Synthesis and Characterization of Epoxy-Amine-Titania Composites

QUAID-I-AZAM UNIVERSITY

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A Dissertation submitted to the Department of Chemistry, Quaid-i-Azam University, Islamabad, in partial fulfillment of the requirements for the degree of

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in

Organic Chemistry

by

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DECLARATION

This is to certify that this dissertation entitled **"Synthesis and characterization of epoxy-amine/titania composites"** submitted by ***Ms. Zakya Rubab*** is accepted in its present form by the Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan, as satisfying the dissertation requirements for the degree of ***Master of Philosophy in Organic Chemistry.***

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ABSTRACT

The present research project encompasses the study of epoxy-amine-titania composites based on diglycidyl ether of bisphenol A (DGEBA), cured with Jeffamine D-400. Titania network was generated ex-situ via inorganic sol gel route. The first type of titania was partially condensed, leaving OH at its surface. The second type was the completely dried and condensed calcined titania network, while coupling agent was grafted onto the surface of the third type of titania namely functionalized titania. The particles were characterized by Attenuated Total Reflection Infra-Red Spectroscopy (ATR-IR), X-Ray Diffraction analysis (XRD) and Atomic Force Microscopy (AFM). The ATR-IR revealed the surface morphology of particles, while XRD gave information about the structure of crystallites. AFM confirmed the functionalization of particles. Namely EAT-1, EAT-2, and EAT-3 three unique composite systems were synthesized by blending titania network with the epoxy amine matrix. EAT-1 system contained epoxy-amine and micro-titania without a coupling agent. EAT-2 system contained epoxy-amine and calcined titania, while a coupling agent was grafted onto the titania filler alongwith the epoxy-amine matrix in the EAT-3 system. The resulting composites were characterized by Attenuated Total Reflection Infra-Red Spectroscopy (ATR-IR), Differential Scanning Calorimetry (DSC), Thermogravimetric analysis (TGA) and mechanical analysis. ATR-IR spectral analysis revealed chemisorption of particles in case of EAT-3, while DSC thermograms showed the transition in the Tg depending upon the type of filler.TGA gave the thermal stability profile. Comparison of the tensile properties with the neat matrix showed the modification in the mechanical properties. Among the three composite systems, the system containing functionalized titania showed best performance owing to stronger interaction between the matrix and the filler.

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1. INTRODUCTION

The development of composite materials and related design and manufacturing technologies is one of the most important advancements in the history of materials. Composites are multifunctional materials having mechanical and physical properties that can be tailored to meet the requirements of a particular application. Many composites also exhibit great resistance to high-temperature corrosion, oxidation and wear. These unique characteristics provide design opportunities not possible with conventional materials. Further, many manufacturing processes for composites are well adapted to the fabrication of large, complex structures, which allows reduction in manufacturing costs.

By definition, composite materials are made from two or more constituent materials that remain separate and distinct on a macroscopic level. There are two categories of constituent materials: matrix and reinforcement. The matrix is the continuous phase and is often but not always present in greater quantity. It surrounds and supports the reinforcement materials by maintaining their relative positions. The reinforcements impart their special mechanical and physical properties to enhance the matrix properties. The major functions of the matrix are to transfer stresses between the reinforcing phase (fibers/particles) and to protect them from mechanical and environmental damage whereas the presence of reinforcement in a composite improves its mechanical and thermal properties such as strength, stiffness, degradation onset, Tg etc. The objective is to make use of the superior properties of both materials without compromising on the weakness of either[1,2].

Among the three types of matrices ceramic, metallic and polymeric matrix the most commonly used matrix materials are polymeric[3]. The reasons for this are twofold. In general the mechanical properties of polymers are inadequate for many structural purposes. In particular their strength and stiffness are low compared to metals and ceramics. These difficulties are overcome by reinforcing polymers with other materials. Secondly the processing of polymer matrix composites need not involve high pressure and does not require high temperature. Also equipments required for manufacturing polymer matrix composites are simpler. For this reason polymer matrix composites developed rapidly and soon became popular for structural applications. The three classes of polymeric matrices, thermosets, thermoplastics and rubbers, are all important as far as polymer matrices are concerned.

For various applications, mechanical and thermal properties of polymer systems are commonly improved by addition of inorganic filler [4-7]. Material properties of the composite are determined by the respective properties of both the constituents and thus depend upon the content of the filler, its adhesion to polymer matrix, uniformity of dispersion, etc. In the last two decades the varieties of elastomers, thermoplastics, linear or cross-linked systems, have been reinforced with inorganic fillers, either formed in situ or ex situ[8].

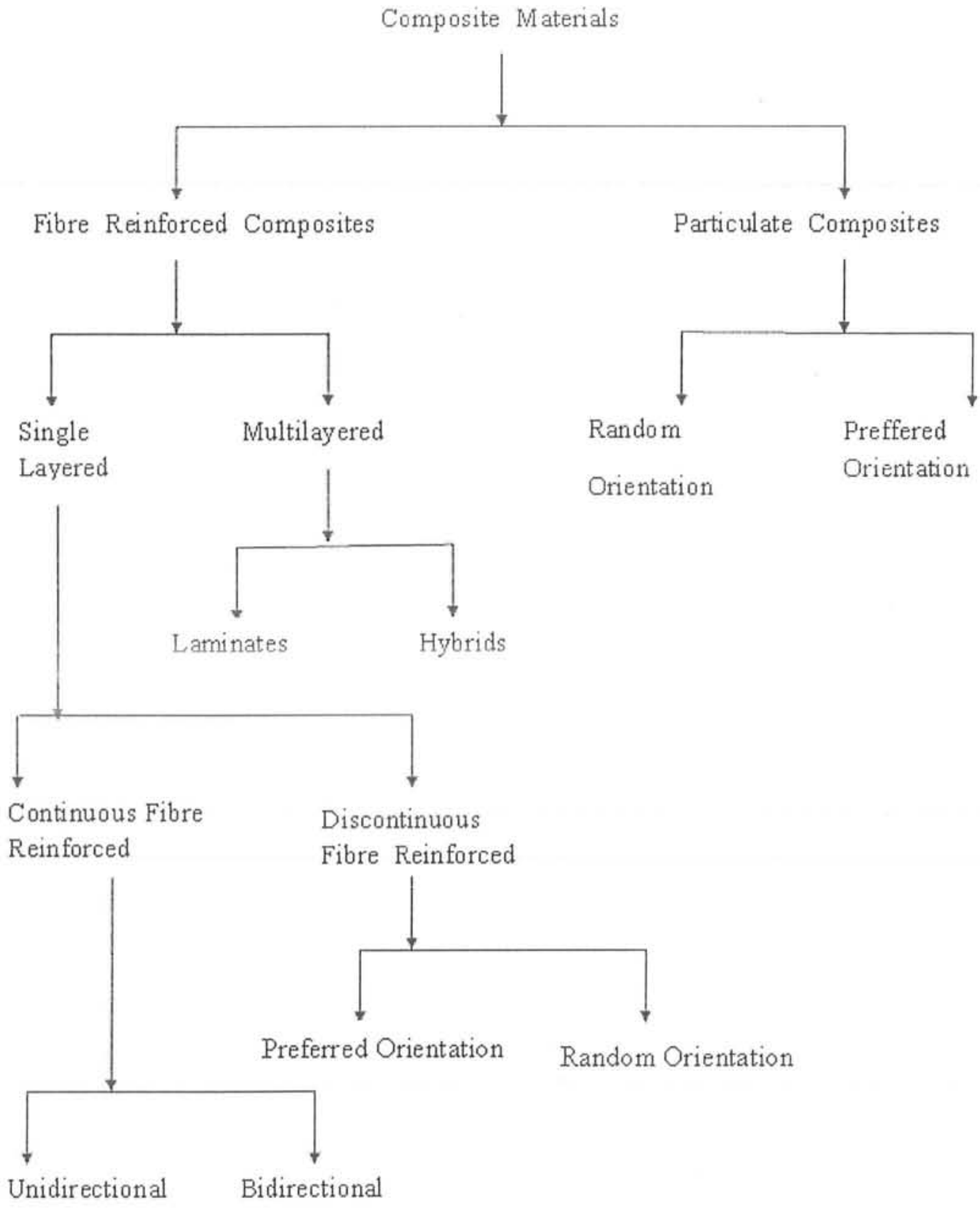


Fig 1.1: General classification of composites[9]

The reinforcing phase may be particulate, fibrous, or clay[10]. Particulate composites, as the name itself indicates, the reinforcement is of particle nature. It may be spherical, cubic, tetragonal, a platelet, or of other regular or irregular shape, but it is approximately equiaxed. Among the particulate reinforcements are metal or metal oxide particles. The fibrous reinforcement comprises of fibres such as glass, carbon, aramid etc. The clay composites contain clay as reinforcing phase e.g. clossite, montmorillonite (MMT) etc.

Industry	**Examples**	**Comments**
Aircraft	Doors, Elevators	20-35% weight savings
Aerospace	Space Shuttles, Space Stations	Great weight savings
Automotive	Body frames, Engine components	High stiffness & damage tolerance
Chemical	Pipes, Tanks, Pressure vessels	Corrosion Resistance
Construction	Structure & decorative panels Fuel tanks etc	Weight Savings, Portable

Table 1.1 Application of composites[1]

1.1 EPOXY RESINS

Epoxy resins are used extensively in composites materials for a variety of demanding structural applications. They are most versatile of all the commercially available matrices. Unsaturated polyesters may cost less and polyimides may perform better at elevated temperatures, but epoxy resins have a broad range of physical properties and mechanical capabilities[12-18].

Epoxy polymers were first synthesized by P.Schlack, the investor of Nylon 6, in 1934[19]. The curing reactions were discovered by P. Castan and polymer products were introduced on the market by Ciba towards the end of World War II.

During 2003-2006, epoxy resins consumption (on an unmodified basis) in the three major regions (United States, Western Europe and Japan) grew at an average annual rate of

3.4%. Epoxy resins consumption in the United States and Western Europe was expected to grow at an average annual rate of about 3.5% and 2.3%, respectively, from 2006 to 2011 [20].

Field of Application	Percent Consumption
Electrical/electronics	12
Composites/structural	15
Industrial protective coatings	15
Powder coatings	16
Building and construction	21
Auto coatings	9
Can coatings	12

Table 1.2: Percent consumption of epoxy resins[21]

Depending on the chemical structures of the resin and the curing agent, the availability of numerous modifying reactants, and the conditions of cure, it is possible to tailor the properties of epoxy resins to obtain toughness, chemical and solvent resistance, mechanical responses ranging from extreme flexibility to high strength and hardness, resistance to creep and fatigue, excellent adhesion to most fibres, and heat resistance. No by-products are formed during the cure and shrinkage due to cure is low.

1.1.1 RESIN MANUFACTURE AND PRODUCTS

Epoxy resin is manufactured by two basic processes. The most important reaction is of epichlorohydrin with compounds containing active hydrogen atoms, such as phenols, or amines and the other is peracid epoxidation of olefins.

The primary resin in epoxy technology is diglycidyl ether of bisphenol A (DGEBA) and its higher analogues. Although a number of different types are commercially available the market is still held by the systems based on reaction products of epichlorohydrin and 2,2-bis(4'-hydroxyphenyl)propane(bisphenolA). Resin is synthesized from the reaction of epichlorohydrin with bisphenol A.

Bisphenol A (BPA) is an important industrial chemical that is used primarily to make polycarbonate plastic and epoxy resins, both of which are used in a wide variety of applications. Polycarbonate and epoxy resins themselves have wide spread applications that mark the worth of bisphenol A. The first reported synthesis of BPA was from Thomas Zincke of the University of Marburg, Germany[22].

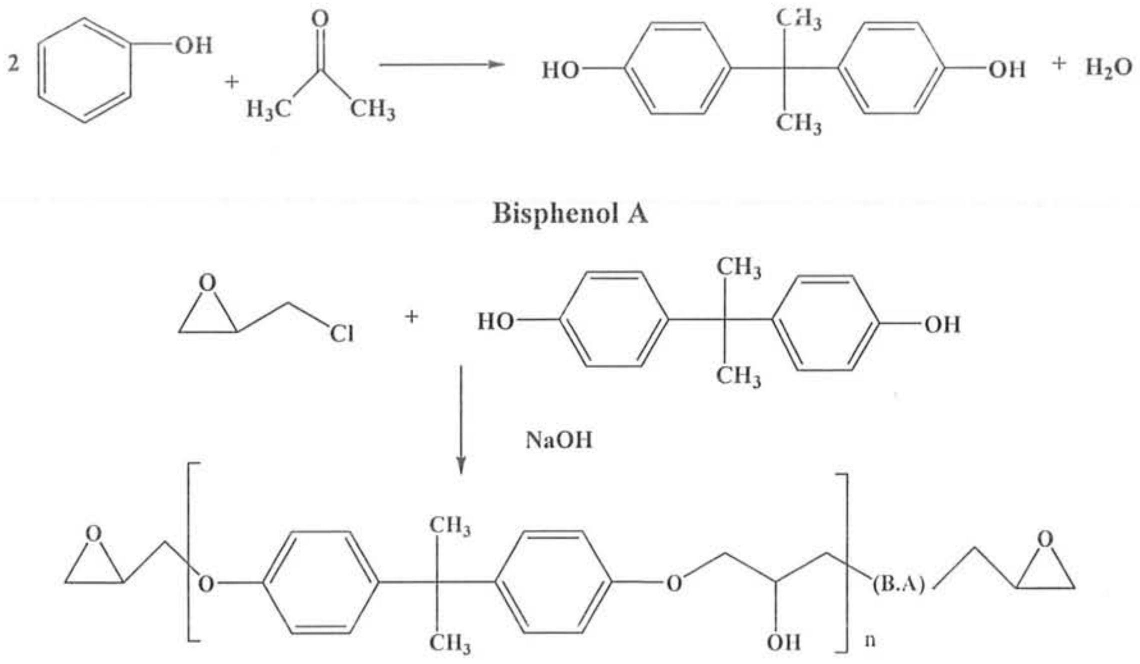


Fig 1.2: Synthesis of Epoxy resins[22]

Depending on the value of n, the polymers are either liquids or low melting point solids. The products with low values of n are the most widely used because, as n increases, melt viscosity also increases and solubility decreases, thus making processing more difficult.

The second most important epoxy resin manufacturing process involves epoxidation of olefins. Peracetic acid is most commonly used for this purpose. Chemo-oxidative oxidation of allyl ethers has also been carried out in recent years to produce glycidyl ethers[23].

The glycidyl ethers of various novolac resins are the second most important class of eoxy resins. They are manufactured by the reaction of epichlorohydrin with various phenolic novolacs, resulting in the chemical structure shown in figure 1.3. The glycidyl novolacs are characterized with better elevated temperature performance than the bisphenol A-based resins.

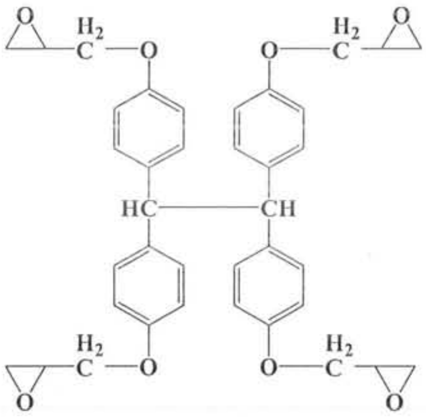


Fig 1.3: Tetraglycidyl ether of tetraphenol ethane

1.1.2 CURING AGENTS

Curing of thermoset adhesives such as epoxy has become increasingly important, mainly arising from application of epoxy as a matrix material for aerospace and marine structural composite components, and more recently as an adhesive and encapsulating sealant for the microelectronics and electronics equipments. In particular, the use of longer curing times for the systems used, is led by the requirement for higher performing systems[24]. Although thermal curing increases the cure rate and thus reduces the cure time, yet this is limited by the fact that the maximum rate of reaction for any given curing system is predetermined at a constant temperature. Microwave assisted curing has been found useful for reduction in the curing time along with retention of properties[24], although some reduction in cure percentage has also been observed[25].

Curing of epoxy resins with amines and other hardeners has been the subject of study for the past thirty years. A better understanding of the topological structure and properties of cured epoxy resins provided with new fundamental concepts about the chemistry of epoxy resins.

Epoxy groups are either structoterminal or structopendant depending on whether crosslinking occurs through the epoxy end group or the hydroxyl end groups. The prepolymer is structoterminal when polyamines are used for crosslinking; in this case curing involves the base catalyzed opening of the epoxide groups.

Hardening occurs primarily through hydroxyl group when an anhydride is used as the cross-linking agent; in this case epoxy prepolymer is considered as structopendant. Phathalic anhydride is often used as curing reagent.

Most of the curing agents in common use can be classified in the following groups:

(a) Primary amines
(b) Polyfunctional amines
(c) Anhydrides
(d) Polymerization catalysts

1.1.2.1 Amines as curing reagents of epoxies

Amines were one of the first hardeners used for the curing of epoxy resins and at present they occupy leading position among the hardeners of this type. The amine hardeners are most likely to be used in future because they are are easily accessible, higly reactive and their properties can be modified.

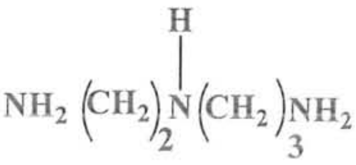
The final structure of the cured resin depends on the structure of crosslinking network, the curing agent, the curing extent, and the time and temperature of curing[26-29]. Since properties of epoxy resin are dependent upon curing agent and reaction temperature a large number of amine curing agents are available varying in structure and performance at different temperatures. The curing agents can be synthesized in–situ as well[30].

As hardeners amines are most versatile in their performance. The curing mechanism with amines and the structure of amine cured polymers have extensively been studied. The systems of epoxy polymers with amine hardeners are widely used in various industrial and home applications.

The aliphatic amines and their derivatives are recommended for ambient temperature curing. Consequently, they would be expected to have a limited pot life or shelf life. Typical applications include wet lay-up laminating operations such as tank linings, patching (repairs) toolings, certain air frames and radomes, and electrical insulations. Pure chemical compounds such as diethyltriamine (DTA) and triethylenetetramine (TETA), when properly post cured display strengths above 100° C/ 212° F.

$$NH_2\,CH(CH_3)\,CH_2\left(OCH_2CH(CH_3)\right)_x NH_2$$

Polyetheramine D-2000 (M*=2000, b.p > 250, m.p. = 29)



$$NH_2(CH_2)_2\overset{H}{\overset{|}{N}}(CH_2)_3NH_2$$

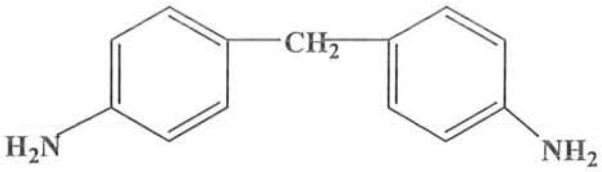
3-(2-Aminoethyl)aminopropylamine (M =117.2, b.p = 221, m.p.= 10)

$$NH_2(CH_2)_3O(CH_2)_2O(CH_2)_3NH_2$$

4,7-Dioxadecane-1,10-diamine (M =176.3,b.p. = 274-276° C, m.p.= 26° C)

Fig 1.4: Aliphatic Diamines (M = Molecular weight) [31]

The aromatic amines are widely used in composite fabrication in both wet and dry lay-up applications for filament winding, electrical, piping, tooling, and whenever maximum chemical resistance is needed. They provide moderate viscosities at room temperature with the liquid resin, long pot life, excellent chemical resistance and electrical properties, good elevated temperature performance [32-33]. High temperature cures and longer cure times are required to obtain these advantages. A representative example is given below.



