CHAPTER 1

INTRODUCTION

1.1 GENERAL

Nanotechnology is one of the most promising areas for technological development in the 21st century. In materials research, the development of polymer nanocomposites is rapidly emerging as a multidisciplinary research activity whose results could broaden the applications of polymers greatly benefiting various industries. Polymer nanocomposites (PNC) are polymers (thermoplastics, thermosets or elastomers) which are reinforced with small quantities (less than 5% by weight) of nano-sized particles having high aspect ratios (L/h > 300) and thus enabling greater retention of the inherent processibility and toughness of the neat resin. PNC represent a radical alternative to conventional filled polymers or polymer blends a staple of the modern plastics industry. In contrast to conventional composites, where the reinforcement is on the order of microns, PNCs are exemplified by discrete constituents of the order of a few nanometers.

The widely used host materials for nanocomposite fabrication include carbonaceous materials like granular activated carbon, silica, cellulose, sands, polymers, and polymeric hosts which are particularly an attractive option partly because of their controllable pore space and surface chemistry as well as their excellent mechanical strength for long-term use. The resultant polymer-based nanocomposite (PNC) retains the inherent
properties of nanoparticles, while the polymer support materials provide higher stability, processibility and some interesting improvements caused by the nanoparticles–matrix interaction.

1.3 ADVANTAGES OF THE COMPOSITES

A composite is a heterogeneous material created by the synthetic assembly of two or more components, selected filler or reinforcing agent and a compatible matrix binder, in order to obtain specific characteristics and properties. The components of a composite do not dissolve or otherwise merge completely with each other, but nevertheless do act in concert. The components as well as the interface can be physically identified and it is the behaviour and the properties of the interface that generally control the properties of the composite. The properties of the composite cannot be achieved by any of the components acting alone.

1.3 MAJOR CLASSIFICATION OF COMPOSITES

Composite materials can be classified into three groups on the basis of matrix material. They are:

- Metal Matrix Composites (MMC)
- Ceramic Matrix Composites (CMC)
- Polymer Matrix Composites (PMC)

1.3.1 Metal Matrix Composites

Metal Matrix Composites have many advantages over monolithic metals like higher specific modulus, higher specific strength, better properties at elevated temperatures, and lower coefficient of thermal expansion. Because of these attributes metal matrix composites are under consideration for wide
range of applications viz. combustion chamber, nozzle (in rocket, space shuttle), housings, tubing, cables, heat exchangers, structural members etc.

1.3.2 Ceramic Matrix Composites

One of the main objectives in producing ceramic matrix composites is to increase the toughness. Naturally, it is hoped and indeed often found that there is a significant improvement in strength and stiffness of ceramic matrix composites.

1.3.3 Polymer Matrix Composites

Most commonly used matrix materials are polymeric. The reason for this are two fold. 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 other materials with polymers. Secondly, the processing of polymer matrix composites need not involve high pressure and doesn’t 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. Composites are used because overall properties of the composites are superior to those of the individual components. Composites have a greater modulus than the polymer component but are not as brittle as ceramics.

Types of polymer composites are:

1) Thermoplastic polymer
2) Thermosetting polymer
3) Elastomers
4) Fibre reinforced polymer
5) Particle reinforced polymer

1.3.3.1 Thermoplastic polymers

Thermoplastics consist of linear or branched chain molecules having strong intra molecular bonds but weak intermolecular bonds. They can be reshaped by the application of heat and pressure and are either semi crystalline or amorphous in structure. Examples include polyethylene, polypropylene, polystyrene, nylons, polycarbonate, polyacetals, polyamides, polyimides, polyethers ketone, polysulfone, polyphenylene sulfide, polyether imide, and so on.

1.3.3.2 Thermosetting polymers

Thermosets have cross-linked or network structures with covalent bonds with all molecules. They do not soften but decompose on heating. Once solidified by cross-linking process they cannot be reshaped. Common examples are epoxies, polyesters, phenolics, ureas, melamine, silicone, and polyimides.

