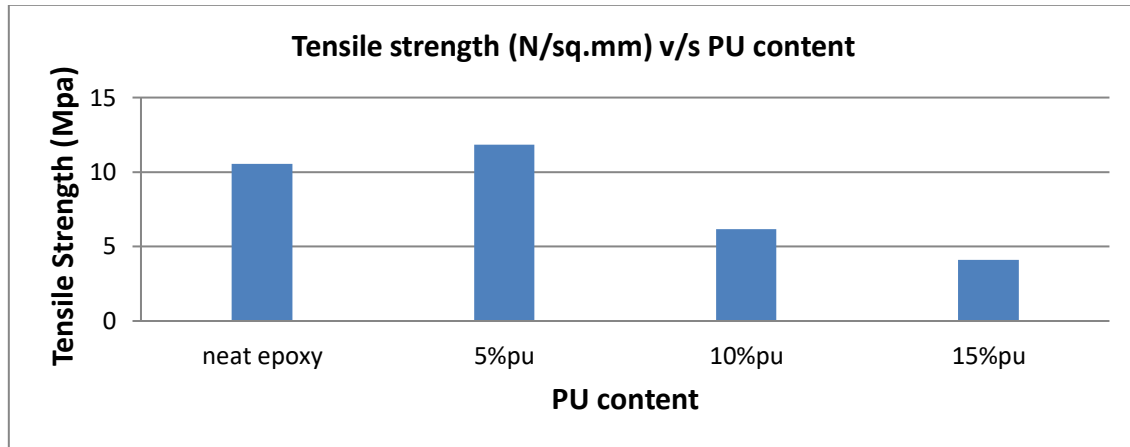
Graph 2

The onset temperature for decomposition of pure Epoxy sample is nearly 270°C and the derivative of thermogram represent at 400°C max. loss in weight. Degradation of Epoxy composite with 5% PU content occurs in two steps, due to modify with PU pre polymer. For first step degradation the onset temperature for decomposition of composite is nearly 290°C and the derivative of thermogram represent at 350°C max. loss in weight. In the second step degradation the onset temperature is 510°C and derivative of thermogram represent at 620°C max. loss in weight. It shows the evenly distribution of the PU prepolymer in the composite and phase separation.

The onset temperature for decomposition of Epoxy composite with 10% PU content is nearly 310°C and the derivative of thermogram represent at 470°C max. loss in weight. The onset temperature for decomposition of Epoxy composite with 15% PU content is nearly 310°C and the derivative of thermogram represent at 470°C max. loss in weight.

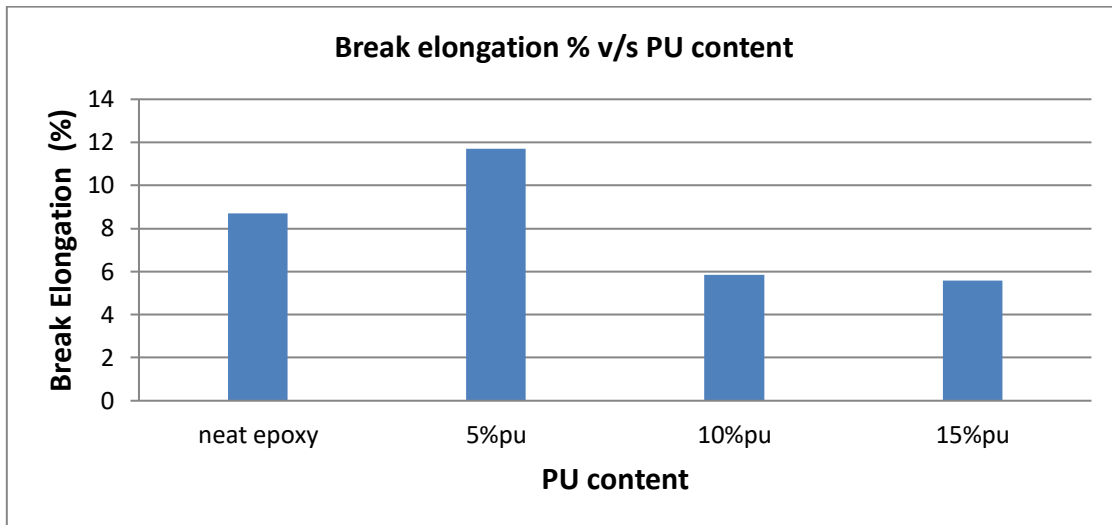
The above results also show that the thermal stability of the epoxy composites incorporated with PU prepolymer increased as compared to the neat epoxy sample. With increase in PU content above 5% in composites, single step thermal degradation is observed, indicating that with increase in PU content the phase separation decreases. It is because, due to reduction in cross-linking density in modified epoxies as concentration of PU increases. (Wang, HH. & Chen, JC. J Polym Res (1996) 3: 133).