4,4'-Diaminodiphenylmethane (M =198.3,b.p. = 398° C, m.p.= 89-91° C)

Fig 1.5: Aromatic Diamine

The **JEFFAMINE** polyetheramines have a proven history in composite applications. One key structural characteristic is the steric hindrance provided by the presence of a methyl group on the amine-bearing carbon. As a result, epoxy-amines curing time for these amines is prolonged than for other aliphatic amines such as ethyleneamines. Another important structural feature is the flexible polyether backbone, which gives reduced brittleness in the cured resins. Good toughness, impact resistance, elongation, and low-temperature characteristics result from this flexibility. Molecular weights of the curing agents ranges from 148 to 5000. Polyether backbones are based on ethylene glycol or propylene glycol, and amine functionality is one, two, or three[34].

Recent advancements in material sciences have not spared the field of curing agents and hardeners. Curing agents modified into nanorods are being incorporated to enhance the quality of the cured resin even more[35].

1.1.3 CURING REACTION

The curing of epoxy resins may either be of epoxy/amine type or of epoxy anhydride type. Another important reaction is homopolymerization of epoxy resin, which requires lewis acid catalyst. The most common reaction is epoxy amine reaction in which each amine reacts with an epoxy group.

A second order mechanism is generally accepted mechanism for this reaction[36]. Mechanism of epoxy amine reaction is generalized in two ways either catalytic addition reaction or noncatalytic. The propositions are based on the following aspects which are widely used in literature. The reactions of primary amines with an epoxy produce a secondary amine which then reacts with another epoxy to produce a tertiary amine[37]. The principle reaction is as follows:

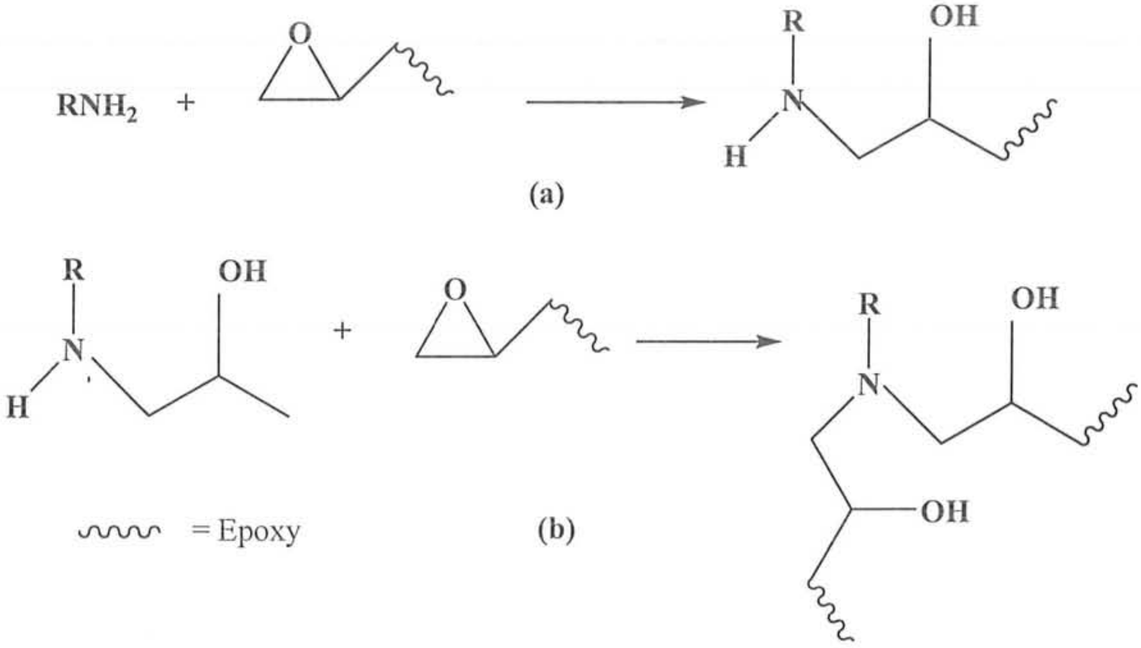


Fig 1.6: Reaction of (a) Primary amine with epoxy (b) Secondary amine with epoxy

The reaction also takes place by two competitive paths, one is catalyzed by hydroxyl groups initially present and those generated during the reaction (rate constants K1 and K2) and the other is non catalytic mechanism (rate constants K1' and K2'). The non catalytic mechanism takes place over entire temperature region[38]. It has higher activation energy (Ea) but is predominant at higher temperature (T<100° C). The catalytic mechanism is predominant at low temperatures. The reactivities of epoxide group in DGEBA are independent. The reactivities of primary and secondary amines can be different, it is called "substitution effect".

The chemistry of curing with anhydride is more complex. Several mechanisms have been proposed for this type of reaction. One proposition is that the anhydride reacts with an alcohol to form half ester, which then reacts with epoxy group to form another ester linkage. The reaction continued in this manner until all of the reactive groups were consumed. Basis of this mechanism was the presence of the hydroxyl either in the resin itself or as an impurity such as water. Another mechanism that was proposed for this reaction was that anhydride reacts with a catalyst to form a carboxyl anion, and the anionic process continues till the completion of cure. This mechanism is in accord with the observed 1/1 stoichiometry of epoxy/anhydride. The kinetic studies have shown that simple first or second order kinetics are absent and the rate of reaction accelerates with the concentration of the catalyst[39-40].

The third curing process to consider is homopolymerization of epoxy group, which requires the presence of a Lewis base (i.e., tertiary amine), inorganic base (i.e.NaOH) or Lewis acid catalysts (i.e., BF_3 complexed with amine)[41].

1.2 FILLERS AND REINFORCEMENTS FOR POLYMERS

According to American Society for Testing and Material Standard ASTM D-883, a filler is realatively inert material added to the matrix to modify its strength, permanence, working properties or to lower cost while reinforcements improve the properties of the matrix[41]. Actually a few fillers are used that do not improve properties, but reinforcing fibres produce a notable improvement in the properties of the composites. There are many different combinations of reinforcements and matrices used to produce composite materials.

Three main types of fibres are used to reinforce polymeric materials: glass, aramid and carbon. Glass is by far the most widely used fibre and it is lowest in cost. Aramid is

In carbon-fibre composites, the fibre imparts the high tensile property for rigidity and strength, while the matrix aligns the fibres and contributes some impact strength. Epoxy is the most common matrix material for the carbon fibres[42].

Many naturally occurring materials have particulate reinforcements e.g., bones have calcium phosphate incorporation within their structure. Synthetic composites have a variety of particulate reinforcements. Particulate reinforcements are usually metal particle or their oxides. Because of the recent availability of nanoparticles, the interest in the polymer nanocomposites has increased. It is well accepted that the composite properties alter with the dispersion state, geometric shape, surface properties, particle size, and particle size distribution.

1.2.1 TITANIUM DIOXIDE (TiO_2) AS PARTICULATE REINFORCEMENT

Titania is one of the most important oxide semiconductor materials, which has been applied in numerous applications such as pigments, catalysts, catalytic supports, membranes, electronic instruments and photocatalysts. The physiochemical properties of TiO_2 strongly depend on its crystal structure and morphology as well as size. There are three crystalline phases of titania: rutile, anatase and brookite. Rutile is the thermodynamically stable polymorph and used as white pigment in making paints, while anatase, as one of the other two kinetic products, has a far high photocatalytic activity[43].

TiO_2 has attracted much attention because of its photocatalytic property[43]. Titania has also been widely used as the reinforcement for enhancing the properties of the composite systems. There are various routes for the synthesis of the titania composites. The titania particles may either be synthesized in-situ or blended with the matrix. Generally the addition of titania enhances the thermal and mechanical properties of the composite systems.

It is usual to tailor the surface of the synthesized particles for betterment of properties. The objective of surface modification is to impart desired properties to the particles and thus enhance the applicability. Solubility in aqueous or organic media of otherwise insoluble particles can be controlled by tailoring the surface with proper ligands [44].

For applications such as use as filler in the composite material the surface of the particles is modified with specific reagents called "coupling agents". The coupling agent acts as a binder that reacts on one of its terminal with the organic and on the other with the inorganic phase. The interaction between the organic and the inorganic phase increases with the use of the coupling agent, so the properties of composite are also improved[45].

inorganic phase. The interaction between the organic and the inorganic phase increases with the use of the coupling agent, so the properties of composite are also improved[45].

There are various routes to the synthesis of particles which include chemical vapour deposition, physical vapour deposition, pyrolysis, gas detonation method and sol-gel reactions. Only sol-gel reaction will be elaborated here.

1.2.2 SOL-GEL SYNTHESIS OF PARTICULATE REINFORCEMENT

The reaction in which a metal alkoxide reacts to form metal hydroxide, which condenses into a metal–oxygen–metal sequence, with the liberation of water or alcohol. The metal may be aluminium, tin, cesium, the transition elements titanium, zirconium, the metalloid silicon etc. Silicon alkoxides have a more controlled and lower reactivity than other metal alkoxide, and hence the majority of understanding of the sol-gel reaction is derived from materials created from silicon based alkoxides.

Sol-gel is the most commonly used reaction by the polymer chemists, since it is a low temperature reaction and can be carried out in-situ with the organic polymerization reaction. Besides this the reaction setup is not complicated and the cost is also low. One of the most attractive features of the sol-gel reaction is the possibility to shape the materials into any desired form. Figure: 1.7 [46].

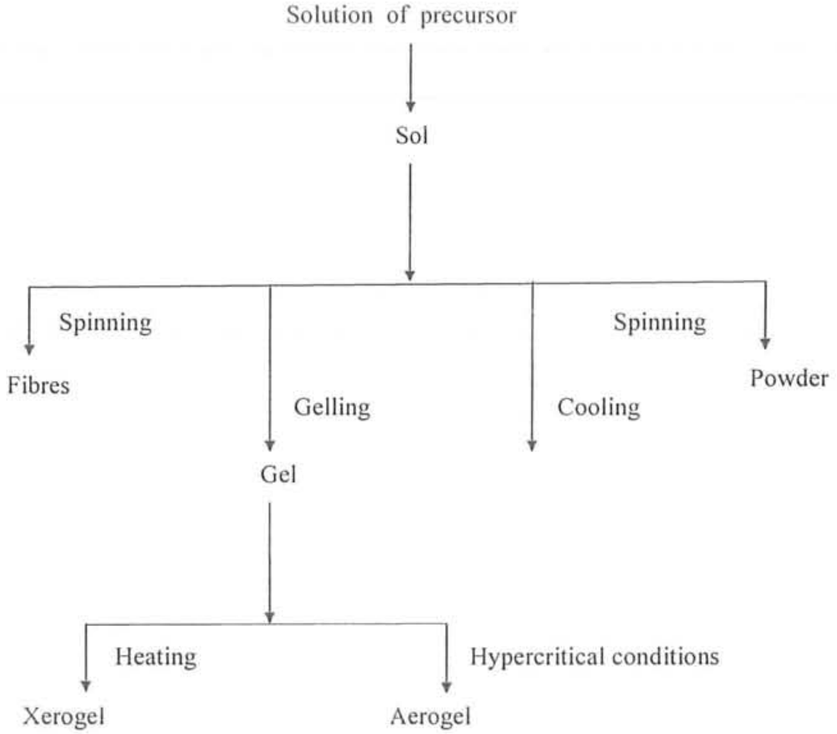


Fig: 1.7: Different possible types of products obtained from sol-gel reaction

1.2.3 CHEMISRY OF SOL- GEL

The first step of the sol-gel reaction is the formation of an inorganic polymer by hydrolysis and condensation reactions, i.e., the conversion of the molecular precursor into a highly cross linked solid. Hydrolysis leads to a sol, a dispersion of colloidal particles in a liquid, and further condensation results in a gel, an interconnected, rigid and porous inorganic network enclosing a continuous liquid phase. This transformation is called the "sol-gel transition". There are two possibilities to dry the gels. If the pore liquid is removed under hypercritical conditions, the network does not collapse and aerogels are produced. When the gel is dried under ambient conditions, shrinkage of the pores occurs, with the formation of a xerogel.

There are various modules of sol-gel reaction depending upon the variations in different parameters. The size, shape, morphology of the final product depends upon the reaction parameters[47-49]. The reaction may be carried out either in aqueous or organic solvents (aqueous and non-aqueous reaction).

The aqueous sol-gel process can briefly be defined as the conversion of a precursor solution into an inorganic solid via inorganic polymerization reactions induced by water. In general, the precursor or starting material is either an inorganic metal salt (chloride, nitrate, sulfate) or a metal organic compound such as an alkoxide. Metal alkoxides are the most widely used precursors, because they react readily with water and are easily available for various metals[50].

In non-aqueous sol-gel chemistry the transformation of the precursor takes place in an organic solvent under anhydrous conditions. In comparison to aqueous sol-gel chemistry, the list of precursors is longer and includes, metal acetates and metal acetyl acetonates in addition to inorganic metal salts and metal alkoxides. The non-hydrolytic sol-gel process is useful for reactions which would otherwise involve precursors of very difficult reactivity. For example, silica-titania and silica-zirconia glasses, where the much faster hydrolysis rates of the transition metals alkoxides lead to predominant formation of metal-oxygen-metal and precipitation of metal oxide[50].

The reaction mechanism also differs depending upon the precursors used i.e., organic and inorganic synthetic procedures. Metal oxides can be prepared by two methods depending upon the nature of the precursor:

1. Metal salt (inorganic route)
2. Metal alkoxide (organic route)

1.2.4 HYDROLYSIS AND CONDENSATION REACTION OF METAL SALT PRECURSORS

The sol-gel reaction of the metal salt precursors takes place by the hydrolysis and condensation pathway. When dissolved in water, metal cations M^{z+}, are solvated by water molecules, and an equilibrium is established which depends upon the acidity of water.

The nature of the species present in the aqueous solution of metal salts is determined by the position of the equilibrium.

$$\overset{+}{M}\!-\!\overset{-}{O}\!-\!\overset{+}{H} + H_2O \rightleftharpoons M\!-\!O^{-} + H_3O^{+}$$

The reaction will proceed towards the right if the overall partial charge on OH is positive. In general hydrolysis increases with increase in charge density on the metal, the number of metal atoms bridged by a hydroxo or oxo ligand, and the number of hydrogen contained in the ligand[50].

Condensation proceeds by either of two nucleophilic mechanisms (addition and substitution) depending upon the coordination state of metal atom. When coordination state of metal is satisfied, then condensation occurs by nucleophilic substitution. The process of condensation can follow either olation or oxolation mechanism.

Olation is a phenomenon in which a hydroxyl bridge is formed between two metal centres. For coordinatively saturated species condensation occurs by S_N substitution where OH^- is the attacking nucleophile and water is leaving group. The smaller the charge and larger the size, the greater the rate of olation, since it depends on the lability of leaving group i.e., H_2O[50].

Oxolation is a condensation reaction in which an oxo bridge is formed between two metal centres. The first step is catalyzed by bases that deprotonate the hydroxo ligand creating strong nucleophile.

$$M\!-\!OH + OH^{-} \longrightarrow M\!-\!O^{-} + H_2O$$

$$M\!-\!O^{-} + M\!-\!OH \longrightarrow M\!-\!O\!-\!M + OH^{-}$$

Fig 1.8: Base catalyzed oxolation reaction

The second step is catalyzed by acids that protonate the hydroxo thus creating better leaving group.

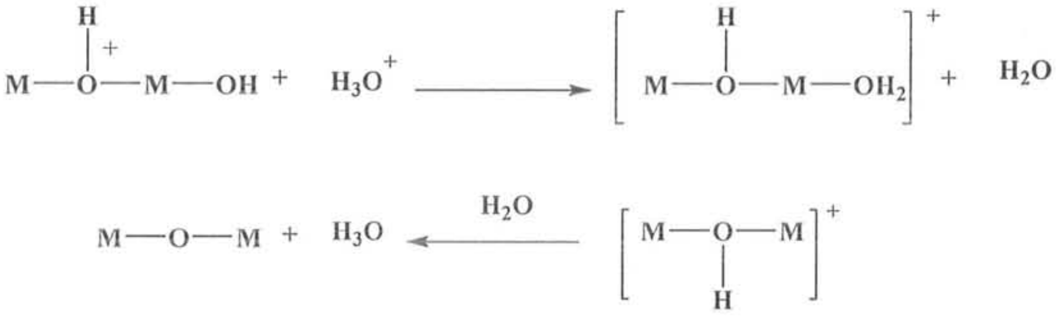


Fig 1.9: Acid catalyzed oxolation reaction

Thus as compared to olation, oxolation occurs at a wide range of pH but due to two step reaction the kinetics are slow[50].

1.2.4.1 Role of the anion

In addition to aquo, hydroxo and oxo ligands the system also contains anions from the dissolution of metal salts in water. These ions compete with aquo ligand for complexation with the metal centre. The complexing ability depends upon the extent of charge transfer from the X^- to the metal centre.

There is possibility of associated complex formation, when metal and X^- are in solution, however the complex can influence the morphology and size of particle atom, if it is stable towards hydrolysis and ionic dissociation. In case the complex is stable counterion can affect the shape, size, crystallite structure as well as surface acidity which are the basis of photocatalytic activity for titanium[50].

1.2.5 SOLUTION CHEMISTRY OF METAL ALKOXIDE PRECURSORS

Transition metal alkoxides especially those of d^0 configuration are widely used as precursors in the ceramics and glasses. Metal alkoxides are generally very reactive due to the peresence of highly electronegative –OR group that stabilizes the metal in high oxidation state and renders it liable to nucleophilic attack.

1.2.5.1 Mechanism of hydrolysis and condensation

Reaction proceeds both by nucleophilic substitution (S_N) and nucleophilic addition (A_N) depending on the coordination state of the metal. Hydrolysis can proceed either by alkoxolation or oxolation. Alkoxolation involves formation of alcohol, while oxolation involves the formation of H_2O. When metal is coordinatively unsaturated condensation occurs by olation.

The thermodynamics of alkoxolation, hydrolysis and oxolation are governed by the strength of entering nucleophile, electrophilicity of the metal and partial charge and stability of the leaving group[50].

1.2.5.2 Reactivity of metal alkoxide

The reactivity of the metal alkoxide can be affected by its ability to increase its coordination number, n, in the network oxide. If z is the oxidation state of the metal atom in the alkoxide, then one can define the degree of unsaturation of metal atom as n-z. Hence increasing the quantity n-z means increasing the coordination number of the metal atom when going from the alkoxide to network oxidation state[50]. For example, the tetra-coordinated alkoxide titanium (IV) butoxide forms a network of TiO_2 in which the titanium is hexa coordinated. This yelds a value of n-z of two. As a general rule, for alkoxides, electronegativity and reactivity are inversely related, i.e., as the electronegativity of metal atom increases, the chemical reactivity of the corresponding metal alkoxide decreases. Since silicon has a high electronegativity and a relatively low degree of unsaturation, sol-gel reactions involving silicon alkoxides are slow. For the same R group, reactivities of metal alkoxides follow the order:

$$Ce(OR)_4 > Zr(OR)_4 > Ti(OR)_4 ;Sn(OR)_4 >> Si(OR)_4$$

Tin has a higher electronegativity than silicon but its alkoxide is much more reactive than the corresponding silicon alkoxide implying that the degree of unsaturation also plays a role in metal alkoxide reactivity.

1.2.5.3 Influence of catalyst

Sol-gel reactions involving silicon alkoxides usually require a catalyst to increase the reaction rate. This can be either a base or an acid. Each influences the sol-gel reactions in a different manner. Acids tend to increase the rate of hydrolysis step, by promoting the protonation of the alkoxy group (OR), while having little effect on the polycondensation step. Bases, on the other hand increase both the hydrolysis and polycondensation step. This occurs due to the presence of –OH and M-O- species which are better nucleophiles than water and silanol, promoting the rapid attack of silicon. Under such conditions, hydrolysis and condensation occurs simultaneously. This promotes a different structure than that formed from the same reactants under acid catalysis. The end result of base catalyzed reactions is generally highly branched, dense particulate species. Under acid catalyzed conditions, the end result is more of a linear species. These structures possess self similarity at different length scales, an attribute known as fractal character [50].