1.3.3.3 Fibre Reinforced Polymer

Common fibre reinforced composites are composed of fibres and matrix. Fibres are the reinforcement and the main source of strength while matrix glues all the fibres together in shape and transfers stresses between the reinforcing fibres. The fibres carry the loads along their longitudinal directions. Sometimes, filler might be added to smooth the manufacturing process, impart special properties to the composites, and reduce the product
cost. Common fiber reinforcing agents include asbestos, carbon / graphite fibres, beryllium, beryllium carbide, beryllium oxide, molybdenum, aluminium oxide, glass fibres, polyamide, natural fibres etc. Similarly, common matrix materials include epoxy, phenolic, polyester, polyurethane, polyether ether ketone (PEEK), vinyl ester etc. Among these resin materials, PEEK is most widely used. Epoxy, which has higher adhesion and less shrinkage than PEEK, comes in second for its high cost.

1.3.3.4 Particle Reinforced Polymer

Particles used for reinforcing the polymer include ceramics, glasses such as small mineral particles, metal particles like aluminium and amorphous materials and carbon black. Particles are used to increase the modules of the polymer matrix, decrease the ductility of the matrix and to reduce the cost of the composites. Reinforcement by ceramics and glasses result in high melting temperature, low density, high strength, stiffness, wear resistance and corrosion resistance. The ceramics are good electrical and thermal insulators also. Some ceramics are magnetic materials, some are piezoelectric materials. A few special ceramics are even superconductors at very low temperatures.

1.4 NANOCOMPOSITES

Nanocomposites are a novel class of composite materials whose reinforcements have dimensions in the range of 1-100 nm. Although nanoscale reinforcements (nanofillers) of nanocomposites have different kinds of fillers such as nanofibres, nanowires, nanotubes and nanoparticles etc, their mechanical behaviors have some common features. The polymer layered silicate nanocomposites, the reinforcing phase, in the shape of
platelets, has only one dimension in nano level. A few weight percent of layered silicates that are properly dispersed throughout the polymer matrix thus, create much higher surface area for polymer/filler interaction as compared to conventional composites (Ray and Okamoto, 2003). Depending on the strength of interfacial interactions between the polymer matrix and layered silicate, can be classified into three types.

1.4.1 Intercalated Nanocomposites

In intercalated nanocomposites (Figure 1.1) (Slia et al 1998), the insertion of a polymer matrix into the layered silicate structure occurs in a crystallographically regular fashion, regardless of the clay to polymer ratio. Intercalated nanocomposites are normally interlayer by a few molecular layers of polymer. Properties of the composites typically resemble those of ceramic materials.

1.4.2 Flocculated Nanocomposites

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

1.4.3 Exfoliated Nanocomposites

In exfoliated nanocomposites, the individual clay layers are separated in a continuous polymer matrix by an average distances that depends on clay loading. Usually, the clay content of exfoliated nanocomposites is much lower than that of intercalated nanocomposites.
1.5 POLYMER NANOCOMPOSITES (PNCs)

Polymer nanocomposites (PNCs) are materials composed of a polymeric host in which particles (buckyballs, carbon nanotubes, semiconductor of metallic nanocrystals and clays) of 1 to several hundred nanometer dimensions are incorporated. Because, the particles and the polymers possess different functionalities, the range of applications are diverse. Applications include membranes, coatings, solar cells, electronic devices, sensing, medicine and structural applications, such as automobile parts. PNCs which contain layered silicates (clays) have been successfully used for different thermal and mechanical applications (Okada 1990).

PNCs are especially interesting because they exhibit properties that are superior to conventional composites with relatively low concentrations of
the inorganic component. The challenges are associated with controlling the composition and spatial distribution of the inorganic component within the polymer. Increase in mechanical, dielectric and transport properties can be understood by knowing the micro structural features, determined by the polymer-particle, polymer-polymer, particle-particle and interfacial interactions. The metal particles reinforcement increases both strength and toughness due to the enormous surface area and the extent of dispersion of metal nanoparticles in the matrix strength.