5.1. Tensile test



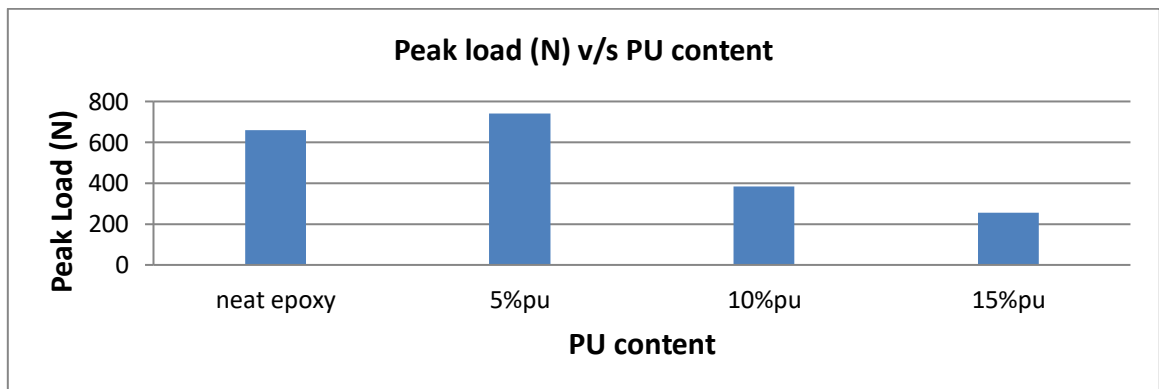
Graph 3

Above graph shows that the composite material of PU prepolymer has increased tensile strength as compared to the neat epoxy sample, because the prepolymer has increased the ductility of the epoxy (brittle) and also increased its toughness. Further increasing the prepolymer content, with increase in PU content above 5% in composites, the composite material became more brittle because, due to reduction in cross-linking density in modified epoxies as concentration of PU increases. (Wang, HH. & Chen, JC. J Polym Res (1996) 3: 133) and as polyurethane and epoxy both are thermosetting polymer, together on bonding they increases the brittleness of material samples with 10% and 15% PU prepolymers shows less tensile strength.