1.2.5.4 Influence of water

Since water is a reactant in the sol-gel process, its presence plays a role in the reaction kinetics and final structure of the material. Increasing the amount of water in the reaction tends to densify the structure. A convenient way to express the amount of water employed in the sol-gel reaction is through the hydrolysis ratio, h, defined as the ratio of moles of water per mole of metal alkoxide. If the value of h is less than two, the alcohol liberating polycondensation reaction is preferred, but for h greater than two, the water forming condensation is favoured [51].

1.2.5.5 Influence of solvent

By varying the solvent in the sol-gel reaction, one varies the types of interactions present. These results in changing the overall reaction rate and in a very general sense the effect of solvent on rate can be ranked by the following:

1-Promoting faster rates, non-polar, aprotic solvents (i.e. dioxane)

2-Promoting intermediate rates, polar, aprotic solvents (i.e. DMF, acetonitrile)

3-Promoting slowest rates, polar protic solvents (i.e.methanol, formamide)

Polar, protic solvents with strong dipole moments tend to deactivate the reactants by stabilizing their charges and solvating the metal alkoxide, hence slowing down the reaction rate. Also hydrogen bonding may take place between a polar solvent (formamide) and the silicon species thereby slowing the reaction by way of steric hindrance [52]. These effects lessen as the opposite extreme is reached, non polar, aprotic solvents, where essentially only dilution of reactants is achieved.

1.2.5.6 Influence of temperature

The temperature of the sol-gel reaction also plays very effective role in determining the structure and morphology of the final product. Generally, for titania the particle size decreases upon increasing the temperature of the reaction[53,54].

The stability of various species in the reaction mixture varies with temperature, for example, anatase polymorphic form of titania being thermodynamically less stable, is retained upto 600-700° C. If the calcination temperature is raised above 650° C, transformation from anatase to rutile takes place. High reaction temperature promotes hydrolysis thus increasing the number of the nuclei and decreasing the size[55].

1.6 SYNTHESIS AND APPLICATION OF TITANIA PARTICLES

The titania particles have been synthesized in a broad range of temperatures. There are several reports about low temperature synthesis of titania[56]. Sun et. al synthesized titania at room temperature by hydrolysis of titanium tetrachloride in a mixed solution of n-butanol and water[57]. Spherical monodisprese particles having diameter in the range 300-400 nm were synthesized by controlled hydrolysis of the dilute ethanolic solution of titanium tetraethoxide. Particle size decreased with the increase in the initial concentration of water. Surface morphology was dependent on the washing procedure. Fresh water washed titania had amorphous interior but a fine layer of crystalline tiania on the surface [58].

The size of particle is the primary concern while designing synthetic strategy. Kim et.al. synthesized partricles by two stage method that have a smaller size than the particles made by single stage method, with the concentration and temperature being size controlling parameters. Higher amount of tetra ethoxy titanate and increased temperature in the second stage reduce the size of the particles[59]. Particle agglomeration and grain growth was prevented by growing particles on the surface of solid NH_4Cl. Hydrated particles were adsorbed on the surface of NH_4Cl, then calcined. NH_4Cl was removed during calcination [44]. The size distribution of particles was controlled by carrying out synthesis in organic solvents with adsorbing ligands[60]. Adsorption of ligands on the surface could improve the efficiency of light absorption but it limited crystal growth because the interaction between the ligand and particles was strong[60]. Another approach to synthesize titania was the combination of sol-gel and hydrothermal method. Hydrolysis was carried out under hydrothermal condition. The final particles were nanosized and had anatase morphology[61]. Not only particles have been synthesized, but films of TiO_2 were successfully deposited on the surface of the host silica particles by heterogeneous nucleation and growth, using $TiCl_4$ as precursor[62].TiO_2 films were prepared on indium-titaniumoxide (ITO) substrate using titanium tetraisopropoxide by spray coating[55].

Meanwhile, TiO_2 photocatalysis became one of the most investigated technologies for remediation of environmental contaminants. Titania absorbs in the UV region thus its photocatalytic activity could be obsereved only under UV. Neither UV nor titania was catalyticaly active separately [63]. The photocatalytic activity of titania depended upon its surface acidity. The surface acidity can be enhanced by doping with various elements such as N-F codopant[64]. Chlorine doped rutile titania nanorods also showed much higher photocatalytic activity than the commercially available titania. It was attributed to the surface acidity and crystal defects which were the result of chlorine doping[65]. Since then, laboratory and field studies have continually confirmed the application of TiO_2 photocatalysis in the destruction of a large variety of contaminants. Titania particles with Pd and Ni modifications were found useful for the degradation of dichloromethane into CO_2 and H_2O[66]. Apart from this TiO_2-SiO_2 cocatalyst could also degrade formaldehyde into CO_2 and H_2O[67] and 2-propanol to acetone and further to CO_2 [68]. The photoreduction of CO_2 was also successfully carried using titania catalyst[69]. Pollutants from the textile industry are an important source of environmental contamination. It is estimated that from 1 to 15% of the dye is lost during dyeing processes and is released in waste waters. For disposal of dyes, nanocrystalline titania with silver doping was synthesized and found efficient for the degradation of methylene blue[70]. In another approach catalytic activity was correlated with the initial concentration of methylene blue, it was observed that degradation increased with the increase in concentration of methylene blue, since the concentration of active centres is the same, the photocatalytic activity depended upon the concentration of methylene blue[71]. Not only titania particles but titania films deposited on polymers, could be used for photocatalytic activity[72-73]. Dye titania films synthesized from plasma enhanced chemical vapour deposition (PECVD) and sol-gel method were successfully applied for the degradation of maleic acid [72]. It was also observed that photocatalytic activity of titania did not depend upon the support size, if supported titania catalyst was used for catalysis[74].

Apart from use as catalyst titania has other applications as well. Examples include disinfection of germs, sensor applications, decomposition of effluents and applications in the field of optics[75-79]. The most attractive feature of titania is its non-toxicity and biocompatibility, which is the bases of many of its applications. Various attempts have been made to use titania in biological systems for purposes such as glucose sensing and hard tissue implants[80-81]. Titania foam with properly tailored surface modification with silica was used as scaffold for tissues[82]. Titania particles were synthesized from the stirred glycerol and NH_4F

electrolyte and surface adhesion with epithelial cells was investigated, however, surface adhesion was found to be low due to stirrings [83].

1.7 TITANIA HYBRIDS AND COMPOSITES

Besides the synthesis of titania particles a large number of hybrids, sols and composites have been synthesized from titania for various purposes. Apart from mechanical and chemical resistance titania also improved the weather resistance of the composite materials[84]. A stable colloid of titania/Poly(acrylic acid) hybrid was synthesized in which chelating bond between matrix and filler was evidenced by IR[85]. The hybrids of titania with acrylic resin were synthesized both by blending and in-situ polymerization. Blending was found more useful for the dispersion of particles and smoother films were formed by this method [85]. The phase separation and gelation were observed to be occurring at different times. when the protocol of reaction was changed. If polymer was added to titania solution, then gelation occured first, but if titania was added to polymer gelation and phase separation occured simultaneously[86]. The effect of annealing temperature was observed on the properties of titania/Poly[2-methoxy-5-(20-ethylhexyloxy)-p-phenylenevinylene] titania/MEH-PPV films. The annealing treatment was effective for a further conversion of titanium isopropxide (TIP) to titania for preparing homogenous MEH-PPV/titania hybrid films[87]. Again in this system the conversion of titanium isopropxide (TIP) to titania was studied in correlation with water concentration, the conversion of TIP to titania increased with the increased of amount of water [88].

Titania composites have generally been synthesized to investigate the effects of filler on mechanical and thermal properties of composites[89].The basis of improvement in properties was the interaction between filler and the matrix, which was evidenced by various technique such as IR [90]. This interaction facilitates load transfer from the matrix to the reinforcement. Since titania has photocatalytic behaviour as well, so some decrease in thermal properties was also observed[91]. Titania hybrids with polyesters showed earlier degradation temperature, which was attributed to the catalytic activity of titania [92].Both the TiO_2 and SiO_2 filler were used simultaneously to overcome the deteriorative feature of titania[93]. Apart from mechanical and chemical resistance titania also improved the weather resistance of the composite materials[94].

1.5 EPOXY-AMINE MATRIX

Epoxy –amine system has versatile properties, so it is used as matrix for a variety of composite formulations with a variety of fillers. The particulate filler may be synthesized in-situ,or prehydrolyzed particles can be added[95-96]. In the later case amine acted as nucleophilic catalyst and agglomerates were formed, because reaction was fast[98]. If the surface of particles was modified with coupling agent, the thermal properties of composite were enhanced further[97]. The thermal properties of the composite system varied with size and surface modification of the particles. The small sized and surface modified particles showed better properties[98-99]. When the curing agent was aliphatic and had flexible structure or the filler acted as plasticizer then the composite was flexibilized instead of toughning[100-101]. Besides this the content of the filler and the conditions under which the filler had been synthesized, also played an important role [102-103].Clay was also incorporated into the epoxy-amine system after modification, which resulted in uplift in the properties of filler[104]. Epoxy-amine system was used not only as thermally and mechanically resistant material, but it was also used as biomaterial e.g., bone cement with silica as reinforcement and for nanoimprint lithography with titania filler[105, 106].

1.6 PRESENT WORK

After a thorough survey it was realized that very little work has been done on epoxy-amine system with titania so it was planned to synthesize and characterize systematically epoxy-amine-titania composites. The curing kinetics of the matrix used was well studied[37], thus it was planned to investigate various factors which influence the mechanical and thermal properties.

The synthesis of epoxy-amine-titania composites was carried out with an aim to study the effect of incorporation of titania filler on the properties of the composite systems. Titania had photocatalytic activity and it imparted negative effect to the thermal stability of the composites[92]. So in the work titania was synthesized ex-situ and then blended with the matrix to minimize the chances of catalytic interference. Two modifications were then made to enhance the intreraction between the matrix and the filler. The first one was to reduce particle size and consequently increase the surface area of particles available for contact with the matrix. The other modification was to tailor the surface of the particles with the coupling agent for better interaction. The properties of the composite systems were studied as a function of the type of the filler.

The matrix used for the composite system was polymeric and the reinforcement was inorganic titania network structure generated by sol gel method. The organic system was represented by epoxy-amine network (matrix) prepared from diglycidyl ether of bisphenol A (DGEBA) and a poly(oxypropylenediamine)diamine, Jeffamine D-400. The particulate reinforcement was synthesized by inorganic route taking $TiCl_4$ as a precursor[77]. The matrix (epoxy-amine) was blended with the particles. The incorporation of the filler resulted in reinforcement of the matrix. Hence the epoxy–amine-titania composites were synthesized with various percentages of reinforcement.

Three types of particles were synthesized. The first type was the partially condensed titania, largest in size having OH moiety at its surface. Second was the finer particles, consisting solely of Ti-O-Ti network and smallest in size of the three (close to nano domain). Third type of particles were those having surface modified with coupling agent (γ-APS) and medium in size. The three types of particles were characterized by IR, XRD and AFM.

Three series of composites were synthesized from the three types of titania. In the case of partially condensed titania, there was possibility of ring opening by the OH moiety so there was some sort of chemical link. In the second case there was no possibility of chemical link between matrix and the filler (Figure 1.10). In the third system interfacial bonding between the two phases was achieved by using γ-aminopropyltriethoxysilane as coupling agent. γ–Aminopropyltriethoxysilane (γ-APS) developed chemical bonding between the titania network and epoxy amine (Figure 1.11). The amino group of γ-APS reacts with an epoxy ring of the DGEBA. The composite series were characterized by DSC, TGA, and SEM as well as mechanical analysis.

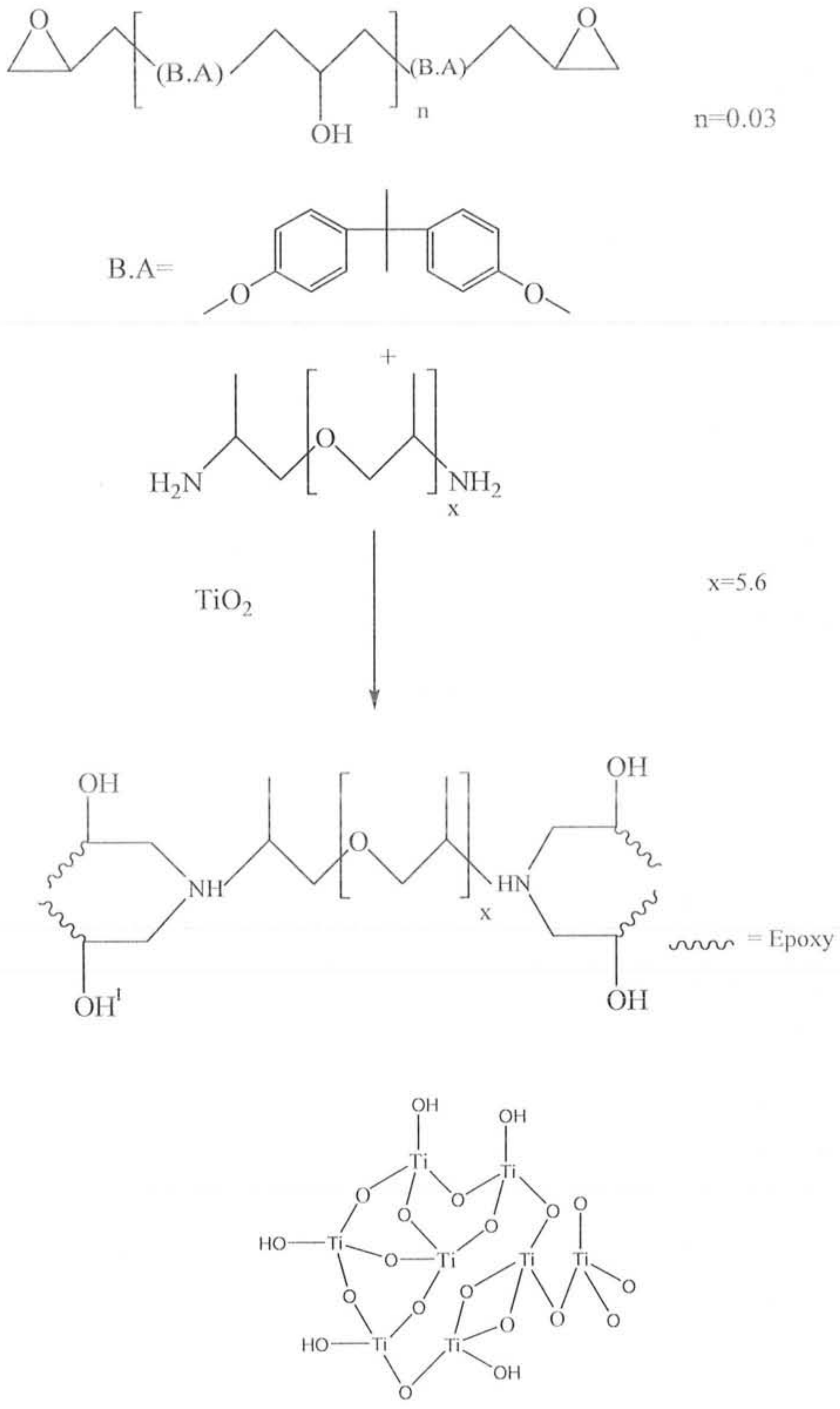


Fig: 1.10 Hypothetical scheme showing the reaction between epoxy-amine and titania developed by sol-gel

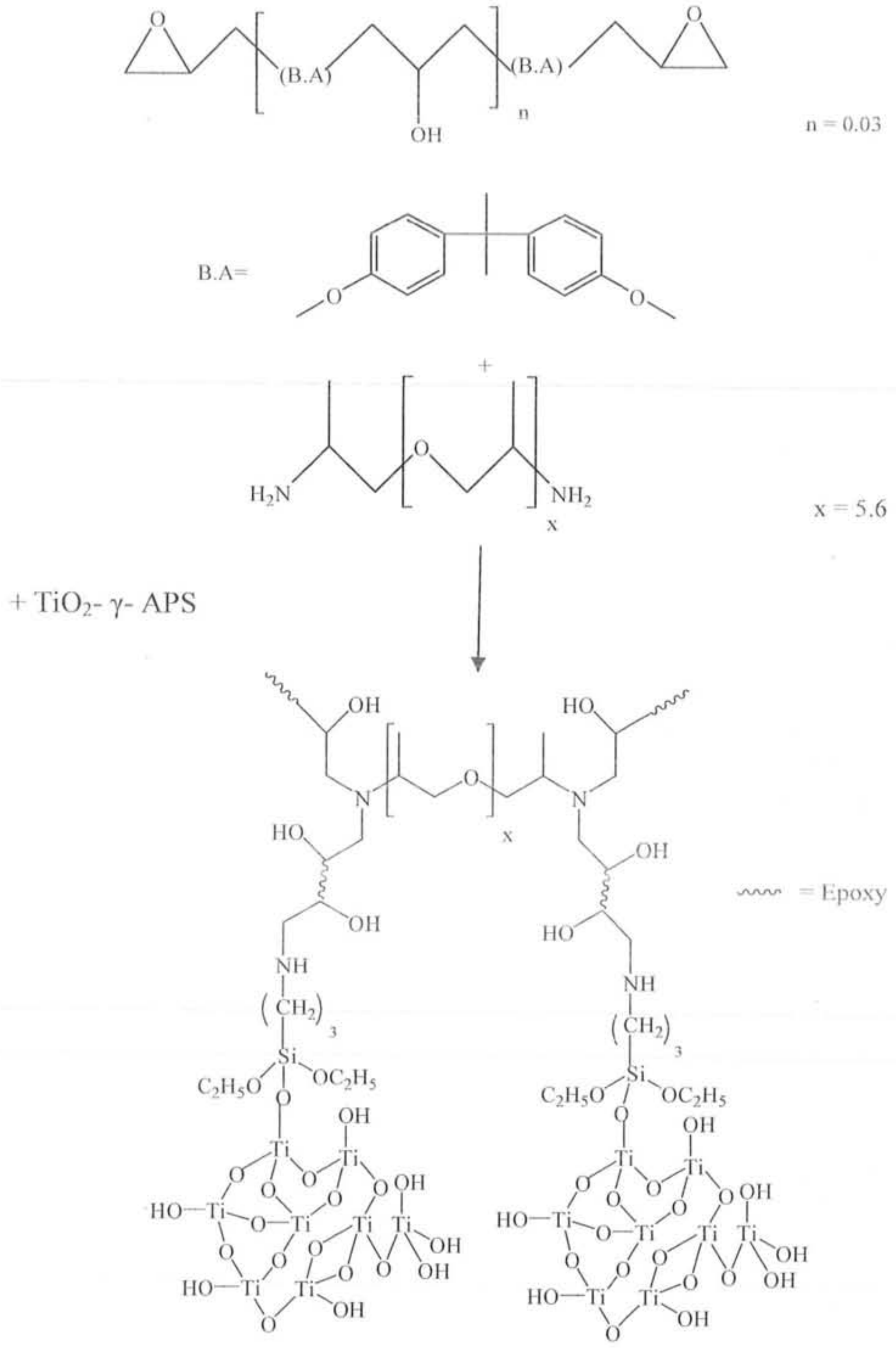


Fig: 1.11 Hypothetical scheme showing the possible reaction between epoxy-amine and γ-APS grafted on titania.

2. MATERIALS AND METHODS

This chapter describes in detail the chemicals used, the procedures adapted for the synthesis of various types of titania and characterization techniques used for the analysis of various types of particles and composites.

2.1 CHEMICALS USED

Diglycidyl ether of bisphenol A, DGEBA (DER 332) was obtained from DOW chemicals and was used as received. It had molar mass of 348.52g/mol, the equivalent weight per functional group was E_E =174.26 g/mol and value of polydispersity index (n) was 0.03.

