

Chapter 1

Introduction

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1. Composites

A composite material is a macroscopic combination of two or more constituent phases, with recognisable interphase between them and with significant characteristics than that of their individual components or phases. The constituent phases in a composite are matrix (continuous phase) and dispersed phase (discontinuous phase). The discontinuous phase enhances the matrix properties and it is stronger and stiffer than the continuous phase. The main function of the continuous phase is to protect the components from the environment, temperature, chemical resistance and transfer load to other phases. Metal and polymer matrices increase yield strength, tensile strength and creep resistance whereas ceramic matrix increases fracture toughness. The properties of composites are a function of the properties of the constituent phases, their relative amounts and the geometry of the dispersed phase¹.

1.1 Types of composite materials

There are four basic types of composite materials - fiber, structural, layered and filled composites.

1.1.1 Fiber reinforced composites

These types of composites are obtained by incorporating fibers into a polymer matrix where the former act as a dispersed phase. The fiber not only enhances the strength and stiffness but also provides fatigue resistance, tensile strength, specific modulus etc. The polymer matrix protects the incorporated fibers by binding them together and transferring the applied load to the fibers thereby increasing the mechanical properties of the fiber reinforced composites. In this type of composite, the fibers reinforce along the line of their length. Reinforcement may be 1-D, 2-D or 3-D.

1.1.2 Structural composites

The properties of structural composites depend on the geometrical design and the properties of their constituent material. Common structural composite types are (a) Sandwich panels and (b) Laminar composites

(a) Sandwich panels: Sandwich panels consist of two or more faces or sheets made up of steel, aluminium alloys, FRPs etc. which are separated and bonded to a core, the latter may be a honeycomb structure that resists stress and provide shear rigidity. These find applications in aircraft and aerospace industry.

(b) Laminar composites: These are composed of layers of materials held together by a matrix. It refers to any flat arrangement of unidirectional fibers in a matrix. These layers have preferred directions to give higher strength to the composites

1.1.3 Layered composites

The sandwich panel is a kind of layered composite consisting of faces and core. A core is a layer of dense material. Strong outer sheets form faces. The stiffness of the composite increases with increase in the thickness of the core.

1.1.4 Filled composites

They result from the addition of filler materials (especially particles) to the matrix. Filler when added to a composite reduces weight and also enhances strength.

1.2 Types of composite matrix materials

1.2.1 Metal matrix composites (MMC)

They are composite materials with at least two constituent phases - a metal and a different metal or another material. The metal matrix is reinforced with the other metal or material to improve strength and wear.

1.2.2 Ceramic matrix composites (CMC)

They consist of ceramic fillers embedded in a ceramic matrix leading to the formation of a ceramic fiber reinforced material. The matrix and the fibers are ceramic materials with low fracture toughness, brittleness and limited thermal shock resistance. Major applications of CMC are in jet and automobile engines, deep-sea mining etc.

1.2.3 Polymer matrix composites (PMC)

Polymer matrix composite consists of a matrix made from a polymeric material. They are divided into three subgroups, namely thermoplastic, elastomer and thermoset. A thermoplastic polymer will soften when heated above T_g and thus can be moulded into a particular shape on cooling. This process is repeatable and so they are reprocessible and recyclable. Thermosetting materials become permanently hard through crosslinking when heated above T_g . Thus thermosetting polymers cannot be moulded by softening. They are not reprocessible and recyclable. Instead, they must be fabricated during the crosslinking process. Elastomer or rubber like resins are lightly crosslinked polymer systems and have properties in between thermosets and thermoplastics. Thermosets are the most popular polymer matrix composite (PMCs) used as aerospace components, high voltage insulation, defence systems etc².

1.3. Nanocomposites

A polymer alone cannot provide all the superior properties like strength, flame retardancy, thermal stability etc. These superior properties are enhanced by the addition of fillers, metals, fibers etc. The effect of fillers on the properties of the composites depends upon their size, weight percentage, shape and their interaction with the polymer matrix^{3,4}.

Depending on the size of the fillers, composites can be classified into micro composites and nanocomposites. If the size of the filler particle is greater than 100 nm, they constitute micro composites and if the size is less than 100nm, it becomes nanocomposite. Depending on the nature of nanofiller, nanocomposites are further classified as follows:

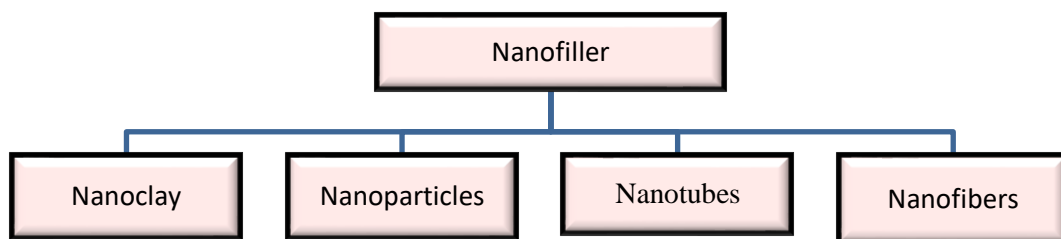


Figure 1.1 Different types of nanofillers.