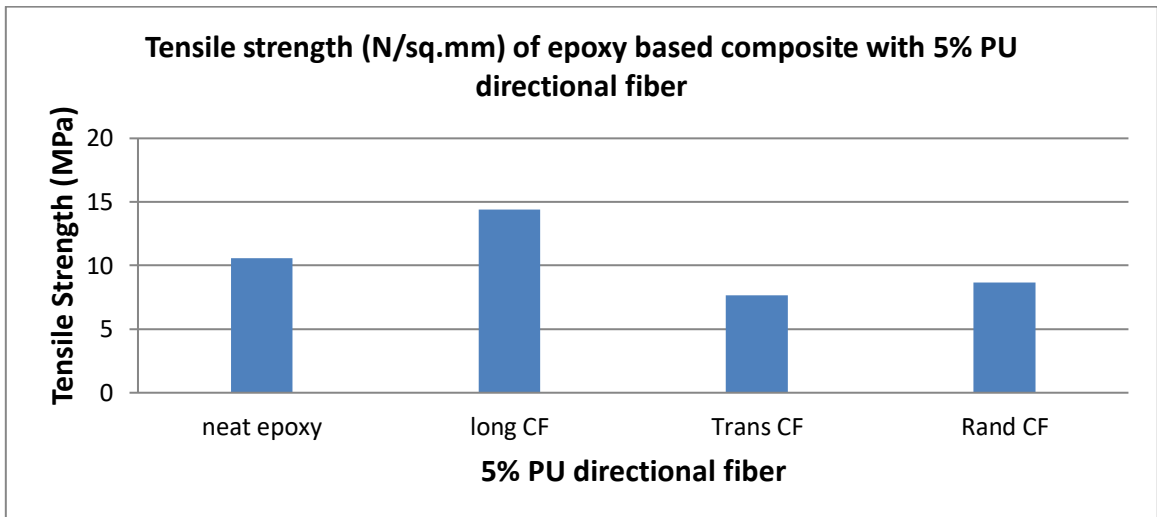
Graph 4

From above graph we can conclude that, the break elongation of the composite with 5% PU prepolymer has increased, due to increase in toughness. Further addition of the prepolymer has reduced the property due to increase in brittleness.



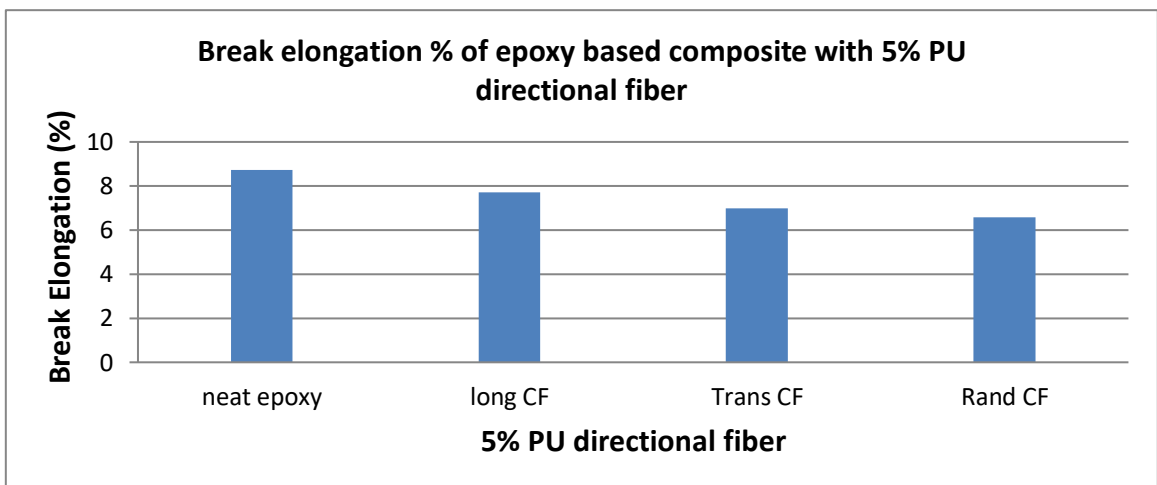
Graph 5

From above graph, we can conclude that the peak load capacity of the 5% PU composite sample has increased because it has increased the ductility of the material. Further addition of prepolymer has made the material more brittle.