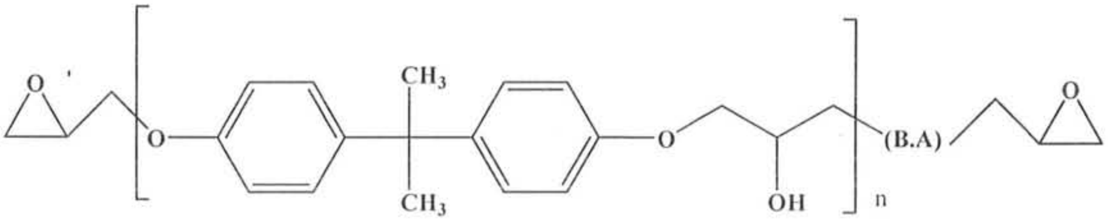


Fig 2.1: Diglycidyl ether of bisphenol A (DGEBA) n=0.03

Poly (oxypropylene)diamine Jeffamine D-400 was obtained from HUNTSMAN and was used as received. It had molar mass of 399 g/mol, the equivalent weight per functional group was E_{NH} = 99.75g/mol and x = 5.6.

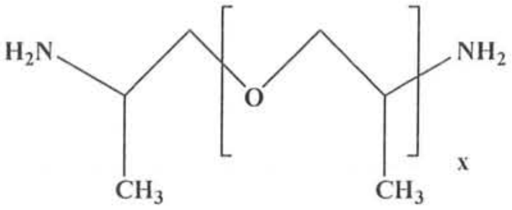


Fig 2.2: (Jeffamine D-400) x=5.6

Titaniumtetrachloride ($TiCl_4$) was obtained from Merck and was used as received. It has molecular weight of 139 g/mol and its b.p was 136.4 °C.

γ-Aminopropyltriethoxysilane (γ-APS) 97% was obtained from ABCR Germany and was used as received. It has molecular weight 222 g/mol and b.p was 122 °C.

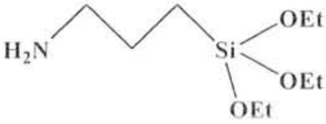


Fig 2.3: γ-Aminopropyltriethoxysilane

HCl 33% was obtained from Fluka and used as received.

2.1.1 DRYING OF SOLVENTS

i) Ethanol was dried on CaO for 6 hours and then distilled[107].

ii) Acetone was dried over $CaCl_2$ and then distilled[107].

2.2 EXPERIMENTAL TECHNIQUES

2.2.1 SYNTHESIS OF PARTICULATE REINFORCEMENT

Titania particles varying in size and surface morphology were used as reinforcement. Inorganic sol gel route was used to generate TiO_2 with titanium tetrachloride as precursor. Firstly a reported procedure was followed [77]. The yield of reaction was very low so the procedure was modified i.e., the solvent was changed (ethanol instead of carbontetrachloride and water was used along with ethanol for faster rate).Three types of particles were synthesized by varying reaction parameters and processing conditions. These three types will be called microtitania, calcined titania and functionalized titania in further discussion for the sake of convenience.

2.2.1.1 Synthesis of Micro-titania

Titania synthesized in this system was partially condensed, leaving -OH and -OC_2H_5 (from solvent) at its surface. The coupling agent was not used for the modification of the surface and drying was carried out at ambient temperature.

2.2.1.1.1 *Procedure:*

In a 100 ml two necked round bottom flask fitted with a septum, 40 ml of ethanol and 5 ml of water was taken. (EtOH : H_2O; 8:1).The flask was then fitted with a reflux condenser and 0.6 mL (0.05mole) of $TiCl_4$ was injected, through the septum along with continuous stirring. The reaction mixture was stirred at 60° C for half an hour. 5 mL (0.1 mole) of NH_4OH was injected drop by drop through the septum to attain a pH of 8. Ageing time of 6 hours was given with stirring. The product was first washed with water (5ml) and then with acetone (5 ml) and solid particles were recovered by centrifugation. The precipitates were sonicated with 0.1 M HCl for 15 minutes to break down agglomerates. Finally the product was dried under vacuum at 120 °C. The actual yield of product was 0.176 g. The yield was found to be 85%.

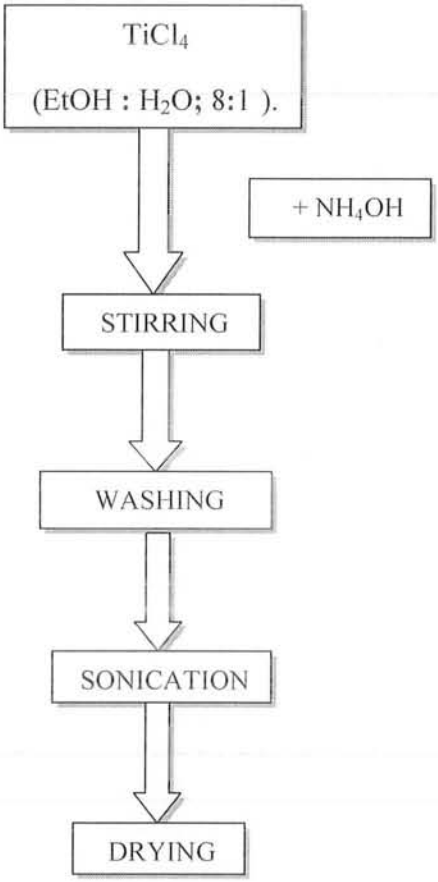


Fig 2.4: Schematic representation of synthesis o. micro-titania

2.2.1.2 Synthesis of Calcined Titania

Titania synthesized in this system was completely hydrolyzed and condensed by calcination at 600 °C for 5 hours. It constituted of Ti-O-Ti network only, without any organic moiety at its surface. The size of the final particles was thus decreased.

2.2.1.2.1 *Procedure:*

The same procediure was followed as for the synthesis of microtitania but instead of drying at 100 °C the product was calcined at 600 °C for 5 hours. The actual yield of product was 0.15 g. The yield was found to be 70%.

2.2.1.3 Synthesis of functionalized titania

In this case, the surface of the particles was modified with coupling agent to facilitate binding with the organic matrix. γ-APS was used as a coupling agent.

2.2.1.3.1 *Procedure:*

In a 100 mL two necked round bottom flask fitted with a septum 100 mg (0.00125 mole) of microtitania (cf: 2.2.1.1) was taken in 10 mL of ethanol as solvent. It was then fitted with a condenser and 0.2 mL (0.02 mole) of γ-APS was injected through the septum. The reaction mixture was stirred at 60 °C for 3 hours. The product was washed with acetone (5 ml). The solid particles were recovered by centrifugation, and then dried at 60° C under vacuum. The actual yield of product was 0.16 g. The yield was found to be 80 %.

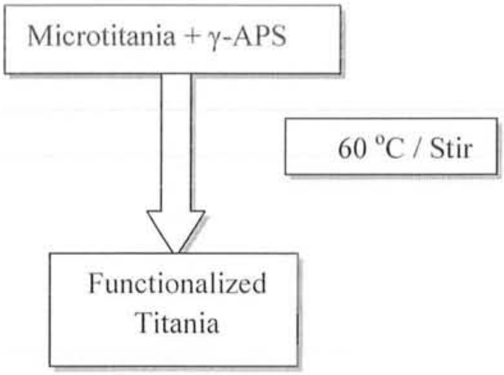


Fig 2.5: Schematic representation of synthesis of functionalized-titania

2.2.2 SYNTHESIS OF NEAT EPOXY-AMINE NETWORK

In order to compare the properties of the epoxy-amine–titania composites, a neat system containing only epoxy-amine was synthesized. The kinetics of the system had already been established[37]. For this purpose stoichiometric ratio NH/E=1 of DGEBA (0.02mole) and

Jeffamine D-400 (0.01mole) was taken in erlenmeyer flask (25ml) and stirred for an hour at room temperature. Then mixture was poured in clean and dried Teflon mould, cured at 100° C for five hours to achieve the complete reaction between epoxy and amine. The film obtained after complete curing was transparent.

Three types of composite systems were synthesized with various percentages (2.5, 5, 7.5 and 10 % wt.) of reinforcement. The phase separation was observed at 10% for EAT-1 and EAT-2 while at 12.5% for EAT-3[*]. The samples obtained were then analyzed by ATR-IR, TGA, DSC, SEM and Mechanical analysis.

(for 10 g, 10 % wt.titania composite)

Sr. No	Titania (g)	DGEBA (g)	Jeffamine (g)	APTES(g)
Neat	-	6.0	3.0	-
EAT-1	1	6.0	3.0	-
EAT-2	1	6.0	3.0	-
EAT-3	0.91	6.0	2.99	0.09

Table 2.1: Percent composition of composites

In the following section the procedures adapted to synthesize the epoxy-amine-titania composites, in the EAT-1, EAT-2 and EAT-3 systems will be discussed.

2.2.3 EPOXY –AMINE –TITANIA COMPOSITES SYNTHESIS

2.2.3.1 Epoxy-amine–micro-titania composite

The epoxy-amine polymer was first modified by the incorporation of micro-titania. In this system no binding agent was added. The system will be abbreviated as "EAT-1". Before curing all reactions were carried out at room temperature. In order to synthesize epoxy-amine-titania networks with various percentages of titania, different proportions of titania were added. At 10 wt % titania composition phase separation was observed, thus no composition was tried further.

As observed by the naked eye

2.2.3.1.1 *Procedure:*

For the synthesis of epoxy-amine-titania composites following procedure was adapted. In a 25 ml erlenmeyer flask, carefully weighed amounts of the DGEBA (0.02 mole) and titania were added. The mixture was sonicated for 15 minutes for proper dispersion of particles. Finally stoichiometric amount of Jeffamine D-400 (0.01 mole) was added to the mixture and stirring was continued for 45 minutes. The mixture was then poured in clean and dried teflon moulds and cured at 100 °C for five hours. The flow chart for the synthesis of EAT-1 is presented in figure 2.6.

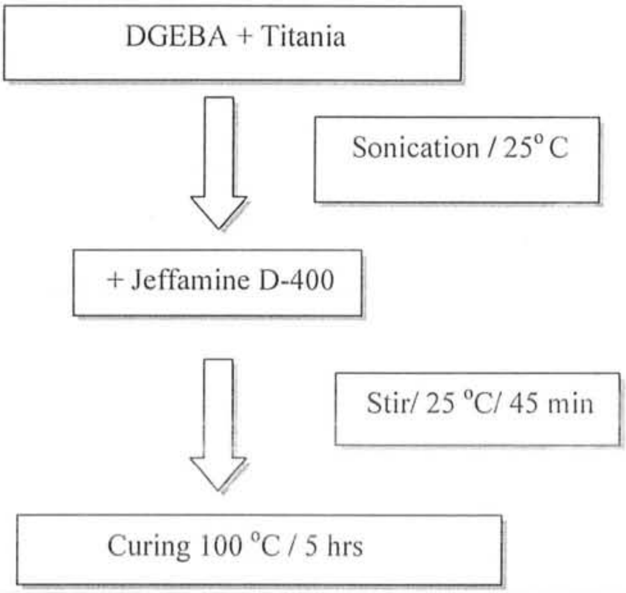


Fig 2.6: Schematic representation of synthesis of composites

2.2.3.2 Epoxy-amine-calcined titania composites

This system was abbreviated as" EAT-2". Before curing of the reaction mixture all reactions were carried out at room temperature. In this system phase separation was observed at 10 % wt. titania hence no composition was tried further. The procedure for the synthesis has been given in figure 2.6.

2.2.3.3 Epoxy–amine–titania composite with functionalized titania

In this system a binding agent was reacted with titania prior to composite synthesis. The aim was to end-link the polymer chains of organic matrix with the titania network. The system was abbreviated as "EAT-3". Before curing all reactions were carried out at room temperature. In order to synthesize epoxy-amine-titania networks with various percentages of titania, different proportions of filler were added. At 12.5 wt % titania composition phase separation was observed, thus no composition was tried further. The procedure for the synthesis of composites was same as described before.

2.3 Film Preparation

Epoxy-amine-titania composite films of controlled thickness were obtained by the measured amount of reaction mixture in teflon moulds and by placing them on carefully leveled surface. The thickness and width of the samples was obtained by measuring the dimension of these films with the help of micrometer and vernier caliper.

2.4 CHARACTERIZATION TECHNIQUES

Various techniques were used for the analysis of particles, matrix and composite systems.

2.4.1 ATTENUATED TOTAL REFLECTANCE INFRA–RED SPECTROSCOPY

Attenuated total reflectance infrared spectroscopy (ATR-IR) analysis of powdered samples was carried out at 25 °C by using Thermo Scientific Nicolet 6700 FT-IR spectrometer.

Attenuated total reflectance (ATR-IR) of composites films was also done by using the same instrument and conditions.

2.4.2 X-RAY DIFFRACTION ANALYSIS

X-ray diffraction analysis was carried out at 25° C using Siemens d 5000 X Ray instrument using Cu K alpha radiation.

2.4.3 ATOMIC FORCE MICROSCOPY

Atomic force microscopic analysis of functionalized titania was carried out. Particles were dispersed in ethanol and thin films of particles were coated on glass surface using spin coater. Analysis of films was carried out at 25° C using Viecco AFM analyzer.

2.4.4 SCANNING ELECTRON MICROSCOPY

Scanning electron microscopic analysis of composite films was done at 25° C using Jeol, JFM 5910, SEM analyzer.

2.4.5 DIFFERENTIAL SCANNING CALORIMETRY

Differential scanning calorimetry (DSC) was carried out with METTLER TOLEDO 823e DSC instrument. 7-8 mg of sample was heated in a sealed aluminum pan in the desired temperature range at a heating rate of 10° C/min, under nitrogen atmosphere.

2.4.6 THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analysis was carried out with METTLER TOLEDO TGA/DSC analyser 851e at 25 °C. 7-8 mg of sample was heated to 700 °C under air atmosphere at the heating rate of 10° C/min.

2.4.7 MECHANICAL TESTING

2.4.7.1 Tensile Measurement

To study the stress-strain response of the hybrid materials as a function of size and morphology of titania mechanical tests were performed at Testometric Universal Testing Machine M350/500. Samples with (15 x 4.5-5.0 x 0.8-1mm) dimension were synthesized. The samples were vaccum dried at 60 °C for two hours. Standard procedures and formulae were used for calculating various tensile properties including stress, strain, %elongation, yield stress, yield strain ,toughness, strength at break, Young's modulus, ultimate tensile strength (UTS) etc.

Data was fed directly into a computer interfaced with the tensile machine. The average of typically 3-5 specimens was determined for each sample and reported.

3. RESULTS AND DISCUSSION

The epoxy-amine matrix network yielded transparent films after curing while epoxy-amine-titania composite systems were opaque but flexible. Transparency of the composites depended upon the particle size of the ceramic like phase and their distribution in the organic matrix. By incorporating the particulate reinforcement the transparency was affected, because the particle size became larger than the wavelength of light. At reinforcement level of 10 wt% phase separation was observed for EAT-1 and EAT-2, while for EAT-3 phase separation appeared at 12.5 wt%.

In this chapter the results obtained for the particles, matrix and composite systems by various analytical techniques will be discussed. The proceeding section is divided into two parts. First part is the analysis of particles, second is the analysis of matrix and composites.

The particles were analyzed by various techniques including IR, XRD, AFM and SEM. IR and XRD were used as qualitative tool for the identification of the synthesized material particles; however, IR of functionalized titania was used as qualitative tool to check the functionalization reaction. Atomic Force Microscopy was also used to get information about the functionalization of particles.

The composites were analyzed by Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), Infrared Spectroscopy (IR), Scanning Electron Microscopy (SEM), and mechanical Analysis. DSC and TGA were used as tool for thermal analysis. Infrared analysis was carried out for qualitative analysis, while tensile tests were performed to study mechanical properties of the composites.

3.1 ANALYSIS OF PARTICLES

Various types of particles were synthesized varying in size and surface morphology. Various analytical techniques were used for the analysis and characterization of different properties.

3.1.1 ATTENUATED TOTAL REFLECTION –INFRARED SPECTROSCOPY

3.1.1.1 ATR-IR of micro-titania

ATR-IR of particles was carried out in order to know about the functional groups present at the surface of the particles. The particles were dried at ambient temperature so some organic groups were present at the surface. Figure 3.1 shows ATR-IR spectrum of micro-titania in the frequency range of 3500-400 cm^{-1}. The vibrational frequencies for various structural units are given in the table 3.1.

The characteristic peaks were stretching vibration of Ti-O-Ti unit at 480 cm^{-1} and O-H stretching vibration in the region of 3400 cm^{-1}. The –OH stretching peak was very broad which shows hydrogen bonding. Other peaks were due to ethoxy (-OEt) unit from the solvent i.e. ethanol. The solvent might have developed H-bonding interaction with the OH of the titania[87]. The presence of peaks for solvent has already been reported[108]. The asymmetric and symmetric stretching vibrations for $-CH_2$ appeared at 3056 cm^{-1} and 2998 cm^{-1} while the –CH symmetric stretching at 2972 cm^{-1} was masked by the peaks due to –OH stretching.

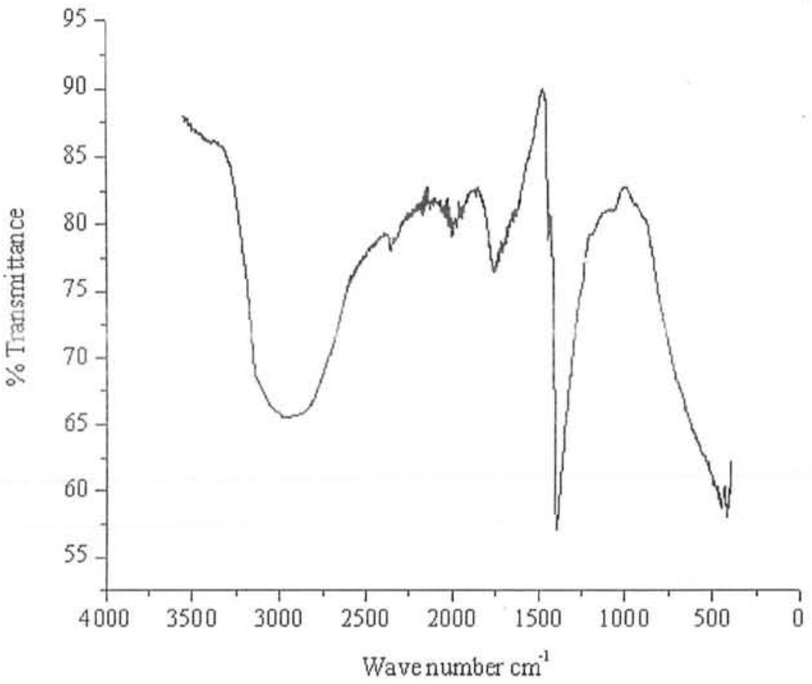


Fig 3.1: ATR-IR of microtitania

However, -CH bending vibration for CH_2 at 1460 cm^{-1} was the evidence of the presence of the alkyl chain.

Structural Unit	Stretching (Str.) / Bending (Bend.) Vibrations	Frequency cm^{-1}
-OH	Sym. Str	3400-3450
$-CH_3$	Asym. Str.	3056
$-CH_2$	Sym. Str. Bend.	2998 1460
Ti-O-Ti	Sym. Str.	480

Table 3.1: ATR-IR spectral data of microtitania

3.1.1.2 ATR-IR of calcined titania

ATR-IR of calcined titania was done to check if any organic functionality was left at its surface, for interaction with the organic matrix. The calcination was carried out at 600° C, so almost all the organic content was burnt off.