1.6 NANOPARTICLES

The synthesis and characterization of nanoparticles have attracted considerable attention in recent years. It is well known that nano-sized particles because of their small size and high surface area, display many unique electrical and magnetic properties (Rudiger et al 2005 Dofrenik et al 2005). The sol-gel synthesis of inorganic nanocomposites based on highly dispersed and nano sized active phases exhibit catalytic, electro-optic, ferroelectric, and non-linear optical properties. Particular attention was addressed to the thin films preparation for the realization of basics of electronic devices. Compared with the conventional ceramic routes, such as co-precipitation, grafting and impregnation the sol-gel exhibits many advantages such as low temperature, high control of purity, composition, microstructure and textural properties of the final materials. Particularly for mixed-oxides this synthesis procedure allows to obtain materials characterized by a high dispersion of the active phase in the matrix on both molecular and nanometer scale. Moreover, the versatility of the sol-gel route makes possible to obtain the final material as powder, bulk and coating films.

In recent years the advances in synthesis techniques and the ability to characterize materials on atomic scale has led to a growing interest in
nanometer-size materials. Polymer nanocomposites combine these two concepts, i.e., composites and nano-sized materials.

Polymer nanocomposites are materials containing inorganic components that have nano-dimensions. Nano fillers can be classified as

1. Symmetric nanoparticles e.g. metal oxides
2. Asymmetric 2-dimensional nanofillers e.g. layered nanoclays
3. Asymmetric 1- dimensional nanofillers e.g. carbon tubes

1.7 PREPARATION OF POLYMER NANOCOMPOSITES

Various methods have been developed and applied for preparation of PNCs. They are broadly classified into two categories: 1. Direct compounding 2. In situ synthesis

1.7.1 Direct Compounding

The direct compounding method has been extensively used to fabricate PNCs because of its convenience in operation, comparatively low cost and suitability for massive production. Nanofillers and polymer supporters are prepared separately at first, and then they are compounded by solution, emulsion, fusion or mechanical forces (Yew 2006; Chan 2002; Wu 2003.). Nevertheless, direct compounding of polymers with nanofillers achieved only limited success for most systems due to the difficulties in deciding the space distribution parameter of nanoparticles in or on the polymer matrix (Chen 2004; Zhang 2004; Liang 2002). The nanoparticles usually exhibit high tendency to form larger aggregates during blending, which greatly diminishes the advantages of their small dimensions. In addition, polymer degradation upon melt compounding and phase separation
of nanophase from the polymer phase is sometimes severe. These limitations should be considered when using the direct compounding method to prepare PNCs (Lee 2002). Various surface treatments to nanoparticles have been adopted in the synthesis procedure and the compounding conditions such as temperature and time, shear force and configuration of the reactor (Wang 2002) can also be adjusted to achieve good dispersion of nanoparticles in polymer matrices.

1.7.2 **In Situ Synthesis**

According to different starting materials and fabrication processes, in situ synthesis can be classified into three types:

1. Metal ions are preloaded within polymer matrix to serve as nanoparticles precursors first, where the ions are supposed to distribute uniformly (Ahmad 2007).

2. The nanoparticles are first dispersed into the monomers or precursors of the polymeric hosts, and the mixture is then polymerized under desirable conditions including addition of appropriate catalyst. Increasing attention is paid to this method because it allows one to synthesize nanocomposites with tailored physical properties. A direct and well dispersion of the nanoparticles into the liquid monomers or precursors will avoid their agglomeration in the polymer matrix and thereafter improve the interfacial interactions between both phases (Luo 2009; Wang 2011).

3. The nanoparticles and polymers could be prepared simultaneously by blending the precursors of nanoparticles and the monomers of polymers with an initiator in proper solvent (Liaw 2007).
1.8 EPOXY RESINS

Epoxy resins are oxirane-containing oligomers, which cure through the reaction of epoxide groups with a suitable curing agent. Epoxy resin is defined as a molecule containing more than one epoxy group capable of being converted to a useful thermoset form. The epoxy compounds are classified into many types namely, glycidyl ethers, epoxy novalac resin, cycloaliphane resins, glycidyl ethers, epoxy novalac resin, cyclo aliphatic resin, glycidyl esters. Some important properties of the epoxy resin are given in Table 1.1.