1.3.1 Nanocomposites with nanoparticles

The development of nanoparticles leads to rapid advances in the field of nanotechnology. To enhance the material properties like mechanical, electrical and thermal properties, significantly less amount of the nanoparticles are used as fillers in nanocomposites⁵⁻⁹.

1.3.2 Nanocomposites with nanotubes

Carbon nanotubes (CNT), the most promising nanofiller, stimulated the development of nanotube reinforced composites in structural and functional applications for both thermoset and thermoplastic polymers. Commonly used nanotubes are CNT, SWCNT (Singlewalled carbon nanotubes), MWCNT (Multiwalled carbon nanotubes) etc¹⁰⁻¹².

1.3.3 Nanocomposite with fibers

The difficulties with the alignment, assembly and processing of nanotubes are overcome by the development of advanced continuous fibers with nanoscale diameter. Electrospinning technology can be used to produce nanocomposite fibrils with various diameters as the conventional mechanical fiber spinning method cannot produce fibers with diameters less than 2 micrometres. Among the methods such as self-

assembly, mechanical fiber spinning, phase separation etc., electrospinning is the efficient, fast, inexpensive and widely used method for producing polymer nanofibers¹³⁻¹⁶.

Exceptional properties of fiber reinforced composites like stiffness, high tensile and flexural strength, resistance to corrosion, high impact strength, fracture toughness etc., made these materials the most promising candidate in various fields of applications.

Suitable fiber with the desired orientation acts as a reinforcing agent and gives protection to the polymer matrix from environmental damages.

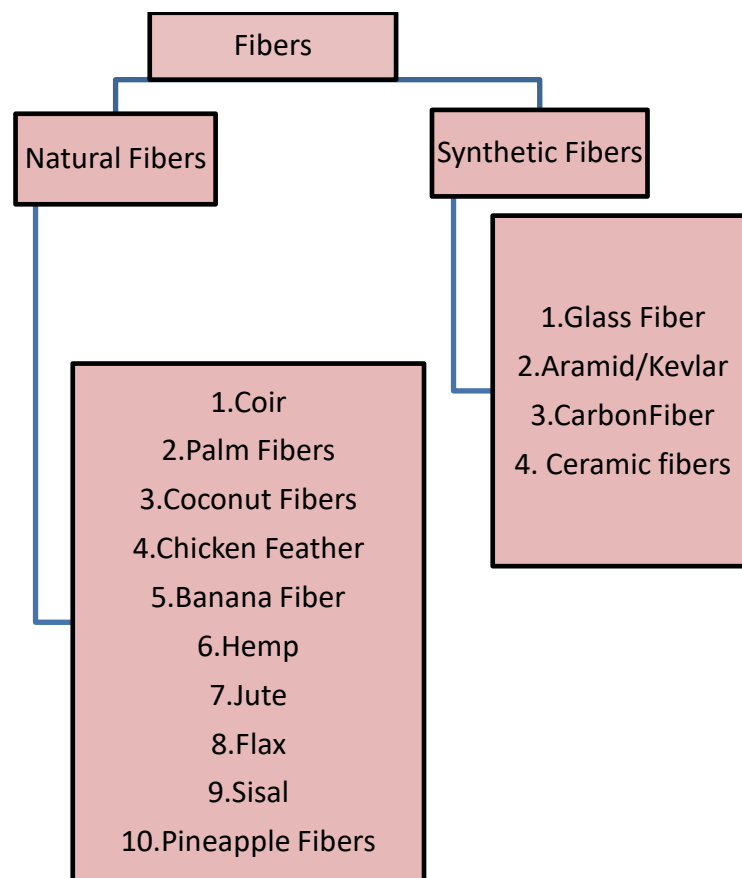


Figure 1.2 Different types of fibers.

The properties that make the glass fiber a high performance, most popular and predominant reinforcement material are (a) high versatility, (b) more flexibility, (c) lightweight, (d) greater specific resistance, (e) sufficient strength, (f) good electrical insulation property (g) less sensitive to variation in temperature (h) incombustibility (i) good compatibility and durability (j) good adhesion property to the polymer matrix (k) good heat resistance and (l) low cost¹⁷.

Based on the composition, glass fibers are classified into different types.