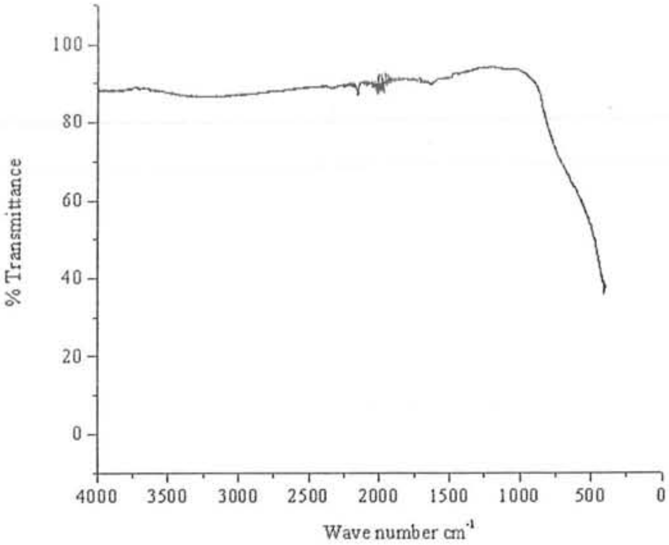


Fig 3.2: ATR-IR spectrum of calcined titania

Figure 3.2 shows ATR-IR spectrum of calcined titania in the frequency range of 4000-400cm^{-1}. The characteristic peak in the IR spectrum of calcined titania was of Ti-O-Ti unit which appeared at 480 cm^{-1}. Any other prominent peak was not present in the spectrum showing that the organic moieties had been removed completely during the high temperature calcination process. The synthesized product was thus pure Ti-O-Ti network.

3.1.1.3 ATR-IR of functionalized titania

ATR-IR of functionalized titania was carried out in order to get information about the completion of the functionalization reaction. The particles were reacted with amino-silane coupling agent, silane moiety underwent hydrolysis and Ti-O-Si bond was formed. Amine functionality remained intact in this reaction.

Figure 3.3 shows ATR-IR spectrum of functionalized titania in the frequency range of 4000-400cm^{-1}. The vibrational frequencies for various structural units are given in the table 3.2.

The characteristic peaks in the IR spectrum of functionalized titania were stretching vibration of OH at 3450 cm^{-1} and symmetric stretching of $-NH_2$ at 3350 cm^{-1} which were merged together. N-H bending was observed at 1508 cm^{-1}. Symmetric stretching and bending at 2998 $cm^{-1}$and 1460 cm^{-1} were due to methylene $-CH_2$ units in the coupling agent. The characteristic peak for Ti-O-Ti appeared at 480 cm^{-1}. Thus the IR spectrum confirmed that the functionalization of titania had been achieved.

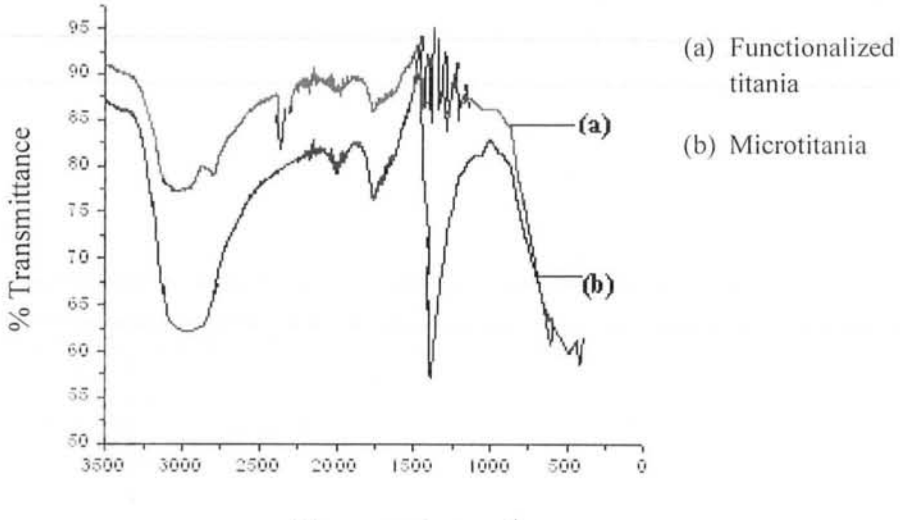


Fig 3.3: Comparative ATR-IR spectra of functionalized titania and microtitania

Structural Unit	Stretching(Str.) / Bending (Bend.) Vibrations	Frequency cm^{-1}
-OH	Sym.Str	3400-3450
$-NH_2$	Sym.Str	3300-3350
$-CH_3$	Asym.Str.	3056
	Bend	1380
$-CH_2$	Sym.Str.	2998
	Bend.	1460
C-N	Bend.	1508
Ti-O-Si	Str.	940
Ti-O-Ti	Str.	480

Table 3.2: ATR-IR of functionalized titania[45]

3.1.2 X-RAY DIFFRACTION ANALYSIS

XRD of particles was carried out as a qualitative analysis tool for the identification of phase of particles, and to get idea about the crystallinity of particles. XRD was correlated with those of references available in the library of the instrument.

3.1.2.1 XRD of micro-titania

XRD of particles was done to check out effect of drying temperature on the surface morphology. It was used as a tool to check whether crystallinity was attained after drying at 120 °C or it required high temperature processing.

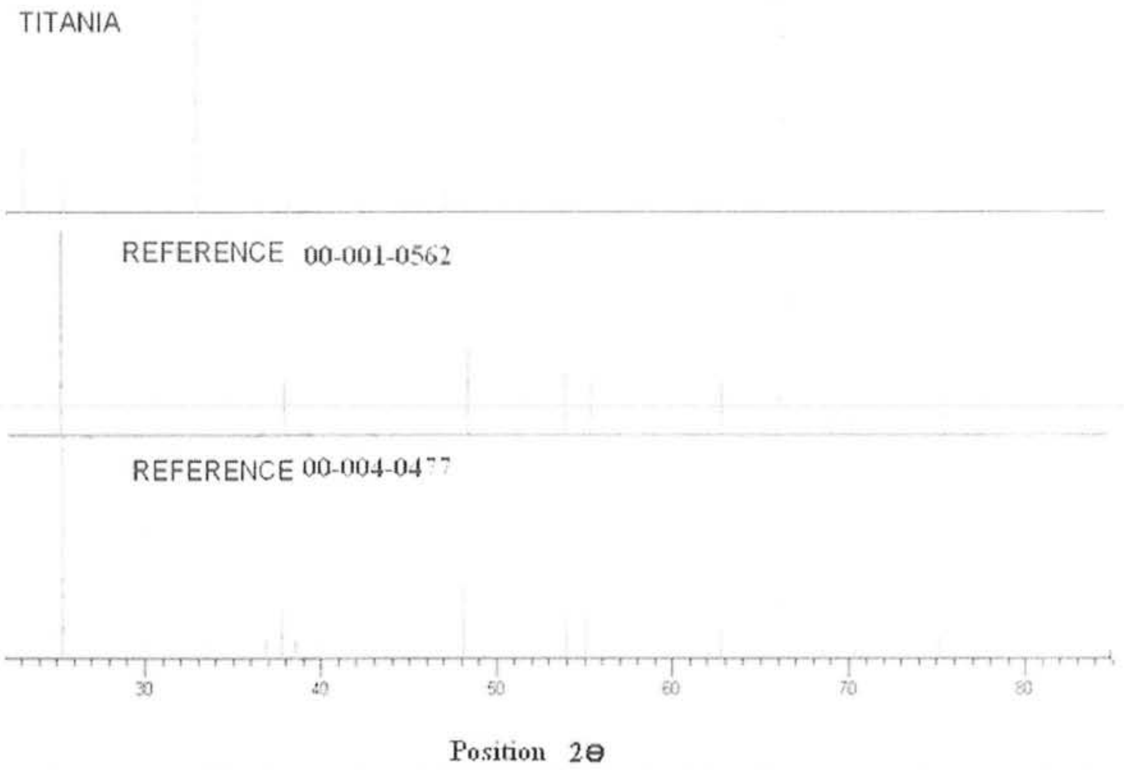


Fig 3.4: XRD peak correlation of micro-titania with the referrence

Figure 3.4 shows XRD peak correlation with that of reference for the micro-titania. The references 00-001-0562 and 00-004-0477 corresponded to peak pattern of anatase polymorph. The peaks pattern did not correspond to those of reference titania. This shows that the synthesized micro-titrania particles was not titanium oxide (TiO_2) rather it was partially hydrolysed titanium hydroxide.

3.1.2.2 XRD of calcined titania

The XRD of calcined titania was used as a qualitative analytical tool for the identification of product. The calcination of titania was carried out at 600 °C. At this temperature all the organic content was burnt off and pure titania network was left. This was confirmed by the XRD peak correlation with those of the reference peaks. Figure 3.5 shows XRD peak correlation with that of reference for the calcined titania.

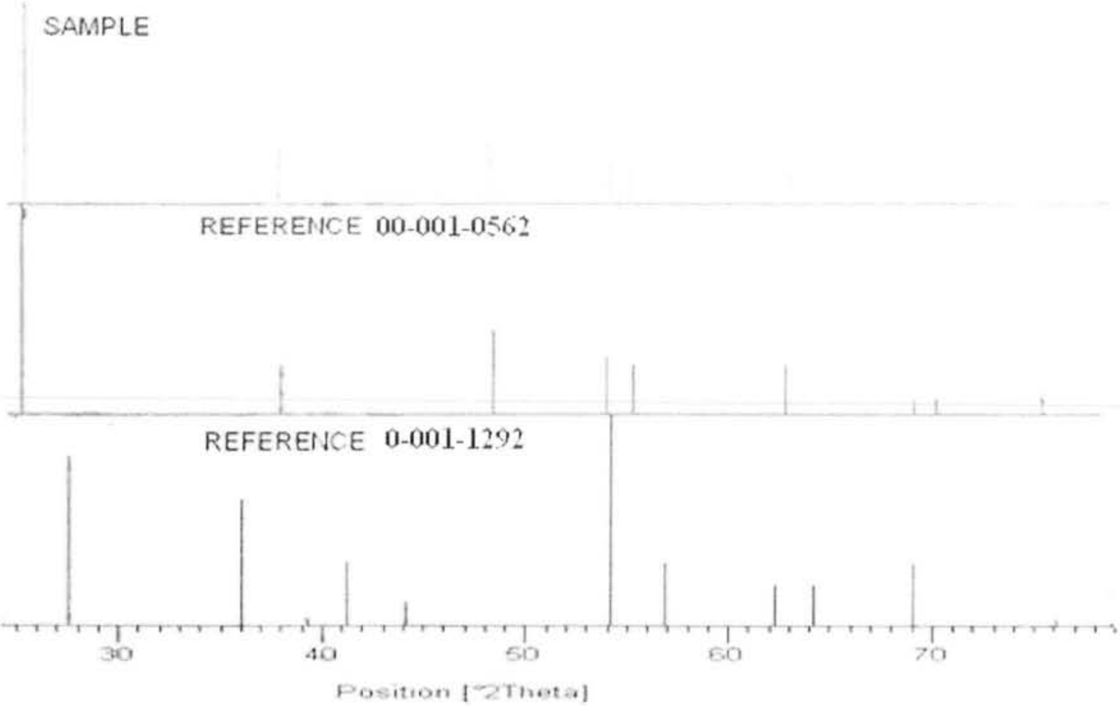


Fig 3.5: XRD peak correlation of calcined titania with the reference

The reference number 00-001-0562 corresponded to peak pattern of anatase titania, while reference number 00-001-1292 corresponded to peak pattern of rutile titania. The peak pattern of synthesized titania matched with that of anatase titania which meant that synthesized titania resembled anatase polymorph. It had empirical formula TiO_2 and crystal system was tetragonal.

3.1.2.3 XRD of functionalized titania

The titania was modified with aminosilane coupling agent. Its surface was expected to be altogether different from that of pure titania. XRD was carried out to confirm this. Figure 3.6 shows XRD peak correlation with that of reference for the functionalized titania.

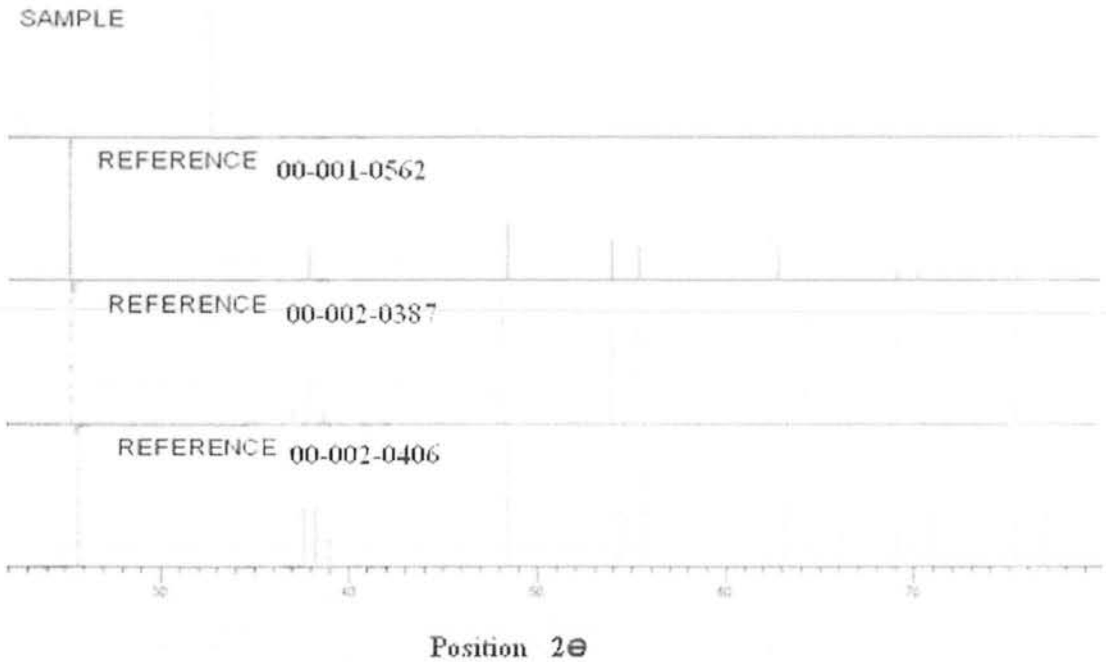


Fig 3.6: XRD peak correlation of functionalized titania with the reference

The references corresponded to peak pattern of anatase titania. The synthesized product did not match with the peak pattern of any of the reported systems which confirmed that it had surface different from that of the reference i.e., it had some other structural units on its structure which was aminosilane coupling agent as indicated by IR analysis. Thus XRD also confirmed the functionalization of particles.

3.1.3 SCANNING ELECTRON MICROSCOPY

3.1.3.1 SEM analysis of microtitania

Figures 3.7 (a and b) presents SEM images of microtitania. As evident by the image the size of particles was greater than 1 μm. Agglomeration was not seen in the images.

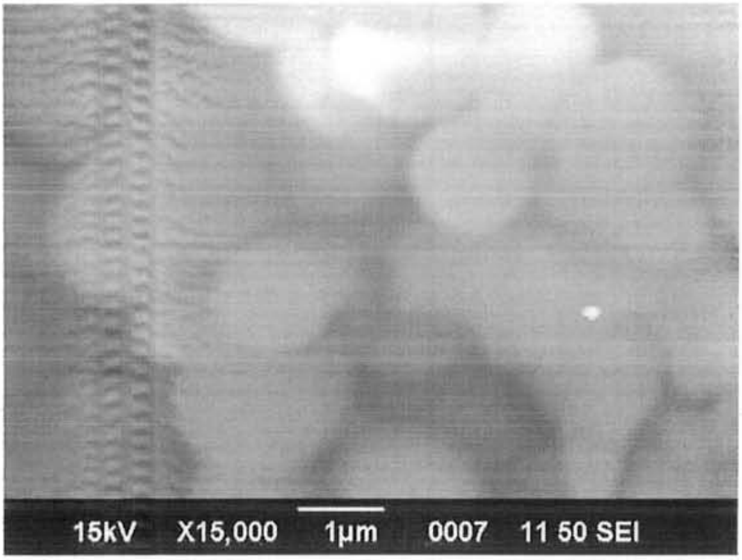
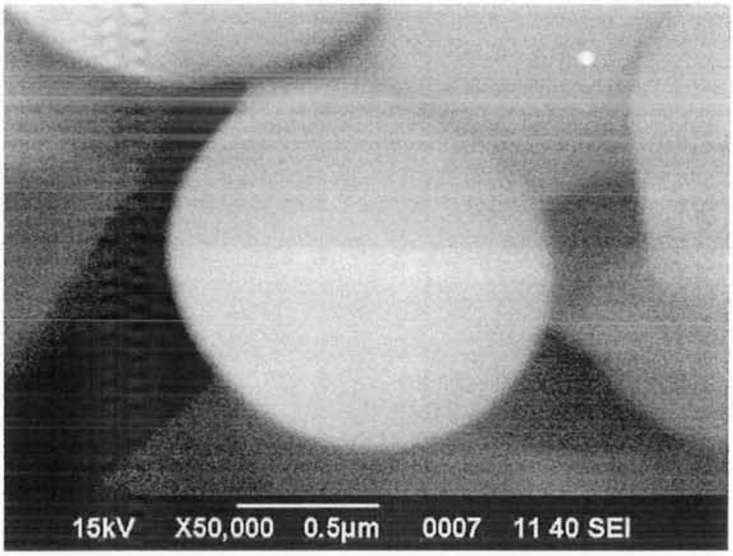


Fig 3.7 (a): SEM images of microtitania; 1 µm resolution



(b)

Fig 3.7 (b): SEM images of microtitania; 0.5 µm resolution

The high resolution image also confirmed the previous observation.

3.1.3.2 SEM of calcined titania

The SEM images of calcined titania showed that the size of titania was much smaller as compared to that of the microtitania. The particles were agglomerated thus it was not possible to determine the size of the particles.

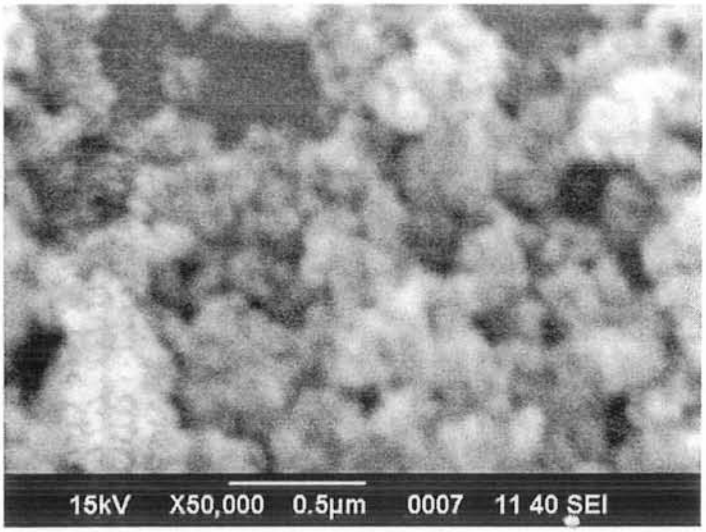


Fig 3.8 (a): SEM images of calcined titania (0.5 μm)

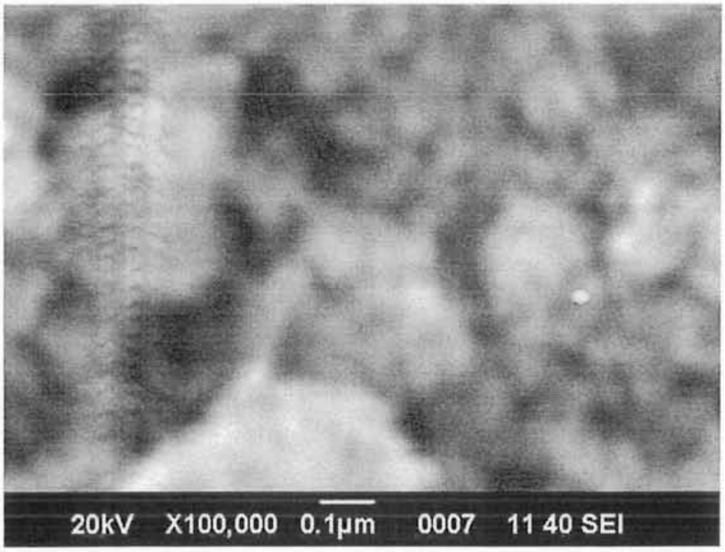


Fig 3.8 (b): SEM images of calcined titania (0.1 μm)

3.1.3.3 SEM of functionalized titania

The SEM images showed the formation of agglomerates so nothing could be said about the size of particles. The surface of particles seemed to be covered with something which could be the coupling agent.