The main advantages of the epoxies are

- Relatively low cure shrinkage that makes dimensional accuracy of fabricated structures easier to obtain
- Inherently polar nature that confers that excellent adhesion to a wide variety of fibres
- No volatile products of the curing reaction to cause undesired bubble or void formation.
- Cross linked structure that confers excellent resistance to hostile environment, both aqueous and non aqueous.

Table 1.1 Typical Properties of cast epoxy resin (Salim Yamini et al 1980)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Gravity</td>
<td>1.2 – 1.3</td>
</tr>
<tr>
<td>Tensile strength, MPa</td>
<td>55 – 130</td>
</tr>
<tr>
<td>Tensile modulus, GPa</td>
<td>2.75 – 4.10</td>
</tr>
<tr>
<td>Poisson’s ratio</td>
<td>0.2 – 0.33</td>
</tr>
<tr>
<td>Coefficient of thermal expansion, $10^{-6}$ m/m/^°C</td>
<td>50 – 80</td>
</tr>
<tr>
<td>Cure Shrinkage, %</td>
<td>1 – 5</td>
</tr>
</tbody>
</table>
1.9 CLASSIFICATION OF EPOXY RESIN

Epoxy resins can be broadly classified into two types such as the glycidyl epoxy, and non-glycidyl epoxy resins. The glycidyl epoxies are further classified as glycidyl-ether, glycidyl-ester and glycidyl-amine. The non-glycidyl epoxies are either aliphatic or cycloaliphatic epoxy resins. Glycidyl epoxies are prepared via a condensation reaction of appropriate dihydroxy compound, dibasic acid or a diamine and epichlorohydrin while, non-glycidyl epoxies are formed by peroxidation of olefinic double bond. Glycidyl-ether epoxies such as, diglycidyl ether of bisphenol-A (DGEBA) and novolac epoxy resins are most commonly used epoxies.

1.9.1 Diglycidyl Ether of Bisphenol-A Resin (DGEBA)

Epoxy resins are compounds containing more than one epoxide group per molecule on average. Commercial epoxy resins contain aliphatic, cycloaliphatic, or aromatic backbones. They are prepared from either epichlorohydrin or by direct epoxidation of olefins with peracids. The most important intermediate for epoxy resins is the diglycidyl ether of bisphenol A (DGEBA) which is synthesized from bisphenol A and excess epichlorohydrin. The epoxy resins (DGEBA) are prepared using different molar ratios of epichlorohydrin to bisphenol A to afford different molecular weight products. The purity of DGEBA is being depended on the excess of epichlorohydrin. The higher molecular weight epoxy resin is synthesized by reacting with epichlorohydrin and bisphenol-A in the presence of NaOH. DGEBA structure is shown in Figure 1.2

![Figure 1.2 Structure of DGEBA](Bejoy Francis et al 2005).
Diglycidyl ether of bisphenol-A resin (DGEBA) are widely used in industry as protective coatings and for structural applications, such as laminates and composites, tooling, molding, casting, bonding and adhesives, and others (Anderson 1968). Treatment with curing agents gives insoluble and intractable thermoset polymers. Some of the characteristics of epoxy resins are high chemical and corrosion resistance, good mechanical and thermal properties, outstanding adhesion to various substrates, low shrinkage upon cure, good electrical insulating properties, and the ability to be processed under a variety of conditions.

1.9.2 Epoxy Novalac

Novolac epoxy resins generally contain multiple epoxide groups and it was glycidyl ethers of phenolic novolac resins. Epoxy novalac resins are synthesised by reacting epichlohydrin with novalac resin in presence of sodium hydroxide as a catalyst. The novalacs range from bisphenol-F to higher molecular weight materials containing twelve phenolic hydroxyls. The multiple epoxide groups allow these resins to achieve high cross-link density resulting in excellent temperature, chemical and solvent resistance. Novolac epoxy resins are having good mechanical, electrical, heat and humidity resistance.