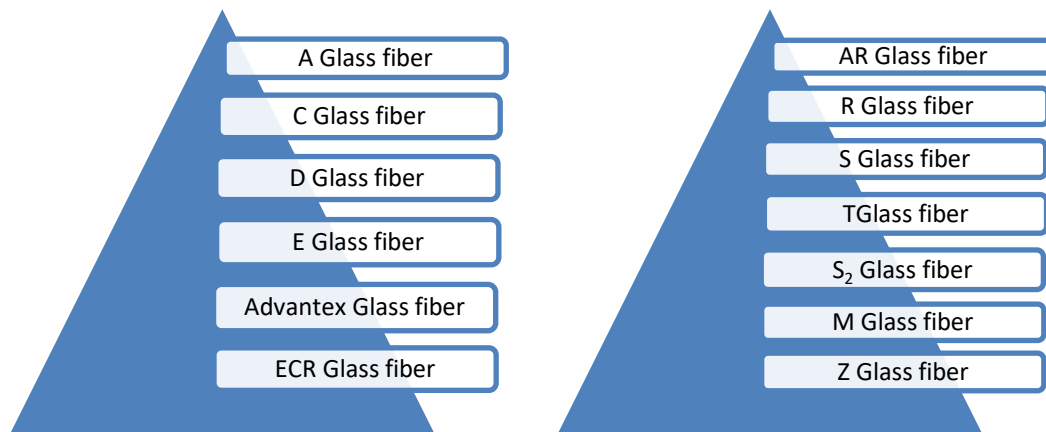


Figure 1.3 Different types of Glass fibers.

Even though different forms of fiberglass are available such as tow and roving form, veil mat form, chopped strand form and woven fabrics, woven fabrics are comparatively stronger reinforcement materials because of their dimensional stability. Among the glass reinforcements, the widely used one is the early developed E glass fiber owing to its low cost and comparable properties.

1.4. Polymer nanocomposites

Polymer nanocomposites consist of a polymer matrix and a dispersed phase of particles or fillers in nano dimensions. Polymer nanocomposites exhibit enhanced mechanical, electrical and thermal properties even at lower nanofiller concentrations.

1.4.1 Thermoplastic nanocomposites

Thermoplastic polymers are of great interest among polymer nanocomposites for scientific research and industrial applications due to their improved thermal and mechanical properties compared to other traditional composites^{18–22}. Polymers such as polyamides, polyolefins, polyesters and polystyrene are used in sensing devices because of their good mechanical properties. Many industrial components such as bearings, seals, gears etc., are produced from thermoplastic matrix composites by injection moulding^{23,24}.

1.4.2 Elastomer nanocomposites

Due to exceptional elongation, ease of deformation at temperatures, flexibility, viscoelastic behaviour, heat resistance, low modulus of elasticity, elastomers can be effectively used as polymer matrices. The processing techniques of elastomer nanocomposites are different from other composites as they need a vulcanisation process. By incorporating different fillers like silica nanoparticles, CNT, layered

silicates etc., the structural and geometrical characteristics of the elastomer get altered and hence can be applied in various industrial, automotive, packaging fields²⁵.

1.4.3 Thermoset nanocomposites

Thermoset nanocomposites are commonly based on glass, carbon or aramid fibers usually incorporated with resins such as epoxies, phenolics, polyesters, vinyl esters, cyanate esters, polyimides etc²⁶. The process by which raw material is converted into a hard, insoluble and infusible one is referred to as curing process. Such materials are irreversibly crosslinked and so their strength is higher than thermoplastics. During the curing process, crosslinking produces a strong three dimensional network structure which eliminates the risk of the product remelting when heat is applied. This makes the thermoset nanocomposites ideal for high heat applications in electronics and electrical appliances. These types of composites are very strong and have very good fatigue strength. They are extremely brittle and have low impact toughness.

1.5. Different types of thermosetting polymers

1.5.1 Epoxy resin

Epoxy resin is one of the most important and widely used matrices of thermoset polymer composites due to their strength, high modulus, excellent chemical and solvent resistance, simplicity in processing²⁷ and good adhesion to substrate make them suitable for applications in aerospace, electronic industries, protective coatings and also used for the fabrication of advanced composites. The limited use of epoxy resins in high performance applications is due to its brittle nature, impact strength, poor weathering resistance and inferior moisture.

1.5.2. Polyimides

Polyimides (PI) are high performance polymers of imide monomers that contain two acyl groups bonded to nitrogen. Polyimides can be synthesised by the reaction between a dianhydride and a diamine²⁸. In addition to high thermal stability, polyimides exhibit excellent mechanical and dielectric properties, high chemical resistance, superior temperature adaptability, increased abrasion resistance, radiation resistance²⁹ and low coefficient of thermal expansion. Certain limitations associated with these polymers are high manufacturing cost, high temperature requirement in processing, specified operating processes at specified temperatures³⁰ and sensitive to alkali and acid attacks.

Due to its electrical insulating properties, thermal stability and excellent mechanical and dielectric properties PI's are widely employed in aerospace and automotive

industry. PI's also find applications in electronics-chip trays, hard disk drive components, wire insulators and printer components³¹. Due to their chemical inertness, high compatibility, mechanical and thermal stability, polyimide based sensor materials have received much attention. Thermoset polyimide tubing and coated wire is a highly versatile product with a wide range of uses in high performance medical devices³². PI films are ideal for insulating circuit boards, transformer manufacturing, high temperature powder coating. PI films are used as a dielectric material in solar cells.