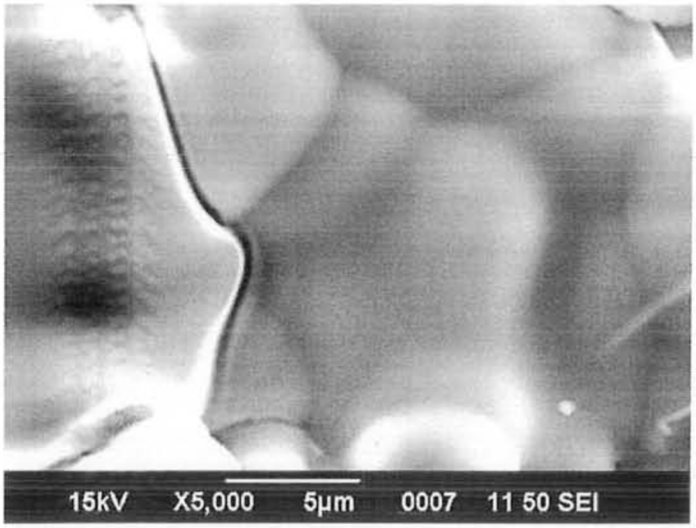


Fig 3.9 (a): SEM images of functionalized titania (5 μm)

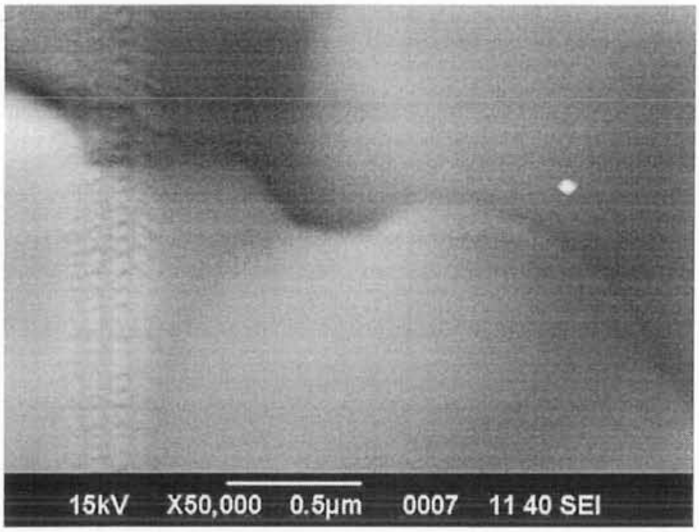


Fig 3.9 (b): SEM images of functionalized titania (0.5 μm)

The high resolution image also confirmed the previous observation.

3.1.4 ATOMIC FORCE MICROSCOPIC ANALYSIS

Atomic force microscopy gave insight into the morphology of the sample. The surface roughness and texture of the sample could be assessed with the help of AFM. The topographic image of the sample gave information about the morphology of the sample i.e., height and width of particles. The phase image gave information about the texture i.e., relative rigidity and softness of the constituents of the sample.

3.1.4.1 AFM analysis of functionalized titania

Atomic force microscopic analysis of functionalized titania was performed in order to get true picture of the synthesized product. It was also used as a tool to investigate the actual size of particle within the envelope of coupling agent.

This topographic image gave information about the morphology by giving picture of the relative height profile i.e., the ups and downs of the surface of the sample that was being analyzed. The phase image gave information about the morphology by depicting relative stiffness of the system as the color intensity of the system. The stiffness increased linearly with the color intensity of the analyte.

Figure 3.10 shows the topographic image of the functionalized titania. Some sort of symmetry was observed which might had appeared by the attachment of 2-3 particles per one molecule of γ-APS. Since there were three ethoxy silane units per coupling agent molecule, there was possibility that 2-3 titania particles might have attached per molecule of coupling agent thus giving rise to some sort of symmetry that appeared in the image.

Two types of structures were visible in the image, figure 3.10 (b). One kind of structure was of smaller size having defined boundary and although of not specific geometric appearance but relatively definite shape. The other type of structure was of larger entities lacking defined boundary and specific shape.

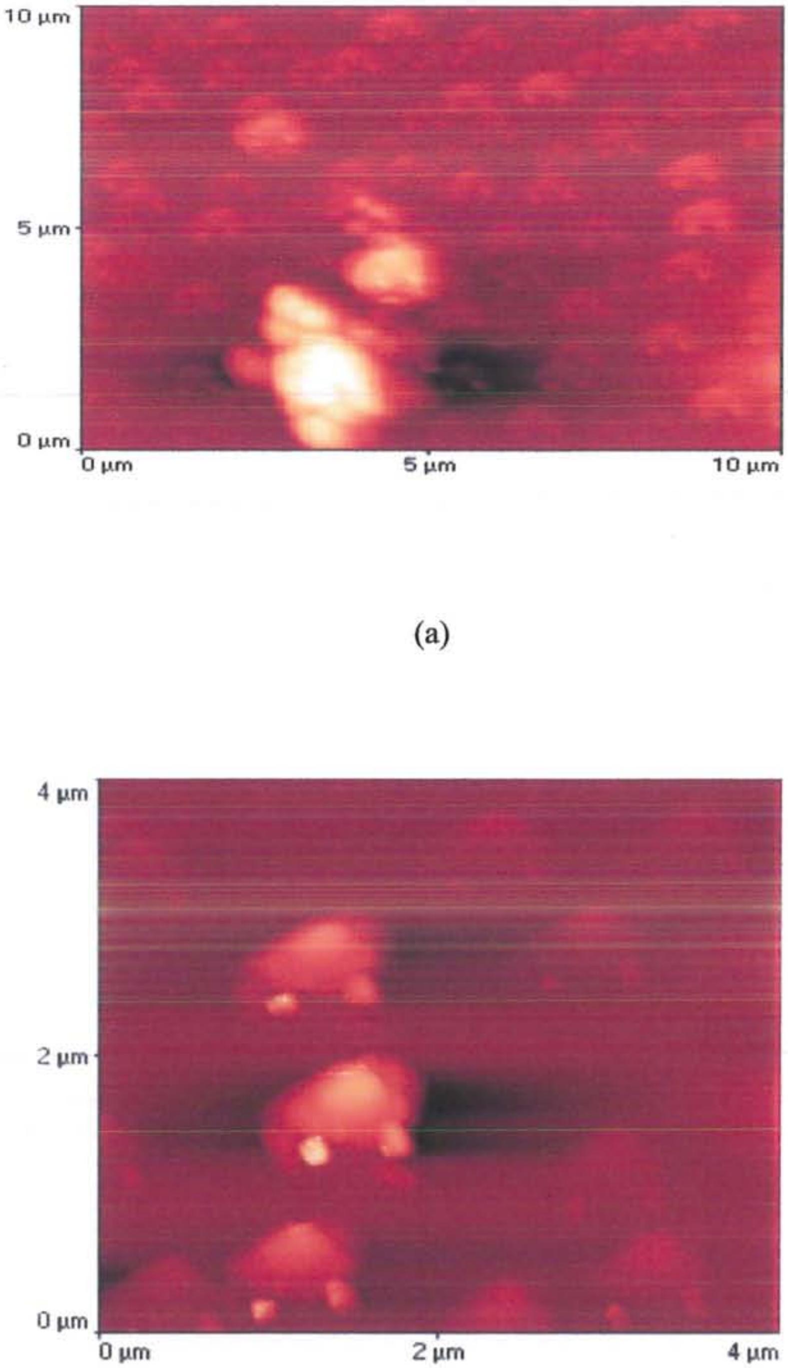


Fig 3.10 (a): Topographic images of functionalized titania

(b): High resolution topographic image

It gave an idea that the small entities enveloped within the larger coverings were titania particles, and larger coverings was the coupling agent. This supported the fact that the surface of particles had been modified by the coupling agent.

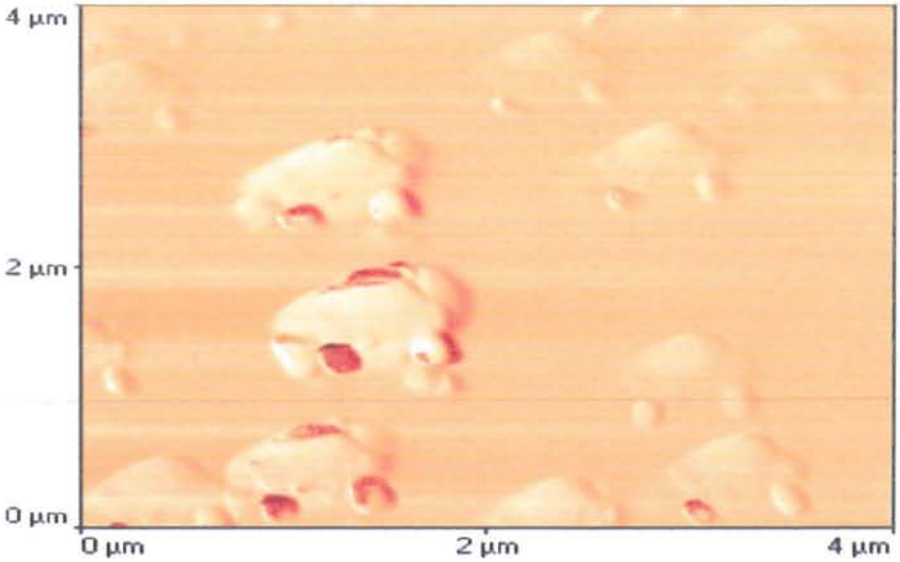


Fig 3.11: Phase image of functionalized titania

Figure 3.11 gives phase image of the functionalized titania. The phase image showed the rigidity and stiffness of the sample as a function of color intensity. The brighter the color, the stiffer would be the substance. The bright portions in the image represented the metallic part, which was also evidenced by the topographic image. The lighter color represented softer part which was the organic coupling agent. This confirmed that titania had reacted with the coupling agent and its surface had been tailored successfully. The cumulative size of the particles was 0.5 µm. The actual size of the metallic particles was 100-120 nm and rest 350 nm was the size of the envelope of the coupling agent.

3.2 CHARACTERIZATION OF MATRIX

The neat-epoxy-amine matrix was used as reference for the epoxy-amine-titania composite systems. The samples obtained in the case of neat epoxy-amine network were analyzed by ATR-IR spectroscopy, DSC, SEM and mechanical analysis. First of all ATR-IR of neat system will be discussed.

3.2.1 ATR-IR SPECTRAL ANALYSIS OF NEAT EPOXY-AMINE NETWORK

Curing of Jeffamine with DGEBA at 100 °C produced three dimensional networks. While curing, D-400 reacts with DGEBA, the NH_2 functionality of amine opened the epoxy ring of DGEBA hence tertiary C-N bond appeared in the final network with the disappearance of primary $-NH_2$ and epoxide groups from D-400 and DGEBA respectively.

In the spectrum, disappearance of asymmetric and symmetric stretching vibrations due to oxirane at 915 cm^{-1} and 863 cm^{-1} respectively and appearance of strong absorption at 3400 cm^{-1} due to O-H formation were observed. The appearance of peak at 1320 cm^{-1} was due to tertiary C-N symmetric stretching and no peaks were observed for primary N-H showing that that the $-NH_2$ functionality of Jeffamine D-400 has been used up in opening the epoxy ring of DGEBA and complete reaction between DGEBA and Jeffamine D-400 had taken place. Symmetric stretching vibrations of CH_3, $-CH_2$ and –CH were observed at 2975 cm^{-1} and 2950 cm^{-1} and 2900 cm^{-1} respectively[109].

The characteristic IR stretching vibrations of bisphenol A part in neat epoxy–amine matrix were also observed. The absorption range from 1608-1511 cm^{-1} was due to Φ C=C and Φ-O at 1250 cm^{-1}.

From the ATR-IR spectral analysis of epoxy-amine matrix it could be concluded that network formation had occurred and reaction between DGEBA and D-400 was complete.

3.2.2 THERMAL ANALYSIS

3.2.2.1 Differential scanning calorimetry "DSC" of EA-neat

DSC thermograms were used to determine the glass transition temperature (Tg) of neat epoxy-amine network. First scan of the composites were reported to start from 0-280° C and the same sample was scanned a second time between 10 – 110° C. As the sample was scanned between 0-300° C in the DSC oven the reaction was completed after this first scan, so the second scan of the system gave the final Tg of the system i.e., Tg of the cured epoxy-amine matrix. It was found to be 45 °C[110].

3.2.3 MECHANICAL PROPERTIES OF NEAT EPOXY-AMINE NETWORK

Tensile testing of the epoxy-amine network was carried out. A brief discourse on the tensile properties of the neat epoxy-amine network is being given in the following section.

3.2.3.1 Tensile properties of EA-neat

Stress-strain behaviour of epoxy-amine matrix was studied. Tensile testing of 3-5 specimens was carried out at 25° C. Parameters studied from Stress-Strain curves were tensile strength, Young's modulus, Stress at 200% elongation, and toughness and found to be almost same as mentioned in reference no. 109.

Mechanical Properties	Observed Values ± 0.03
Tensile Strength	11.67 MPa
Young's Modulus	1128.45 MPa
Stress at 200% elongation	4.72 MPa

Table 3.3: Tensile properties of epoxy-amine neat

3.3 EPOXY-AMINE-TITANIA COMPOSITES WITH MICRO-TITANIA "EAT-1"

A composite system, based upon epoxy-amine-titania, containing partially condensed titania was synthesized and abbreviated as **"EAT-1"**. The hydrolysis and condensation of $TiCl_4$ was carried out at 60 °C and drying was carried out at 120° C. The partially condensed particles were blended with stoichiometric amounts of DGEBA and Jeffamine D-400 while ensuring the formation of homogenous mixture. The mixture was then poured into the uniform sized moulds for shaping into thin strips for mechanical analysis. The samples obtained were analyzed by IR, DSC and TGA.

3.3.1 ATR-IR ANALYSIS OF "EAT-1"

To study the effect of incorporation of titania in the epoxy-amine matrix without coupling agent, ATR-IR spectroscopy was performed.

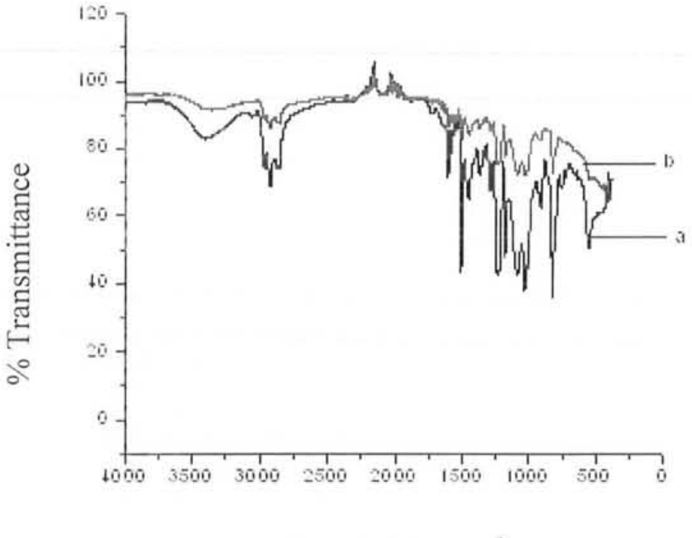


Fig 3.12: ATR-IR spectra of (a) Epoxy-amine neat (b) 10 wt% epoxy-amine-titania composite "EAT -1"

Figure 3.12 shows the overlapped ATR-IR spectra of 10 wt% epoxy-amine–microtitania composites and the neat epoxy-amine matrix in the frequency range of 3500-400 cm^{-1}. The absorption bands at 1320 cm^{-1} corresponding to C-N stretching vibrations respectively confirmed the formation of epoxy-amine network. The peaks due to bisphenol A could also be observed as mentioned before (See Section 3.2.1) showing that incorporation of titania phase had no effect upon the formation of organic matrix.

The characteristic stretching vibrations for titania were present in the region 410-490 cm^{-1} showing that basic network skeleton of titania remained intact during the formation of the composite.

From the spectral analysis of epoxy-amine neat and epoxy-amine-microtitania composite it was thus concluded that the presence of reinforcement in the matrix did not interfere with the formation of the matrix itself. From spectrum (b) it was clear that peaks observed for titania in the 10wt % composite were absent in the spectrum of the neat epoxy-amine network.

3.3.2 CURING BEHAVIOUR OF THE EPOXY–AMINE TITANIA MATRIX

In order to determine the effect of titania on the curing of the epoxy amine matrix, DSC was performed on initial mixture of epoxy-amine-titania before curing (t=0). Figure 3.13 (a)

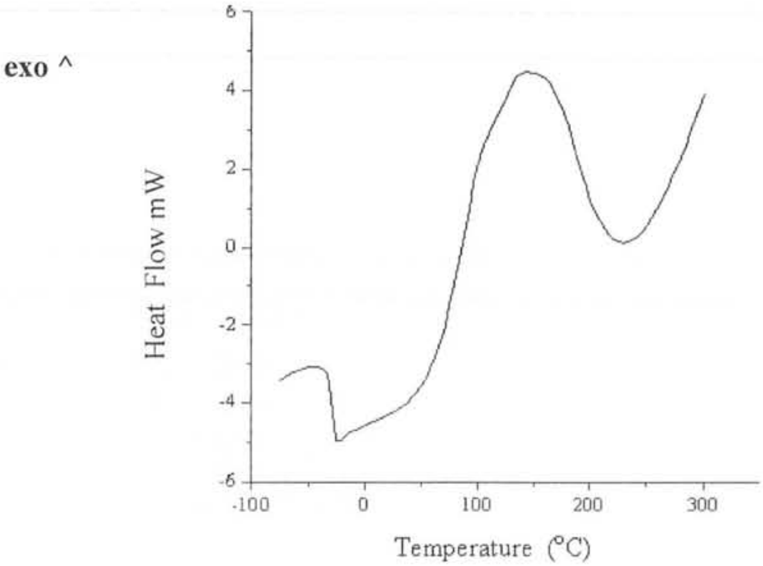


Fig 3.13 (a): First DSC scan of the epoxy–amine-titania (2.5 wt. %) at t=0

In the first scan of scan of DSC an exotherm appeared to start at 50 °C and continued till 220 °C showing that the reaction had been completed in this range. Now curing could be done either by giving longer times at 100 °C or by giving heat treatment at 150 °C for shorter time. Another transition was also present in the DSC scan of the epoxy-amine-titania composite, which was initial Tg (Tg of the system which had unreacted precursors) of the system. The curing was then carried out at 100 °C for 5 hours and completion of reaction was checked by IR and DSC of cured composite films.

The second scan given in figure 3.13 (b), gave information about the glass transition temperature Tg, of the system since the reaction had been completed during the first scan. The scan showed that the Tg of the final system (41 °C) had been decreased a little as compared to that of neat epoxy-amine matrix i.e., 45 °C[110]. This was due to the reason that the titania was partially condensed, it had –OH, which played its part as flexibilizer thus decreasing the Tg of the system. Also there was possibility of release of water by the condensation of O-H groups at the surface of titania[101].