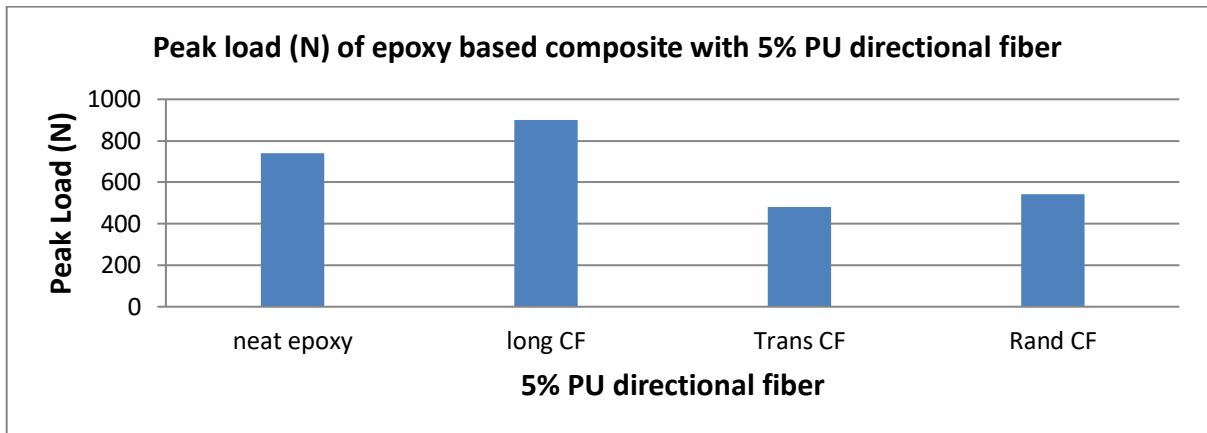
Graph 6

Addition of carbon fiber in different direction has shown considerable changes in tensile property. The tensile strength of the composite reinforced with longitudinal carbon fiber has increased as compared to other reinforced fiber because of better load distribution by the fiber in longitudinal direction.



Graph 7

Break elongation has decreased with reinforcing by carbon fiber, due to the reason that carbon fiber is stiff and resists elongation.

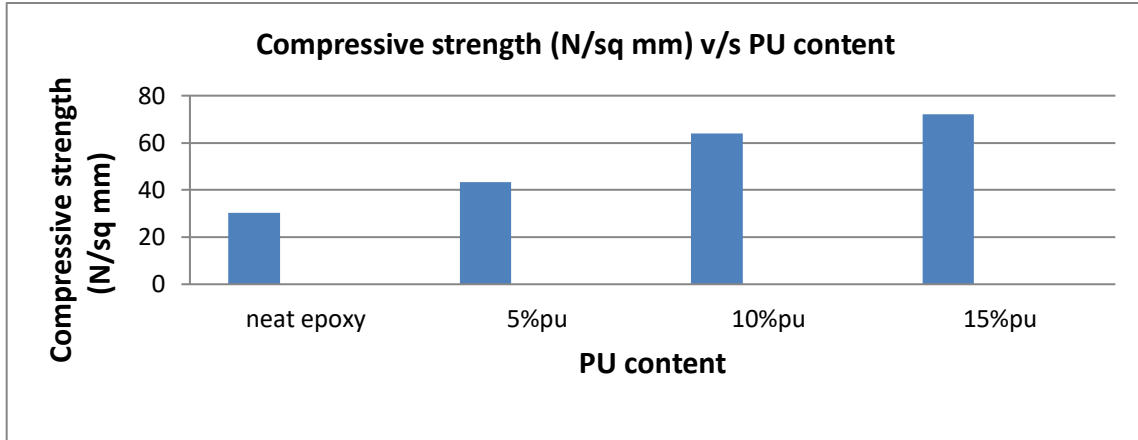


Graph 8

Longitudinal reinforced carbon fiber PU epoxy composite has shown highest load bearing capacity as compared to the other samples made, due to good load distribution by the carbon fiber in the longitudinal direction.

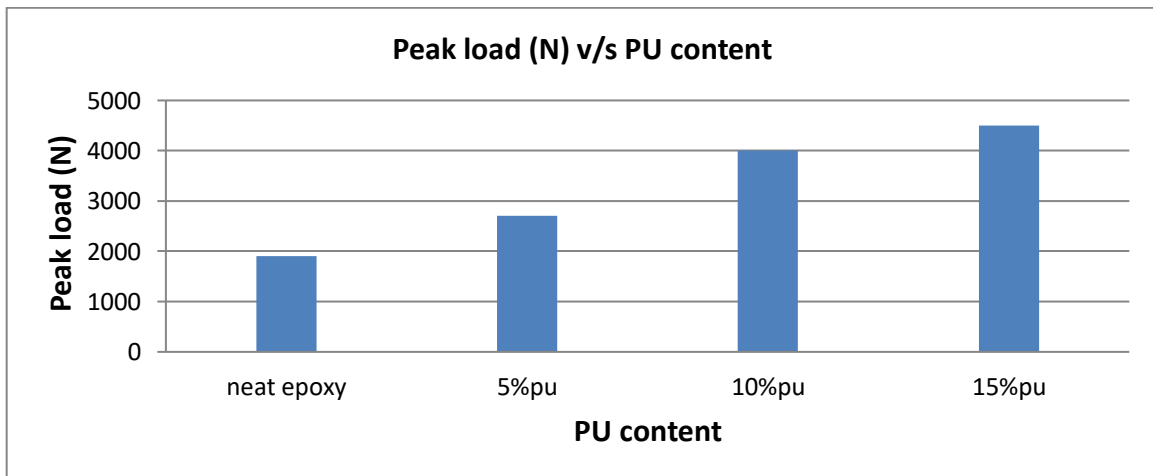
From above graph, we can conclude that, the properties shown by the composite made by incorporating 5% PU content shows excellent properties. The PU reacts with the resin chemically, which increases its molecular weight, and leads to the phase separation, it also ensures intrinsically strong chemical bonding throughout the rubbery phase/resin matrix interface. The tensile modulus gradually decreases with an increase in the content of PU. The decrease of modulus in PU-modified epoxy network is due to the effect of the soft segment phase present in the PU-modifier another reason for decrease in the tensile strength in the epoxy network with the addition of PU prepolymer because further increasing the prepolymer content, above 5% in composites, the composite material becomes more brittle because, due to reduction in cross-linking density in modified epoxies as concentration of PU increases. (Wang, HH. & Chen, JC. J Polym Res (1996) 3: 133) and as polyurethane and epoxy both are thermosetting polymer, together on bonding they increase the brittleness of material samples with 10% and 15% PU prepolymers show less tensile strength. [26-30].