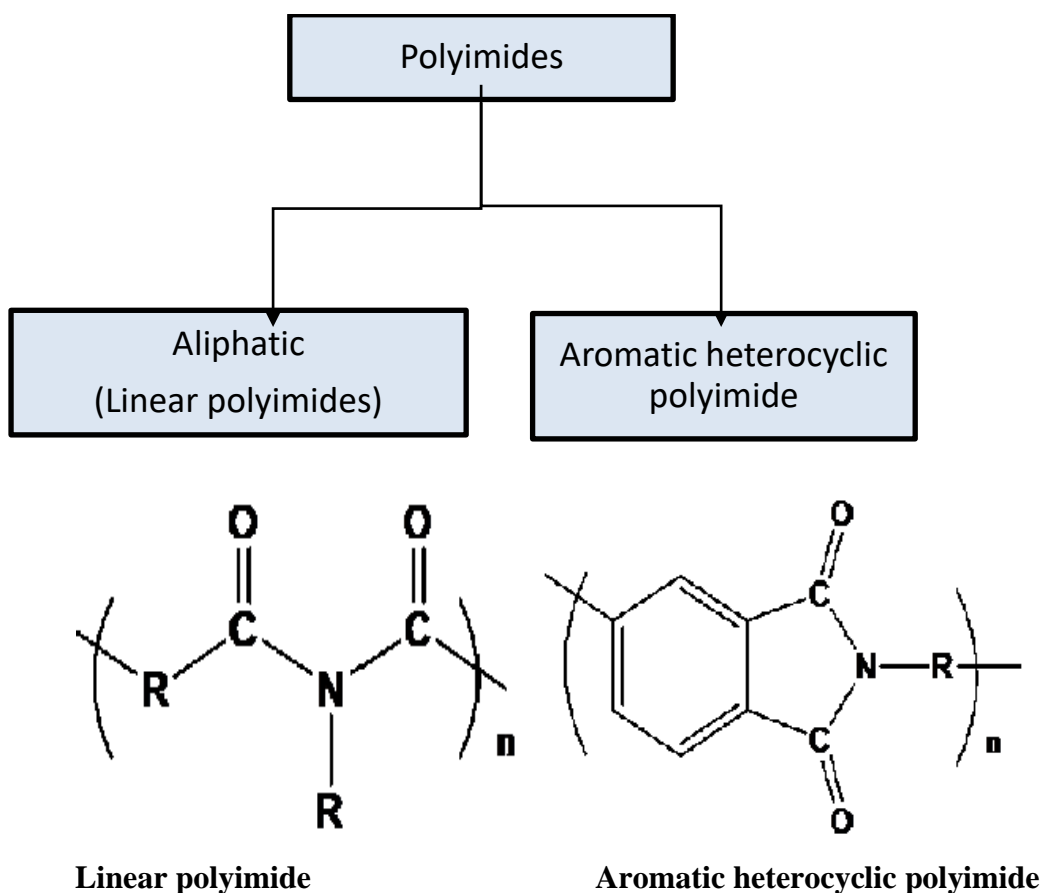


Figure 1.4 Classifications of Polyimide.

The high performance applications of PI's in electronics, aerospace and automotive industries due to their remarkable thermal and mechanical properties come from strong intermolecular forces between the polymer chains and from the stiffness of the aromatic segments.

1.6 Bismaleimide and epoxy resin blends

Bismaleimide resins (BMI), being one of the widely accepted thermosetting high performance polyimide for advanced composites in aerospace and electronics industry, possess excellent oxidative stability, rigidity, thermo-mechanical properties,

low moisture absorption, high glass transition temperature, highest service temperature capability, retention of physical properties at elevated temperatures as well as in wet conditions.

The low molecular weight BMI monomer with maleimide end groups can form a highly crosslinked network through homopolymerisation or co-polymerisation reactions by applying heat. As a result of high crosslinking density, BMI resins are brittle in nature. The high crosslinking density is responsible for the high temperature performance of the resin³³.

In order to overcome the brittleness, many resins such as epoxies, aromatic amines, polysiloxanes^{34,35}, cyanate esters³⁶ etc., were blended with BMI. Many allylic derivatives of phenols have also been used to blend with BMI, resulting in a considerable reduction in brittleness and the retention of high heat resistance³⁷.

Epoxy resins are the most important and versatile class of thermosetting resins with properties like easy processability, toughness³⁸, handling convenience, excellent mechanical properties³⁹⁻⁴², chemical and solvent resistance and good adhesion to substrate²⁷ make them suitable for applications in aerospace, electronic industries, protective coatings and fabrication of advanced composites.

The limited use of epoxy resins in high performance applications is due to its poor weathering resistance and inferior moisture absorption. The higher the number of epoxide groups, the more functional is the epoxy resin. Various types of epoxies can be derived with respect to the number of epoxide groups. Diglycidylethers of bisphenol-A (DGEBA) and bisphenol-F (DGEBF) are the most commonly used due to their high mechanical strength, heat and corrosion resistance. Curing of this type of epoxide functional resins depends on the selection of hardner as well as temperature. The curing process occurs by the reaction between a di-epoxide and a primary diamine or an anhydride referred to as hardner. Further crosslinking can take place by the reaction of the resulting hydroxyl groups that are generated by the opening of the epoxy ring. The epoxy prepolymers or hardners with highly reactive functionalities leads to the highly crosslinked, stiff and tough epoxy network suitable for aerospace applications. It is used in military and commercial applications. Epoxy-reinforced concrete, glass fiber reinforced and carbon fiber reinforced epoxy composites are used in building and bridge structures. Epoxy composites have high strength, density,

tensile, compressive, flexural and impact strength. They are used in printed circuit board laminating, electrical encapsulation, adhesive and coatings for metal to protect from corrosion, erosion or chemical attack at high continuous operating temperatures.