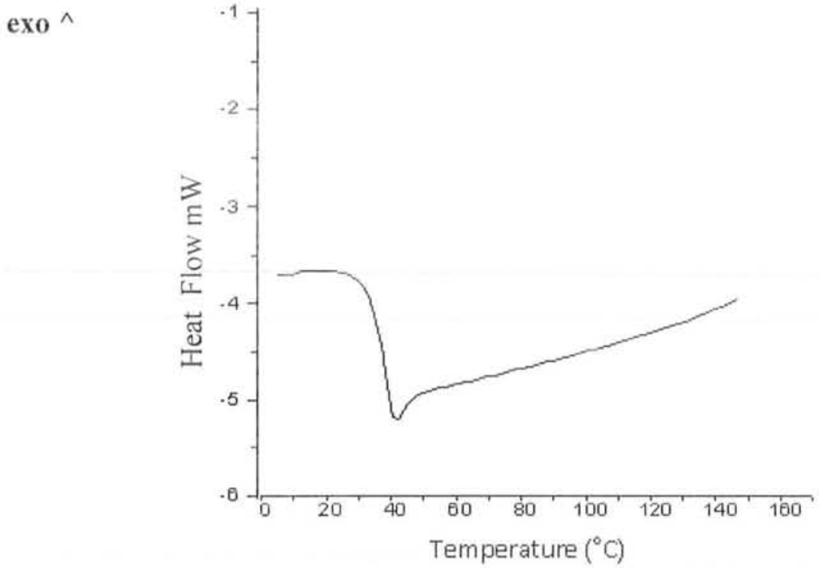


Figure 3.13 (b): Second DSC scan of the epoxy- amine-titania

3.3.3 SCANNING ELECTRON MICROSCOPY

SEM of EAT-1 series was done in order to see the influence of addition of micro-titatnia on the type of interaction between the matrix, filler and the final size of the particles.

It was also indicated by the image that particles were homogenously distributed in the matrix i.e., any region without filler was not visible, however, the particles were agglomerated so the interaction between the matrix and the particles was not so strong. Since particles in the gel phase were added to the matrix, there was a probability that D-400 might have acted as nucleophillic catalyst for completion of the hydrolysis of the particles[96]. The result was fast growth and hence agglomeration of the particles.

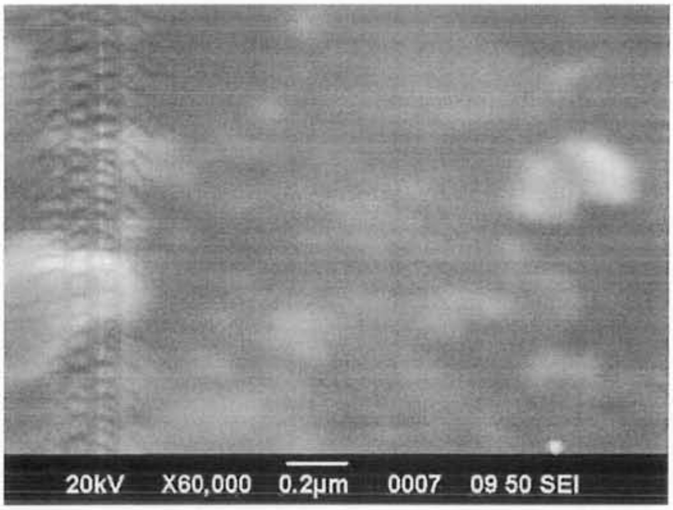


Fig 3.14 (a): SEM image of EAT-1 (10 wt. %, 0.2 µm)

Also the surface of the particles was not modified i.e., coupling agent was not used so the probability of strong interaction decreased.

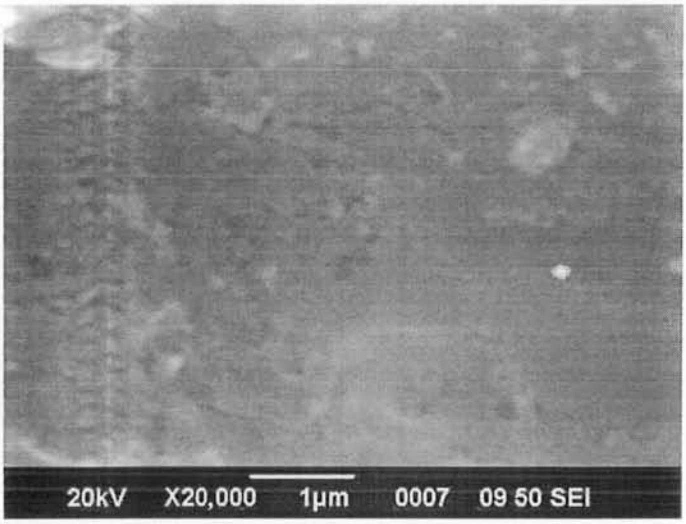


Fig 3.14 (b): SEM image of EAT-1 (10 wt. %, 1 µm)

3.3.4 THERMOGRAVIMETRIC ANALYSIS OF "EAT-1"

TGA analysis of the epoxy-amine-microtitania composites was carried out to investigate the thermal stability, the onset of degradation and the weight loss behaviour. TGA was done in the air atmosphere. The TGA showed that the thermal stability depended greatly on the content of the filler. TGA of the two representatives for the series "EAT-1" i.e., 5 wt. % and 10 wt. % microtitania composite are compared in figure 3.15.

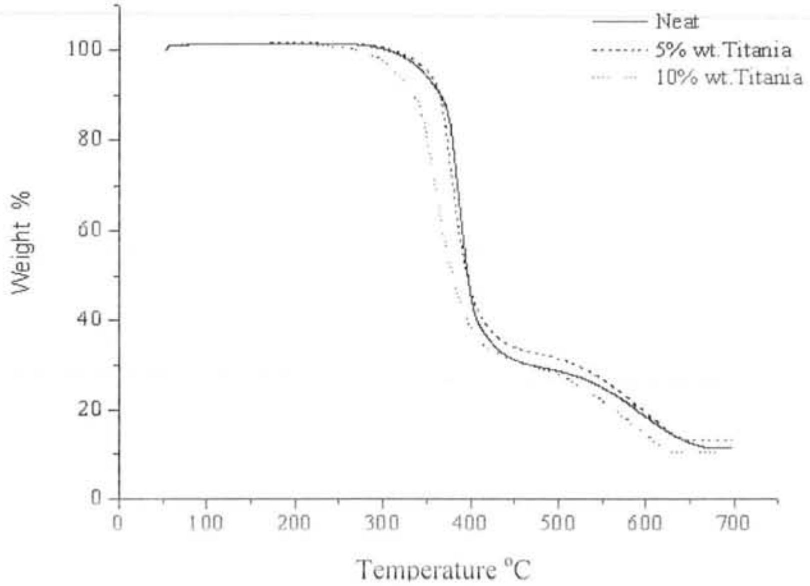


Fig 3.15: TGA of microtitania 5 wt. %, 10 wt. % and neat epoxy-amine matrix

The onset of degradation started at about 300 °C for the neat epoxy matrix, showing the thermal stability of matrix itself. The onset of degradation for 5 wt% microtitania was about the same as for matrix. This shows that titania upto 5 wt% did not alter the thermal properties of the matrix to a larger extent. The onset of degradation for the 10 wt% titania composition was earlier than the matrix. Since the titania used was partially condensed it had plasticizing effect. Instead of increasing thermal stability, it would rather increase the mechanical properties. Secondly it was reported that if prehydrolyzed particles were added then amine that was being used as curing agent would act as nucleophilic catalyst and agglomerates would form which lower the thermal properties of the system so this observation was in accord with the reported one [96]. Apart from this fact water was also being formed by the condensation of the OH groups present at the surface of titania, this water also played an important role in plasticizing the composite system thus formed[101].This effect was more pronounced in the 10 wt% titania composite, showing that the higher the content of the filler, the greater the plasticization of the composite

SYSTEM	T_{50} °C	T_{10} °C	T_{max} °C
5 % weight EAT-1	375	370	360
10% weight EAT-1	350	330	340
Neat Epoxy-amine	380	375	370

Table 3.4: Thermal stability parameters for "EAT-1"

The T_{10}, T_{50} and T_{max} values also confirmed the plasticization of matrix by the reinforcement. The maximum weight loss for 10 wt. % occurred at lowest temperature. The T_{50} and T_{10} values also depicted the least thermal stability of the 10 wt. % composite.

3.3.5 DIFFERENTIAL SCANNING CALORIMETRY OF "EAT –1"

DSC of the samples was carried out to get information about the glass transition temperature of the composite systems. Here in this system the curve for the heat evolution or absorption was not visible. (See Annex) It is attributed to the fact that the organic polymer chains were bound to the particulate reinforcement and chain mobility was highly restricted that is why Tg was not visible. Although quantitative results could not be drawn, yet the invisibility of Tg might be affect of filler, since the presence of the filler restricts the motion of the polymer chains[90].

3.3.6 MECHANICAL PROPERTIES OF EPOXY-AMINE-MICRO-TITANIA "EAT-1" COMPOSITES

Tensile testing of the epoxy-amine network was carried out. Following section gives a brief discourse on the tensile properties of the network.

3.3.6.1 *Tensile properties of "EAT-1"*

The parameters studied from the stress-strain curve are given in table: 3.5. The tensile strength for the EAT-1 composite formulations exceeded the value for the neat epoxy-amine matrix system (section 3.2.3.1), showing the improvement in mechanical properties.

All the parameters showed an increase, giving an evidence that the addition of filler had resulted in the enhancement of tensile strength. It was attributed to the fact that that the micro-titania acted as plasticizing agent. It lent flexibility to the polymer chains thus enhancing the chain mobility as compared to those in the neat epoxy-amine matrix which was relatively rigid.

Mechanical Properties	Observed values ± 0.05
Tensile Strength	23.98 MPa
Young's Modulus	1321.86 MPa
Stress at 200% elongation	18.08 MPa

Table 3.5: Tensile properties of "EAT-1"

3.4 EPOXY-AMINE-TITANIA COMPOSITE WITH CALCINED-TITANIA "EAT-2"

A composite system, based upon epoxy-amine-calcined titania, containing completely condensed titania, was synthesized and abbreviated as "EAT-2". The hydrolysis and condensation of $TiCl_4$ was carried out at 60 °C and calcination was carried out 600 °C. The particles were completely dried to study the effect of the size reduction only keeping all the other factors constant. The calcined particles were blended with stoichiometric amounts of DGEBA and Jeffamine D-400 to ensure formation of homogenous mixture. The mixture was then poured into the uniform sized moulds for shaping into thin strips for mechanical analysis. The samples obtained were analyzed by IR. SEM and TGA of samples was also carried out.

3.4.1 SCANNING ELECTRON MICROSCOPY OF "EAT-2"

Figure 3.16 shows SEM of "EAT-2" series composite. The particles were agglomerated which indicated the poor interaction between the particles and the matrix.

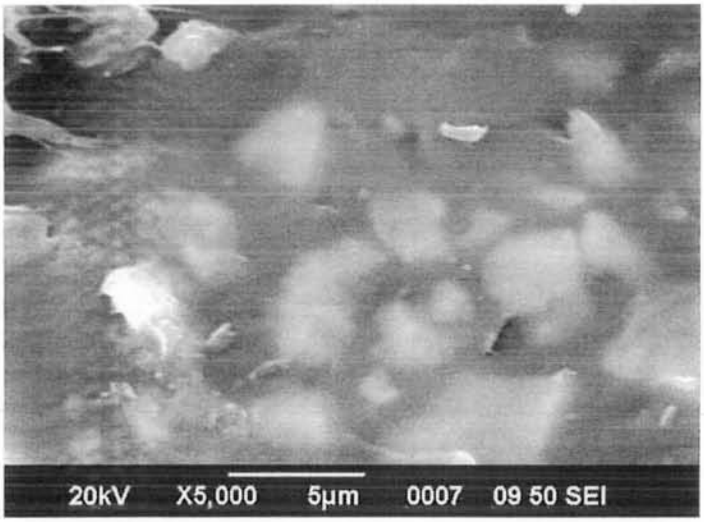


Fig 3.16 (a): SEM image of epoxy-amine-calcined titania composite (10 wt. %, 5μm)

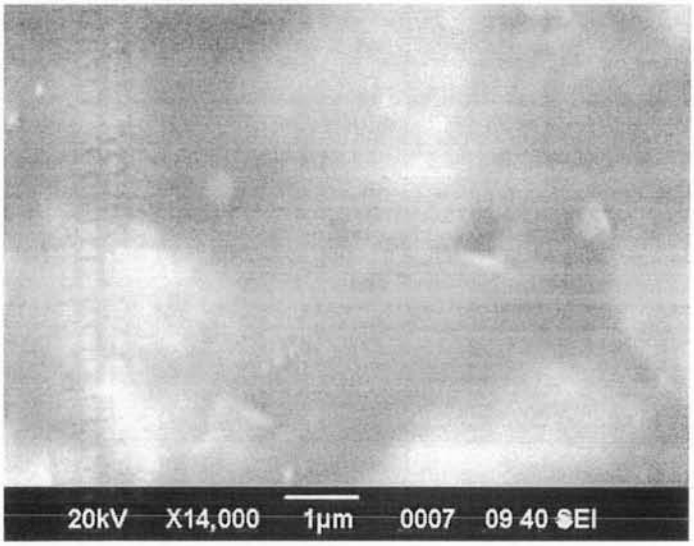


Fig 3.16 (b): SEM image of epoxy-amine-calcined titania composite (10 wt. %, 1 μm)

There was no chance of interaction between matrix and the filler because the filler was purely Ti-O-Ti network without any organic moiety to interact with the matrix. The inorganic domains were dispersed in the organic matrix.

3.4.2 THERMAL ANALYSIS OF "EAT-2"

Thermal behavior of the epoxy-amine-calcined titania composites was studied to see the effect of the calcined titania. The binding agent was not used in this series.

3.4.2.1Thermogravimetric Analysis of "EAT-2"

Figure 3.17 shows the TGA of the calcined titania composites in comparison with the neat epoxy-amine matrix. The onset of degradation for the calcined composites was higher than the neat matrix, showing that the particles conferred extra thermal stability to the composites. This was attributed to the fact that the ceramic content increased in the composite system. The thermal stability in case of 10 wt. % titania was better than the 5 wt. % composite, showing that the higher the content of the filler, the greater the stability of the composite. This was due to the fact that the filler was ceramic in nature which had higher thermal resistance than the organic constituents.

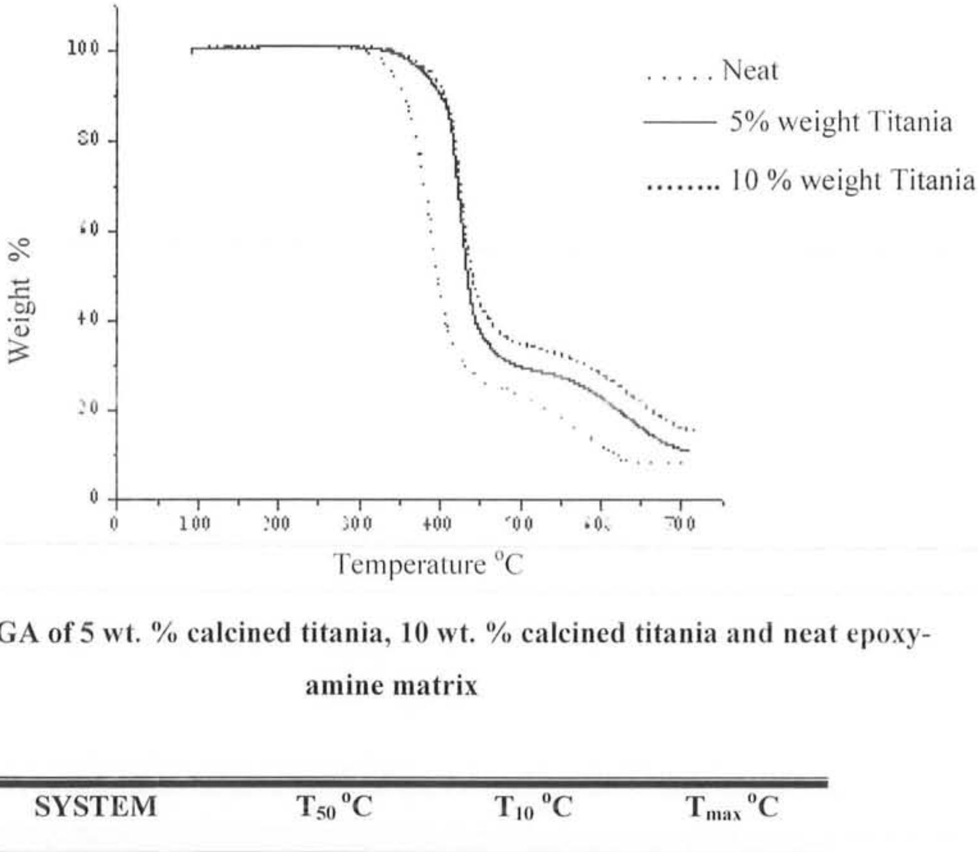


Fig 3.17: TGA of 5 wt. % calcined titania, 10 wt. % calcined titania and neat epoxy-amine matrix

SYSTEM	T_{50} °C	T_{10} °C	T_{max} °C
5 % weight EAT-2	420	400	410
10% weight EAT-2	420	400	410
Neat Epoxy-amine	380	375	370

Table 3.6 Thermal stability parameters for "EAT-2"

The DSC results for EAT-2 are still awaited for.

3.4.3 MECHANICAL PROPERTIES OF EPOXY-AMINE-CALCINED TITANIA "EAT-2" COMPOSITE

Tensile testing of the epoxy-amine network was carried out. Following section gives a brief discourse on the tensile properties of the network.

3.4.3.1 ***Tensile properties of "EAT-2"***

The tensile properties showed a negative trend as compared to those of neat epoxy-amine matrix. Both the tensile strength and Young's modulus had decreased. This was due to the fact that although the ceramic content increased, yet there was poor dispersion which imparted rigidity instead of flexibility to the composite system. The system became even more brittle than the matrix and hence its tensile strength decreased. Table: 3.7 shows the values of different parameters for EAT-2.

Mechanical Properties	Observed values ± **0.05**
Tensile Strength	9.62 MPa
Young's Modulus	562.25 MPa
Stress at 200% elongation	4.15 MPa

Table: 3.7 Tensile properties of "EAT-2"

3.5 EPOXY-AMINE-FUNCTIONALIZED TITANIA COMPOSITES "EAT-3"

A composite system, based upon epoxy-amine-functionalized titania, containing binding agent to connect filler particles to the polymer backbone, was synthesized and abbreviated as "EAT-3". The hydrolysis and condensation of $TiCl_4$ was carried out at 60° C and drying was carried out at 120 °C. The as-synthesized particles were reacted with γ–APS to modify the surface. The modification was done to enhance the binding capability of the filler with the matrix. The functionalized particles were blended with stoichiometric amounts of DGEBA and Jeffamine D-400 till the formation of homogenous mixture. The mixture was then poured into the uniform sized moulds for shaping into thin strips for mechanical analysis. The samples obtained were characterized by IR, SEM, TGA and DSC.

3.5.1 ATR-IR ANALYSIS OF "EAT-3"

To study the effect of incorporation of titania in the epoxy-amine matrix with the coupling agent, ATR-IR spectroscopy was performed. Figure 3.18 shows the combined ATR-IR spectra of 10wt% epoxy-amine–functionalized titania composites and epoxy-amine matrix in the frequency range of 4000-400 cm^{-1}.

The absorption bands at 1320 cm^{-1} corresponding to C-N stretching vibrations respectively confirmed the formation of epoxy-amine network. The peaks due to bisphenol A could be observed as mentioned earlier. The coupling agent had amine functionality in it, but the peak for N-H absorption was not found in the IR of composite system showing that the amine of coupling agent also took part in the reaction.