5.2. Compression test



Graph 9

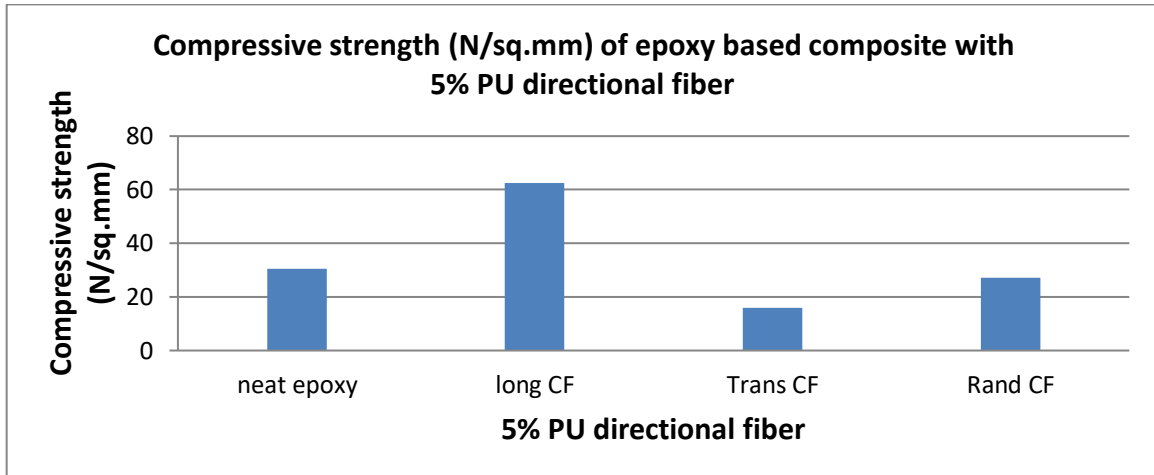
From above graph it can be concluded that, as the PU content in epoxy has increased, the epoxy has become ductile upto 5% PU content, because the tensile property of the same sample has also increased while, for other samples the tensile property has decreased but the compressive strength has increased confirming that the samples has become brittle in nature.