Carbon fiber reinforced epoxy systems are widely used in the aircraft and aerospace industries but the brittleness, moisture absorption, limited impact strength and weathering resistance nature of epoxy limits the performance of these systems⁴³. Different approaches have been reported by researchers and attempts have been made to toughen epoxy resins by the addition of rubber⁴⁴⁻⁴⁷ as well as thermoplastics⁴⁸⁻⁵² but the addition of these polymers results in reduction in T_g and retention capability of hot-wet property. In order to balance between the thermal and mechanical properties and to overcome the deterioration in properties, researchers developed thermoset-thermoset blend⁵³ with intercrosslinked and interpenetrated networks which exhibit synergistic effects resulting in improvements in properties compared to the individual resins⁵⁴.

Epoxy resins are limited by their low glass transition temperatures so that they can only be used safely at around 140°C⁵⁵. Due to poor hot/wet performance and high moisture sensitivity, they are not used for applications in high temperature conditions. In most engineering applications, especially in aerospace industries, temperature and pressure are greater than 177°C and 100psi respectively stands as a major disadvantage of using epoxy composites. BMI can withstand high temperatures but they possess poor processability compared to epoxies. Blending the two resins- BMI and epoxy will lead to a matrix with beneficial characteristics of the two components.

The most important class of epoxy resins are diglycidyl ether of bisphenol A (DGEBA) and its homologues⁵⁶⁻⁶⁰. Compared to high temperature epoxies, copolymers of BMI and 2,2'-diallyl bisphenol (DABA) developed by Ciba-Geigy Company demonstrated greater toughness and heat resistance. Due to better elevated temperature performance than bisphenol A (BPA)⁶¹ based resins, glycidyl ethers of novolac resins^{54,62} come under the second most important class. Blend resin of 2,2'-diallyl bisphenol A (DABA) with BMI has been investigated in detail by many researchers^{34,57,63-65}.

Based on lots of previous investigations, blending epoxy resin to BMI has proved to be a common and effective method to endow polymer matrix with excellent and

desired physical properties. In this research work, the BMI-epoxy resin system has been chosen as the polymer matrix to balance the advantages and disadvantages of both epoxy and BMI resins. A thorough analysis of the studies based on the research of BMI-epoxy composites reveals a lot of modified properties of the BMI-epoxy intercrossed matrix. A few advantages are given below

- 1) Thermal degradation temperature of the bismaleimide modified epoxy system is increased with increasing BMI concentration which may be ascribed to the formation of interpenetrating network between BMI and epoxy resin^{66,67}.
- 2) An increase in glass transition temperature may be due to the polymer chain interlocking effect of BMI network with the epoxy networks and effective compatibility⁶⁸.
- 3) Increase in heat distortion temperature due to high crosslinking density and rigidity imparted by bismaleimides⁶⁹.
- 4) Good resistance to moisture absorption due to the presence of rigid aromatic hydrophobic structure of BMI⁷⁰.
- 5) Enhanced tensile strength, flexural strength and decrease in fracture toughness due to the formation of intercrosslinking network between BMI and epoxy resin^{60,71}.
- 6) SEM micrograph of the fracture surface of BMI-epoxy matrices indicated no separate phase domains and suggested the formation of homogeneous morphology of the intercross linked network within the system⁶⁹.

BMI and epoxy resin have a low dielectric constant, limiting their applications as embedded capacitor devices, printed electronic devices like printed circuit boards (PCB) and printer wiring boards (PWB), advanced dielectric capacitors, pulsed power capacitors, sensors and high energy storage devices.

Different methods have been proposed in the past decades to increase the dielectric constant (k) of polymer matrices. One methodology to develop high k polymer composites is the use of ferroelectric polymers like polyvinylidene fluoride (PVDF), polyvinylidene fluoride-trifluoroethylene (PVDF-TrFE) with a fairly high dielectric constant compared to the earlier mentioned polymers⁷². With the increase of temperature, these ferroelectric polymer based composites show an increase in dielectric constant with poor temperature stability. They also showed a large loss

tangent, i.e., a large amount of heat is dissipated that can affect the performance of the composites. The most widely used dielectric polymers are polystyrene (PS), polypropene (PP), polyethylene (PE), epoxy resin and polyimide (PI).

Attention has been turned to the possibility of incorporating nanofillers with high dielectric constant into the BMI-epoxy matrix to enhance the physical properties like thermo-mechanical and dielectric properties of the composites. Several papers have been published devoted to the study of the effect of nanofiller in BMI-epoxy matrices.