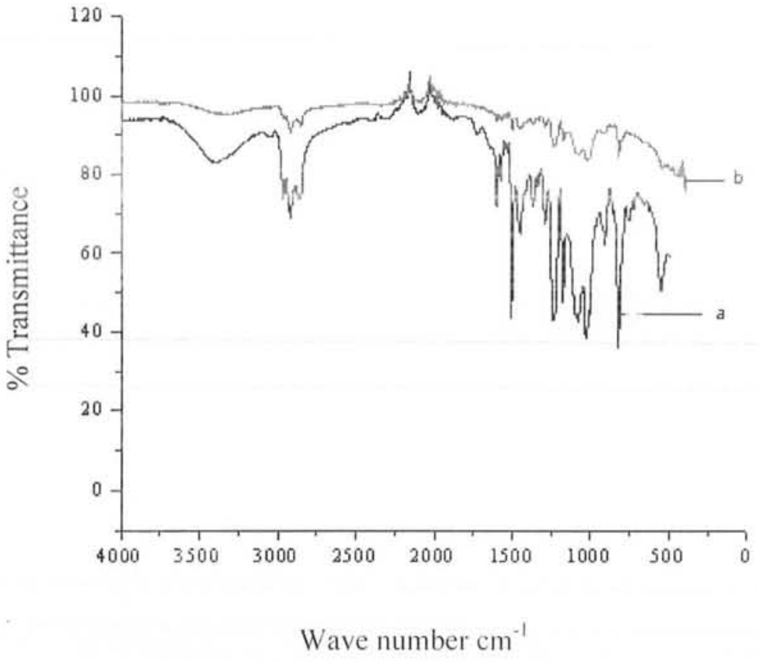


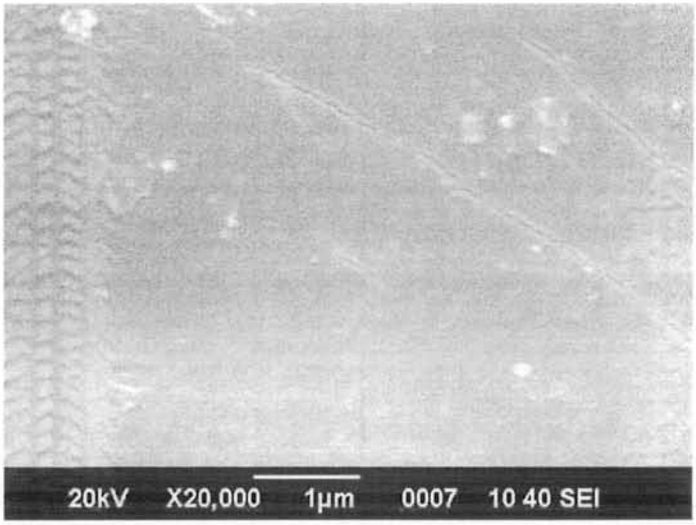
Fig 3.18: ATR-IR spectra of (a) epoxy-amine neat (b) 10 wt% epoxy-amine-functionalized titania composite "EAT-3"

The characteristic stretching vibrations for titania were present in the region 410-490 cm^{-1} showing that basic skeletal network of titania remained intact during the formation of the composite. The O-H stretch present in the IR of matrix was absent in the IR of composite since there was possibility of interphase bonding through the OH group[111].

From the spectral analysis of epoxy-amine neat and epoxy-amine-functionalized titania composite it was thus concluded that the amine group in the coupling agent reacted with epoxy group of the DGEBA thus establishing chemical link between the matrix and the reinforcement.

3.5.2 SCANNING ELECRON MICROSCOPY OF "EAT-3"

SEM of the composites was carried out with the aim to study the effect of tailoring the surface of particles on the interaction between the matrix and the filler.



(a)

Fig 3.19 (a): SEM image of "EAT-3" (10 wt. %, 1μm)

Figures 3.19 (a and b) show the SEM images of "EAT-3". Even at higher resolution particles were not visible which confirms the breakdown of agglomerates and reduction in size due to interaction between the matrix and the filler. The particles were well diffused in the matrix showing the strong chemical interaction between particles and matrix due to functionalization of the particles.

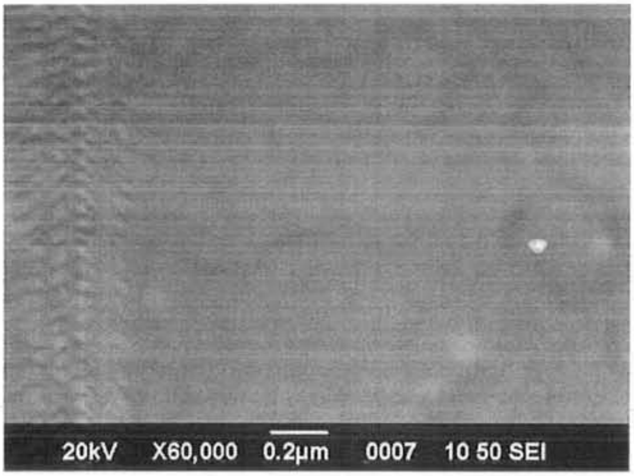


Fig 3.19 (b): SEM image of "EAT-3" (10 wt. %, 0.2 µm)

3.5.3 THERMAL ANALYSIS OF "EAT-3"

Thermal analysis of the composites was carried out in order to study the effect of introduction of the coupling agent on the thermal properties of the composites. The coupling agent had modified the surface properties of the particles thus modifying the properties of the composites also. This affect was studied by the TGA and DSC of the samples.

3.5.3.1 Thermogravimetric Analysis of "EAT-3

The comparative TGA thermograms for EAT-3 and neat system are given in figure 3.20. The thermal properties of the composites showed a negative trend. The onset of degradation was earlier than the neat epoxy-amine matrix for both the 5 wt% and 10 wt% composites. Although the binding between the organic and the inorganic constituents increased due to the coupling agent, but the weight loss behaviour was governed by metallic content in the reinforcement.

SYSTEM	T_{50} °C	T_{10} °C	T_{max} °C
5 % weight EAT-3	380	375	370
10% weight EAT-3	360	325	340
Neat Epoxy-amine	380	375	370

Table 3.8: Thermal stability parameters of EAT-3

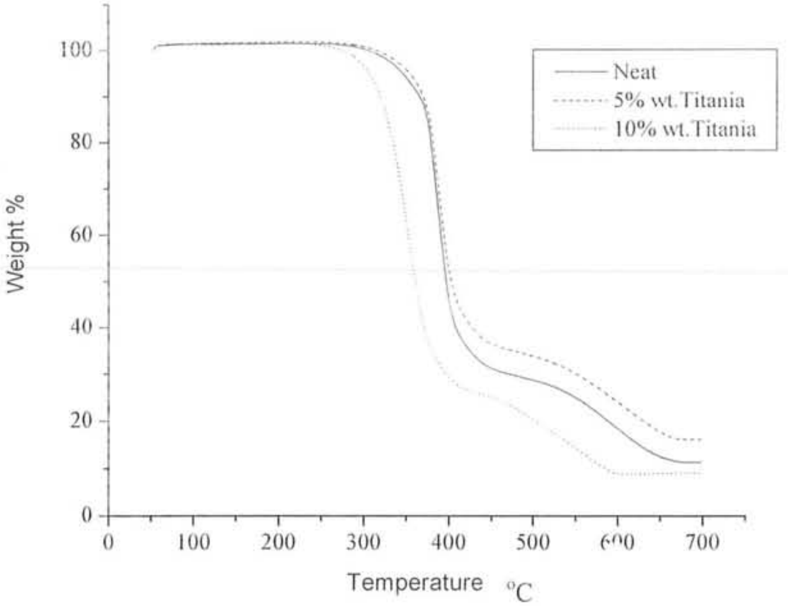


Fig 3.20: TGA of epoxy-amine matrix, 5 wt. % and 10 wt. % functionalized titania composites.

The coupling agent γ-APS, reduced the weight % of the inorganic phase (titania network) in the overall weight of the particles. This in turn reduced the inorganic content in the composite system which adversely affected the thermal properties of the composites. The higher the content of the organic part, the linear the decrease in the content of the inorganic phase and thus lower the thermal stability of the composites. This was also evidenced by the observation that the thermal stability of the 10 wt% composite was even lesser than the 5 wt % composite. The values in table 3.8 also confirmed this observation.

3.5.3.2 Differential Scanning Calorimetry of "EAT-3"

DSC analysis of the composites was done in order to get information about the Tg of the composites. Tg was also affected by the modification of the reinforcement.

Figure 3.21 shows the DSC thermogram of the epoxy-amine-functionalized titania composite. The Tg of the 5 wt. % composite was 51 °C. The Tg of neat epoxy-amine matrix was 45 °C[110]. This shows that the Tg of the system had increased indicating restricted movement of polymeric chains. It was attributed to chemical linkage between titania and organic network. The polymer chain mobility was hindered and chain movement occured at higher temperature accounting for an increase in Tg. The Tg of the 10 wt. % composite system was 67 °C.

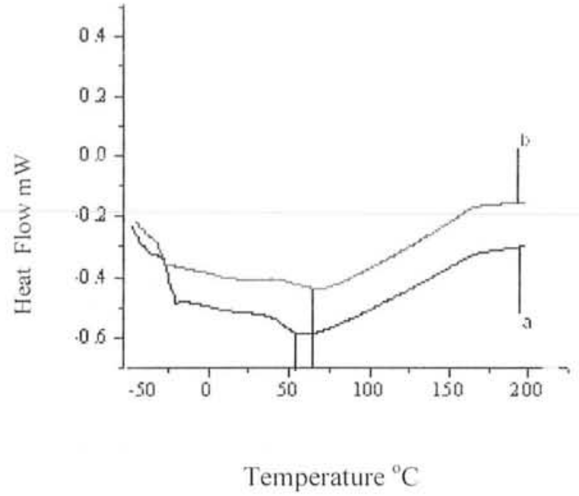


Fig 3.21: DSC Thermogram of EAT-3 (a) 5 wt. %; (b) 10 wt. %

The Tg showed linear increase with the content of the filler. It was due to the reason that as the content of the filler increased, the bound polymer layer increased too. The bound polymer layer was actually the amount of polymer that stuck to the filler. The chain mobility was restricted with the increase in bound polymer layer which in turn increased the Tg.

3.5.4 MECHANICAL PROPERTIES OF EPOXY-AMINE-FUNCTIONALIZED TITANIA COMPOSITE

Tensile testing of the epoxy-amine network was carried out. Following section gives a brief discourse on the tensile properties of the neat epoxy-amine network.

3.5.4.1 ***Tensile properties of EAT-3***

Table 3.9 gives the values of the different parameters regarding the tensile strength of the EAT-3 series. The data showed that the tensile strength of the composite systems had increased. It was attributed to two reasons. Firstly, the particles are chemically bound to the matrix system and thus enhanced the mechanical strength of the composite system. Secondly, the particles had aliphatic coupling agent chain associated with them which imparted flexibility to the system. Hence the mechanical properties increased as a combined affect of both the factors.

Mechanical Properties	Observed values ± **0.05**
Tensile Strength	30.18 MPa
Young's Modulus	1437.7 MPa
Stress at 200% elongation	1.38 MPa

Table 3.9: Tensile properties of "EAT-3"

3.6 COMPARATIVE ANALYSIS OF THE PROPERTIES

Now a comparative overview of the properties of the composites would be given. The study of the properties of the composites could be generalized in two ways. The properties of the composites within the same series and the comparison of properties between different series.

The properties of composite within the same series did not show any linear trend. Both the thermal and mechanical properties showed irregular behaviour. This was due to the reason that epoxy-amine matrix itself was a comparatively thermally stable system. Although it was relatively rigid system yet it exhibited good mechanical properties. It was generally difficult to obtain a linear trend in the properties of composites of an already stable matrix system, so any trend could not be generalized.

The properties of the composites among different series could be generalized on the basis of the properties of the filler particles. The state of dispersion and distribution of filler particles and the type of interaction between matrix and filler was shown by the SEM images of the composite series. The SEM images of EAT-1 indicated agglomeration and poor interaction between matrix and the filler. There was poor interaction between matrix and filler in EAT-2. The composites containing the functionalized particles, however, showed better adhesion between matrix and filler.

The composites containing the functionalized titania performed the best in the mechanical analysis. This was attributed to the stronger interaction between the matrix and the filler. Although the degradation temperature was lowered due to the decrease in the inorganic content of the filler, the Tg was increased. The mechanical properties were improved because the polymer bound layer increased strength and the aliphatic coupling agent lent flexibility. Due to increased strength the mechanical properties were improved.

The composite system containing calcined titania performed the poorest in the mechanical analysis. This was due to the reason that calcined titania made the system more rigid and increased the brittleness due to agglomeration. However, the onset of degradation for this system was shifted to higher temperature because the ceramic content increased, hence improving the thermal stability. The mechanical properties of composite containing the microtitania were better than the neat epoxy-amine system but thermal properties were lower. It was attributed to the fact that the addition of filler improves the mechanical properties due to plasticization but deteriorates the thermal properties.

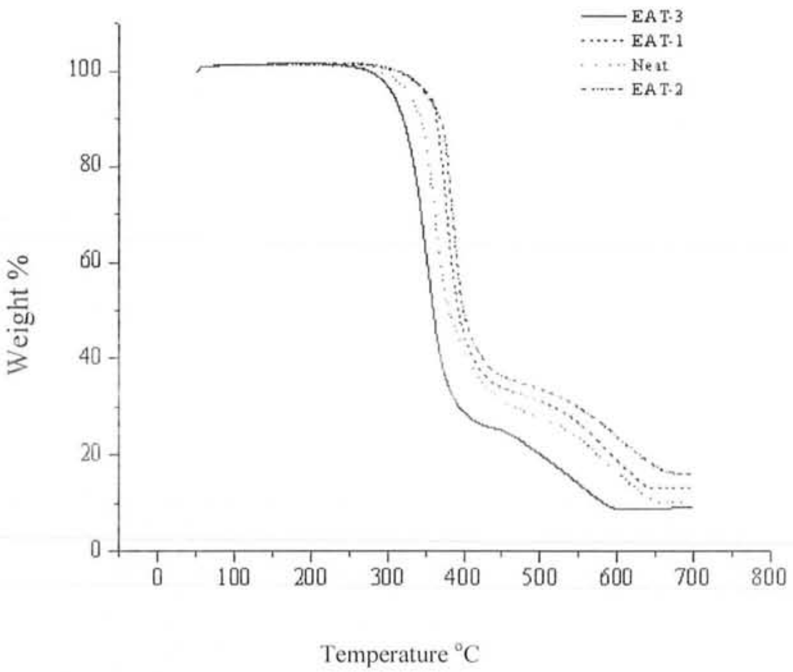


Fig 3.22: Comparative TGA thermograms of composite series and neat matrix.

Figure 3.22 shows the comparative TGA analysis of composite series and neat epoxy-amine matrix. The performance of "EAT-2" composite was the best in TGA. The performance of "EAT-1" and "EAT-3" was even lower than the matrix because of the plasticizer effect of filler.

The char yield was highest for the epoxy-amine-calcined titania composites, which indicated the thermal stability imparted to the composite system by the incorporation of the calcined titania. The char yield was lowest for the epoxy-amine-functionalized titania composite supporting the fact that the coupling agent had some organic content in it. The organic content decreased the thermal stability, despite the fact that it increased Tg. The char yield for EAT-1 lies in between that for EAT-2 and EAT-3 showing moderate thermal stability of the system.

PROPERTIES	NEAT	EAT-1	EAT-2	EAT-3
Tensile strength(MPa)	11.67	23.98	9.61	30.18
Young's Modulus(MPa)	1128.45	1321.86	562.25	1437.7

Table 3.10: Comparative tensile data for composites and matrix.

The mechanical properties increased in the opposite order. The performance was observed in the order EAT-3 > EAT-1 > Neat > EAT-2 owing to the varying effects of filler.

3.7 CONCLUSION

The recent work has provided much insight as to know about the effect of addition of titania as reinforcing phase on various properties of epoxy-amine network. Titania was generated outside the matrix via inorganic sol-gel route. Different procedures were tried and different types of particles were synthesized varying in size and surface morphology. At the end this work can be summarized by a few basic yet important conclusions.

1. In general addition of the titania reinforcement improved the properties of the composites.
2. Better adhesion between reinforcement and filler was achieved by functionalizing the surface of the particles.
3. Addition of binding agent promotes miscibility. In absence of coupling agent phase separation was observed at 10 wt%, while in the presence of the coupling agent phase separation appeared at 12.5 wt%.

5 The smaller size of the reinforcement provided an increased surface area for interaction with the matrix, but use of coupling agent was more useful to achieve binding between matrix and filler.

6 The system that performed best mechanically was the epoxy-amine-functionalized titania system. The increase in the mechanical properties was attributed to the increased interaction between the matrix and the filler. The epoxy-amine-calcined titania composite system performed the best in thermal analysis owing to the highest content of ceramic.

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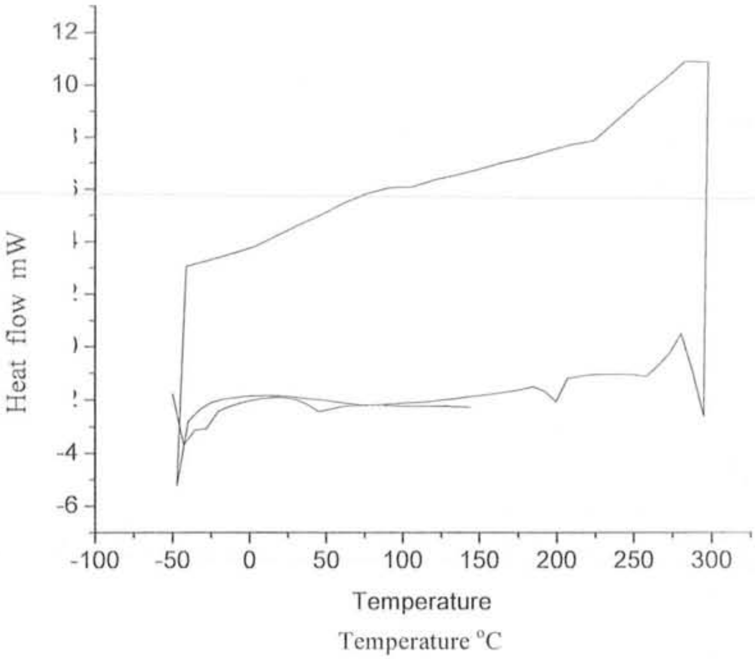
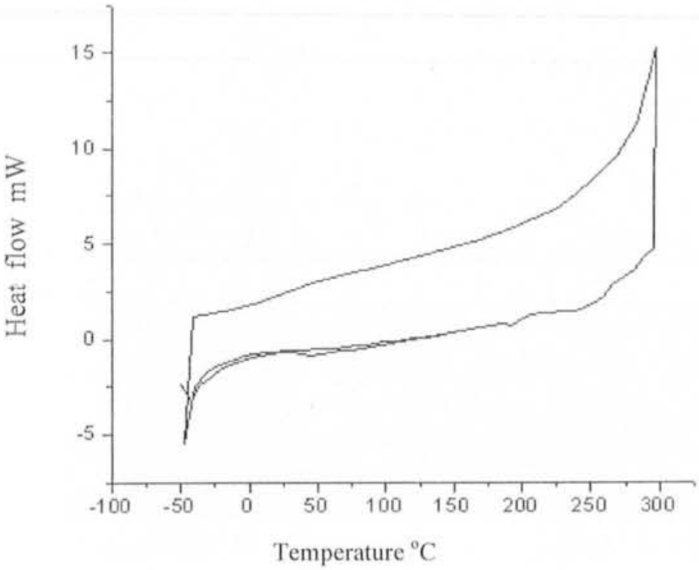


DSC for EAT-2 (5 wt. %)



DSC for EAT-2 (10 wt. %)

2. STRESS-STRAIN CURVES FOR EAT-3


Load-Position
N
200
180
160
140
120
100
80
60
40
20
0
0
0.3
0.6
0.9
1.2
1.500000
1.800000
2.100000
2.400000
2.700000
mm