Graph 10

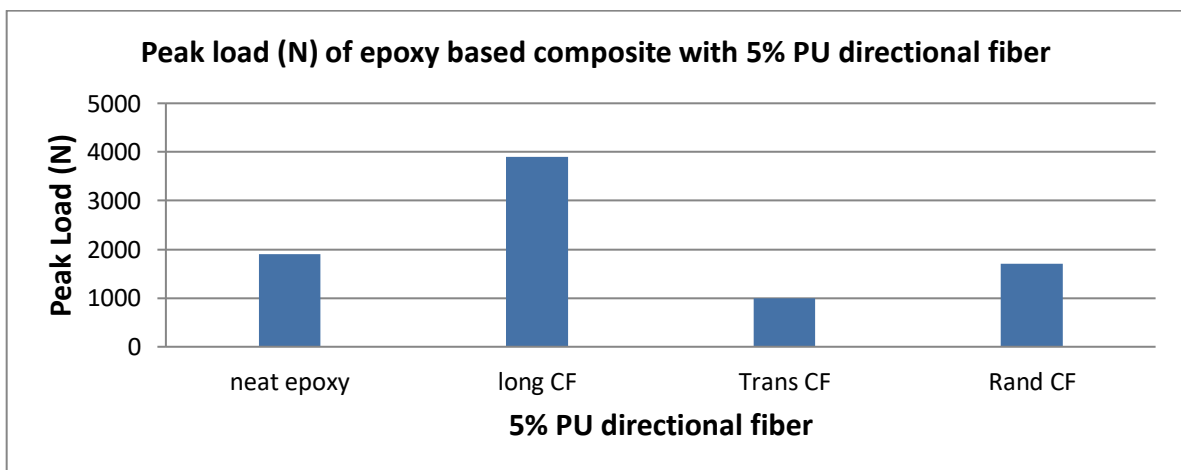
From above graph it can be concluded that, as the PU content in epoxy has increased, the epoxy has become ductile upto 5% PU content, because the tensile peak load of the same sample has also increased while, for other samples the tensile peak load has decreased but

the compressive peak load has increased confirming that the samples has become brittle in nature.



Graph 11

Addition of carbon fiber in different direction has shown considerable changes in compressive property. The compressive strength of the composite reinforced with longitudinal carbon fiber has increased as compared to other reinforced fiber because of better load distribution by the fiber in longitudinal direction.



Graph 12

Addition of carbon fiber in different direction has shown considerable changes in compressive property. The compressive peak load of the composite reinforced with

longitudinal carbon fiber has increased as compared to other reinforced fiber because of better load distribution by the fiber in longitudinal direction.

CHAPTER 5. CONCLUSION

Epoxy modified with hydroxyl-terminated polyurethane (HTPU) can increase the load bearing capacity, as well as the tensile strength of the modified epoxy resins with PU content. The PU-modified epoxy resin reinforced with Carbon fiber in longitudinal direction has shown the increase in tensile strength and load bearing capacity further. While, the samples reinforced with carbon fiber in random direction has shown significant increase in tensile property and also in load bearing as compared to the transverse direction. However, at higher prepolymer content, the tensile strength, toughness and load bearing capacity has decreased and the plastic deformation of the PU in the epoxy samples incorporated by PU prepolymer is restricted. However, the addition of PU prepolymer particles does not greatly affect the thermal degradation of the epoxy samples incorporated by PU prepolymer. The decrease in the properties of the composite material with increased content of polyurethane (PU) pre polymer above 5% is due to reason that, further increase in PU content above 5% in composites, the composite material becomes more brittle because, due to reduction in cross-linking density in modified epoxies as concentration of PU increases. (Wang, HH. & Chen, JC. J Polym Res (1996) 3: 133) and as polyurethane and epoxy both are thermosetting polymer, together on bonding they increases the brittleness of material samples with 10% and 15% PU prepolymer show less tensile strength and more brittleness.

CHAPTER 6: FUTURE SCOPE

Different types of materials (rubbery particles) or the combination of different materials can be used for modifying the properties of the epoxy resin. The reinforcement can also be incorporated in the modified epoxy to obtain the composite (s) with enhanced properties and better finishing. Operations like drilling, turning, vibration testing, cutting, etc. can be performed to know the composite material behavior and to utilize them in various engineering applications. Further, as the reinforcement material used was Carbon fiber, so the studies can be made to determine conductivity of the resulted composite samples.