We adopted the most frequently employed method to prepare polymer composites with high dielectric properties by loading fillers with high dielectric constant. Among the dielectric ceramic particles like BaTiO₃ (BT), barium strontium titanate (BST), boron nitride (BN), lead zirconate titanate (PZT), BT has wide spread applications due to its high dielectric constant and high piezoelectric coefficient. Moreover, being a non-lead material, BT is virtually free from the environmental pollution and adverse effects as in the case of PZT^{73,74}.

1.7 Barium titanate (BT)

Barium titanate (BT) is the most common and well known ferroelectric perovskite oxide (figure 1.4) in fields such as energy storage devices like multilayer ceramic capacitors (MLCC)⁷⁵, gate dielectrics⁷⁶, piezoelectric nanogenerators⁷⁷⁻⁷⁹, positive temperature coefficient resistors⁸⁰, dynamic random access memory (DRAM)⁸¹, frequency modulation in communication devices^{82,83}. As a well suited material for thin film electroluminescent (EL) devices (TFED), BT became a part of a more energy efficient and sustainable electroluminescent emerging technology.

As the temperature increases, the ferroelectric ceramic material BT shows a phase transition from cubic to tetragonal to orthorhombic and finally to a rhombohedral structure. All other crystal structures except the cubic phase exhibit ferroelectric behaviour whereas the latter exhibits paraelectric behaviour.

BT is the first discovered ferroelectric oxide with a perovskite structure. Goldschmidt et al., in 1920's have done the first structural study on the perovskite BT. The ideal perovskite structure possesses atomic parameters such as divalent cation (0,0,0), tetravalent cation (1/2,1/2,1/2) and oxygen atoms (0,1/2,1/2), (1/2,0,1/2) and (1/2,1/2,0) and has a simple cubic lattice with one formula weight per cell. At 20°C

BT exists in a tetragonal phase with one formula weight per cell exhibiting the identical atomic parameters as that of the cubic phase. Transformation of cubic phase to tetragonal phase can be easily attained by simply stretching the c axis and this usually occurs at high temperatures⁸⁴. Naray-Szabo confirmed from X-ray diffractograms of BT that it exhibits a slight distortion from cubic structure still it comes under cubic symmetry⁸⁵. BT has a low Curie temperature, T_c , at 120-135°C⁷⁴. The phase transition of BT depends mainly on temperature. The phase transition temperatures of cubic, tetragonal, orthorhombic and rhombohedral structures are 130, 5 and -90°C respectively.

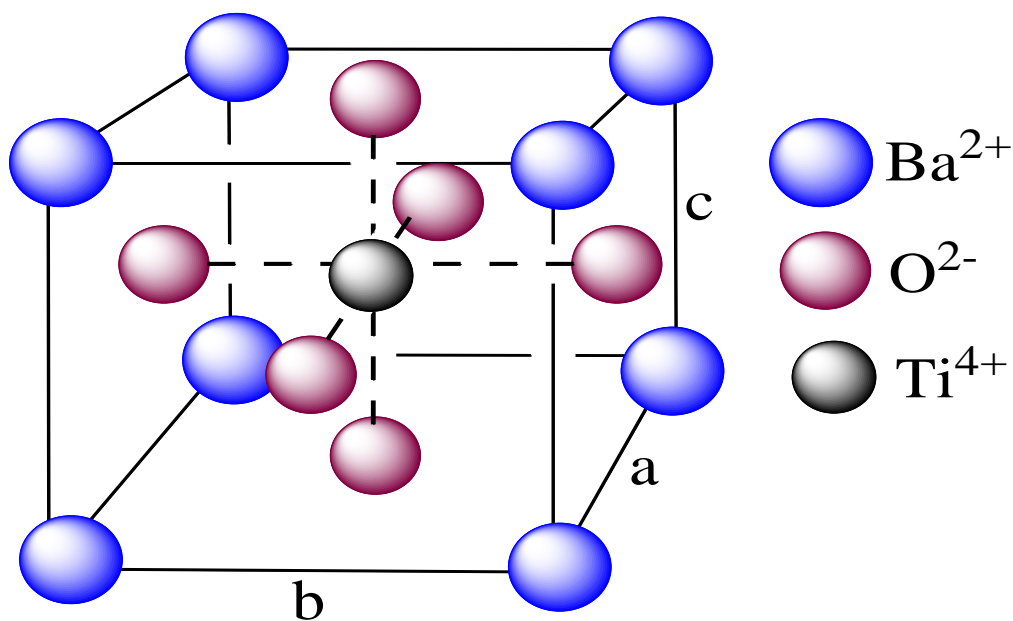


Figure 1.5 Perovskite structure of $BaTiO_3$ (BT).

Different crystal structures of BT was studied by Xiao et al⁸⁶ and found that the tetragonal phase is stable at room temperature. In tetragonal structure, BT exhibits its excellent ferroelectric and piezoelectric properties^{87,88} and strong dielectric properties^{75,89} in its perovskite phase and so we can improve the dielectric properties of the composites by incorporating the perovskite BT during their fabrication. In order to obtain flexibility and durability, BT ceramics in the form of nanoparticles has been blended with BMI-epoxy matrix.