REFERENCES

- 1- Subita, B. and Pardeep, K.. Effect of Graphite Filler on Mechanical Behaviour of Epoxy Composites. International Journal of Emerging Technology and Advanced Engineering.2013
- 2- Ranganatha, S. R. and Ramamurthy V.S. Investigation on Mechanical Behavior of Filler Al₂O₃ in CFRP Composites. International Journal of Advanced Engineering Technology/IV/III/July-Sept.,2013 pp.105-107.
- 3- Shokrieh M.M., Daneshvar A. and Akbari, S., Carbon 59 .2013, pp. 255.
- 4- Shams S.S. and El-Hajjar, R.F., Composites Part A, 49, 2013pp.148.
- 5- Kaman M.O., Eng. Fract. Mech., 78 (2011) 2521. Yashir S. and Ogi, K., Composites Part A, 40 (2009) 938.
- 6- Dey B., Zhou Y., Jeelani S., Kumar A. and Stephenson L.D., Mater. Lett., 62 (2008) 3659.
- 7- Broughton W.R., Koukoulas T., Woolliams P., Williams J. and Rahatekar S.S., Polym. Test., 32 (2013) 1290.

- 8- Zhang K., Gu Y., Li M. and Zhang Z., *Mater. Design*, 54 (2014) 624.
- 9- Kucher N.K., Zemtsov M.P. and Zarazovskii M.N. *Mech. Compos. Mater.*, 42 (2006) 407.
- 10- Mangalgi, P. D. (1999). *Composite Materials for Aerospace Applications*, *Bulletin of Materials Science*, 22 (3): 657–664.
- 11- Kim, R. Y., Crasto, A. S. and Schoeppner, G. A. (2000). Dimensional Stability of Composite in a Space Thermal Environment, *Composites Science and Technology*, 60(12): 2601-2608.
- 12- L. Brown, “Applications of,” pp. 39–59, 1984.
- 13- K. K. Chawla, “Composite Materials,” *Adv. Mater. by Des.*, p. 73, 2012.
- 14- R.-M. Wang, S.-R. Zheng, and Y.-P. Zheng, “Introduction to polymer matrix composites,” *Polym. Matrix Compos. Technol.*, pp. 1–548, 2011.
- 15- H. H. Wang and J. C. Chen, “Polyurethane-modified epoxy resin and their polymer particle filled epoxies,” *J. Polym. Res.*, vol. 3, no. 2, pp. 133–138, 1996.
- 16- Xiao, H. X. Gao, X. M. *Polym Eng Sci* 1994, 22, 752.
- 17- Ho, T. H. Wang, C. S. *Polymer* 1996, 37, 2733.
- 18- J. K. Kim and R. E. Robertson, *J. Mater. Sci.*, 27, 161(1992).

- 19- J. K. Kim and R. E. Robertson, *J. Mater. Sci.*, 27,3000 (1992).
- 20- Tibbetts, G. G. (1989). Vapor-grown carbon fibers: Status and prospects. *Carbon*, 27(5),745–747
- 21- Selzer, R. and Friedrich, K., Effect of moisture on mechanical properties and fracture behavior of carbon fibre reinforced polymer composites. *Advanced Composites Letters*, 1993, 2(1), 10- 13.
- 22- Selzer, R. and Friedrich, K., Influence of water up-take on interlaminar fracture properties of carbon fibre-reinforced polymer composites. *Journal of Materials Science*, 1995, 30, 3344338.
- 23- Ma, C.-CM. and Yur, S.-W., Environmental effects on the water absorption and mechanical properties of carbon fibre reinforced PPS and PEEK composites. *Polymer Engineering and Science*, 1991, 31(1), 34-39.
- 24- Shirrell, C.D. and Halpin, J., *Moisture Absorption and Desorption in Epoxy Composite Laminates*, ASTM STP 617. American Society for Testing and Materials, Philadelphia, PA, 1977, pp. 514-528.
- 25- Li, D. and Xia, Y. “Electrospinning of Nanofibers: Reinventing the wheel.” *Adv Materials* 16 (1151-1170).
- 26- J. K. Kim and R. E. Robertson, *J. Mater. Sci.*, 27, 161(1992).
- 27- J. K. Kim and R. E. Robertson, *J. Mater. Sci.*, 27,3000 (1992).
- 28- M. E. Nichols and R. E. Roberston, *J. Mater. Sci.*, 29,5916 (1994).

29- H. X. Xiao, K. C. Frisch and H. L. Frisch, *J. Polym.Sci., Polym. Chem. Ed.*, 21, 2547 (1983).

30- D. S. Kim, K. Cho, J. H. An and C. E. Park, *J. Mater.Sci. Lett.*,11, 1197 (1992).