The structure and desired properties of BT for different applications will mainly depend upon the synthesis methods adopted⁹⁰. Dielectric constant values of BT

nanoparticles depend on particle size and purity, which in turn depends on the different synthesis routes.

Different processing techniques can be employed to synthesise BT nanoparticles like sol-gel⁹¹⁻⁹³, ball milling⁹⁴⁻⁹⁶, solvothermal^{97,98}, microwave heating⁹⁹⁻¹⁰³, polymer precursor method^{104,105}, hydrothermal¹⁰⁶⁻¹¹⁰, micro-emulsion¹¹¹, solid state reaction methods¹¹²⁻¹¹⁴, precipitation methods¹¹⁵⁻¹¹⁷, solution phase processes^{118,119}, low temperature direct synthesis method¹²⁰ etc. Both the advantages and disadvantages of each method were reported by Emre¹²¹.

A mixture of BaCO₃ and TiO₂ calcined at temperatures in the range of 1000-1200°C^{122,123} and thermal decomposition of barium-titanyl oxalate carried out at 800-1100 °C are the common conventional processing techniques for the synthesis of BT powder. The product obtained from these solid state reactions is further subjected to milling to achieve particle sizes < 1µm. This method may result in particles with a wide size distribution, irregular morphology, high degree of aggregation, large size leading to powders with high impurity and poor characteristics¹⁰⁹.

In solution-based synthesis such as precipitation or co-precipitation and sol-gel methods, the product obtained should also undergo calcination and milling to control the size similar to that in solid state reaction methods, which resulted in much lower improvements in powder quality¹²⁴⁻¹²⁶. In sol-gel processing techniques, gels are prepared by the hydrolysis of alkoxide. The major difficulty in this process is to avoid precipitation of solid particles by controlling the hydrolysis kinetics.⁹²

In precipitation methods, the size of the particles that are precipitated from solution depends on the rates of crystalline growth and nuclei formation which in turn depends on concentration, mixing conditions and temperature. Synthesis of particles in nano dimensions will result only from proper control of the above parameters.

The major advantage of the micro-emulsion method is the confinement of particles on a nanometer scale with disadvantages like high cost of production, poor yield of products¹¹¹ etc.

BT nanoparticles, in this work, have been synthesised by hydrothermal method. The hydrothermal process was carried out in a teflon lined steel autoclave under elevated pressure and temperature, ensuring better control over the size and distribution of the

products obtained¹²⁷. The high temperature and pressure inside the autoclave provide a better environment for enhanced chemical reactivity owing to which preparation of various compounds/materials that otherwise remain difficult turns out to be much easier. The high temperature and pressure inside the autoclave also facilitate better solubility of poorly soluble substances¹²⁸. The hydrothermal method allows isolation of metastable state, intermediate state, specific phase and specific condensed state products during synthesis. Appreciable control over size, shape and crystallinity of products could be tuned by adjusting the nature and type of solvent, surfactant, precursor, reaction time and temperature¹²⁹.

1.8 Surface hydroxylated Barium titanate nanoparticles (BTOH)

In order to avoid aggregation and to improve the dispersion capabilities of BT nanoparticles, the surface of the BT nanoparticles can be modified either by surfactant adsorptions, polymer coatings or chemical modification. There are several ways for surface modification of BT nanoparticles such as hydroxylation by H₂O₂^{48,106–110}, silanisation using different silane coupling agents^{134–136}, dopamine modification¹³⁷, 2,3,4,5-tetra fluorobenzoic acid (F4CBT)¹³⁸, fluorinated phosphonic acid modification¹³⁹, modification with a non-ionic and hydrophilic surface agent like polyethylene glycol (PEG)¹⁴⁰, surface aminated BT nanoparticles (BT-NH₂)¹⁴¹ and by further chemical modification of the hydroxylated BT nanoparticles, using titanate coupling agents¹⁴², modification by ligand exchange reactions¹⁴³, by palmitic acid¹⁴⁴, by sodium oleate (SOA)^{145,146} etc.

The nanocomposites embedded with these surface hydroxylated and chemically modified nanofillers and nanofibers exhibit significant enhancement in the dielectric properties which may be ascribed to the improved interfacial interaction between the filler and the matrix, thereby increasing the uniform dispersion of nanoparticles with a reduction in agglomeration. These nanocomposites also exhibit high dielectric constant, breakdown strength, low dielectric loss and good compatibility.

Among the various chemical modification processes, silanisation using silane coupling agents is the most accepted method because further activation of the particle surface can be done by introducing different functional groups into it. The silane coupling agents are usually added to surface hydroxylated BT nanoparticles (BT-OH) because they are more prone to silanisation than BT because of the polarity of the

former. Current research reveals that silanisation of nanoparticles strongly depends on the reaction kinetics such as reaction time, temperature, different silane coupling agents and solvent effects.

In this work, surface modification of BT was carried out by hydroxylation using H_2O_2 . It is the simplest and easiest method of surface modification compared to silanisation. The interfacial dipole layer that emerged from the surface hydroxylated BT particles play an essential role in the dielectric properties of the fabricated BMI-epoxy composites.

As BT lacks reactive functional groups, modification using organic reagents only leads to physisorption on the particles either by van der Waal's forces or by the electrostatic force of attraction. The synthesised BT nanoparticles contain a low concentration of hydroxyl groups on the surface but this will not significantly improve the surface activity. For effective modification of BT, more hydroxyl groups are to be associated on the surface of BT nanoparticles that can be achieved by treating BT with H_2O_2 .

1.9 Rochelle salt crystals

In order to attain large tunability of dielectric constant, attempts were made to incorporate readily available, more common, less expensive and ecofriendly material sodium potassium tartarate tetrahydrate commonly called seignette or Rochelle salt (RS).

RS, used in gramophone pickups and microphones, was the first piezoelectric material discovered. RS is highly soluble in water and deliquescent. So in damp conditions, transducers made of this material may deteriorate. Being the only known, long time old ferroelectric, it finds several applications as a laxative, in organic synthesis, in silvering of mirrors, ingredient of Fehling's solution, ingredient of Biuret reagent etc.

The optically active RS shows abnormally high values of dielectric constant parallel to the axis between $-10^{\circ}C$ and $+25^{\circ}C$. RS has poor mechanical strength, low disintegration temperature and absorbs water. The decomposition temperature of RS is about $55^{\circ}C$ and it has two Curie points $+24^{\circ}C$ and $-18^{\circ}C$. Hydrogen bond plays a vital role in the ferroelectric behaviour of RS.

In 1824, Sir David Brewster, using RS demonstrated the piezoelectric effect. Later in 1919, Alexander McLean Nicolson developed microphones like audio related devices and speakers using RS. In 1921, Valasek discovered ferroelectricity in RS from which he introduced the term Curie temperature. Valasek has shown that the piezoresponse of RS crystal increases to a maximum between -20°C and $+20^{\circ}\text{C}$ and a sharp drop to zero above and below this temperature. In DC fields, a rapid increase in the dielectric constant is also found between the same temperatures. From this, it is inferred that the piezoelectric and dielectric properties of RS crystals strongly depends on temperature¹⁴⁷.

The complete structure of sodium potassium tartrate tetrahydrate (RS) was investigated by C.A. Beevers and W. Hughes (1940)¹⁴⁸. It was revealed that one of the carboxyl groups of RS molecule exists as a dipole and the tartrate molecules are bonded directly to potassium and sodium atoms through water molecules (figure 1.5). The abnormal dielectric properties of the RS crystal may arise due to the reversal of the carboxyl-water-water dipole chains.

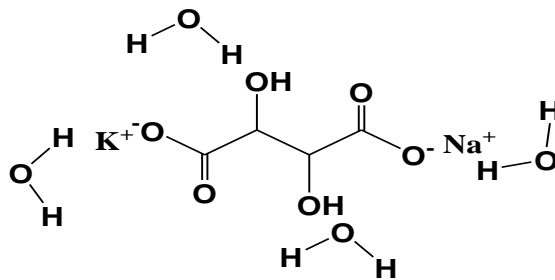


Figure 1.6 Structure of sodium potassium tartrate tetrahydrate (Rochelle salt).

In this work, the proportion of BMI and epoxy were always kept constant and the effect of various loadings of different nanofillers on mechanical, thermal and dielectric properties have been studied in detail.

1.10 Objectives of the present research

The specific objectives of the research work include

- To develop a new polymer nanocomposite as a substitute for ceramic insulators with enhanced electrical and mechanical properties for high dielectric applications.

- Synthesis of BaTiO₃ by hydrothermal method and surface hydroxylated BaTiO₃ by using H₂O₂ and their characterisation using SEM, EDAX and FTIR.
- Fabrication of nanocomposite with bismaleimide-epoxy as polymer matrix and BaTiO₃, Rochelle salt and surface hydroxylated BaTiO₃ as nanofillers for improving the dielectric properties.
- BMI-epoxy nanocomposite reinforced with E glass fiber (EGF) and silane-coated E glass fiber (SC-EGF) fabrication as per ASTM standards for different compositions of nanofillers.
- Morphological study of the synthesised reinforced and non-reinforced composite using SEM and structural study using XRD, EDAX and FTIR.
- Evaluation of the effect of different nanofillers and the reinforcement (EGF and SC-EGF) on thermal stability and mechanical properties such as tensile strength, flexural strength.
- Studies on dielectric constant, dielectric loss factor (tan delta) and dielectric breakdown strength of the synthesised composite.
- Analysis of dielectric behaviour, ac conductivity and electromagnetic interference shielding effectiveness (EMI-SE) of the fabricated BMI-epoxy nanocomposites with optimised weight percentages of the nanofiller.
- Effect of MWCNT on thermo-mechanical, electrical and EMI SE of BMI-epoxy composites with different nanofillers such as BT, RS and BTOH.
- To study the suitability of the synthesised BMI-epoxy nanocomposites in relevant fields.

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