1.9.3 Glycidyl Esters

Glycidyl esters are prepared by the general mechanism of the reaction of epichlorohydrin and the carboxylic acids. This reaction was two stage process, first stage being the formation of intermediated in the presence of base via chlorohydrins. The reaction then completed dehydrohalogenation. A number of acids have been made to undergo this reaction, but only the glycidyl esters derived from phthalic, terephthalic and isophthalic acids, and
tetra and hexa-hydrophthalic acids have found some significant practical applications in epoxy resin technology.

1.9.4 Glycidyl Amines

Glycidyl amines can be prepared from aliphatic and aromatic primary and secondary amines. Among the glycidyl amines, aromatic based on aniline and diaminodiphenylmethane (DDM) are of industrial importance. There are two main varieties diaminodiphenyl methane four glycidyl amine (resin), three glycidyl aminophenol (TGAP) and Tetra glycidyl diaminodiphenylmethane (TGDDM). Its characteristics are cured heat resistance, mechanical strength is better than bisphenol A epoxy resin. Accordingly diamine by polycondensation with epichlorohydrin is obtained. They are mainly used for the production of aircraft, space vehicles and equipment and sports equipment.

Glycidyl amines can be prepared from aliphatic and aromatic primary and secondary amines. Among the glycidyl amines, aromatic amines based on aniline and diaminodiphenylmethane (DDM) are having practical importance. Tetra glycidyl diaminodiphenylmethane (TGDDM) is widely used commercially available glycidyl amino resin. They have following general structure (Figure 1.3).

Figure 1.3 Structure of TGDDM (Attias et al 1990)
They are mostly used with anhydrides to give products with good strength retention at high temperature and good to nuclear radiation. They are used for wet lay-up lamination and filament winding.

1.10 CURING AGENTS

The epoxy resins can be cured using a range of materials with different types of curing conditions. The choice of curing agents (also called ‘hardeners’) depends on the curing conditions applicable and the final application of the resin. Epoxies can be cured with amines, thiols, and alcohols (Mika 1973). The reaction proceeds through the cleavage of the oxirane ring through a nucleophillic addition reaction. Due to the involvement of an addition reaction, no volatile byproducts are formed during the curing of epoxy resins. Because the reactions of the epoxy monomers with the respective hardener are sometimes not fast enough for a specific application, accelerators are often added to the resin formulations. Cure temperatures influence the morphology considerably and has a significant effect on the mechanical properties (Dehoff 1961; Mika 1973; Dasgupta & Mital 1964, Penn & Chione 1990).

Amines are widely used as hardeners for epoxy resins. During the curing reaction, two epoxy rings react with a primary amine. The first step is the reaction between the primary amine hydrogen with the epoxy group, followed by a reaction between the secondary amine hydrogen with another epoxy. Although a single activation energy and heat of reaction are experimentally obtained for both steps, the reactivities of primary and secondary amino groups may be different (Potter 1970; Ashcroft 1993). The hydroxyl groups generated during the cure can also react with the epoxy ring, forming ether bonds (etherification). The etherification reaction competes with the amine–epoxy cure when the reactivity of the amine is low or when there is an excess of epoxy groups. The tendency of the etherification reaction
to occur depends on the temperature and basicity of the diamines, and increases with the concentration of epoxy in the mixture. Secondary alcohols (continuously formed during cure) also catalyse the amine–epoxy reactions; this is called ‘autocatalysis’. Thus the curing reaction occurs by two competitive mechanisms: an autocatalytic reaction (catalysed by the hydroxyl groups initially present in the epoxy prepolymer or those generated during the reaction) and a non-catalytic mechanism, which is second order in nature. The autocatalytic mechanism involves a ternary transition complex.

The reactivity of the amine increases with its nucleophilic character: aliphatic > cycloaliphatic > aromatic. Thus, appropriate curing temperatures and catalysts (called ‘accelerators’) must be employed for curing.

### 1.10.1 Aliphatic Curing Agent

The advantage of aliphatic amines both primary and secondary amines is that they can cure epoxy resins at ambient temperature. Other amines mostly require heat curing. Heat curing is difficult and impractical for fabrication of certain structures, and requires a significant amount of energy.

Some of the most common amines used are diethylenetetramine (DETA, functionality=5), triethyleneteramine (TETA, functionality=6), hexamethylenediamine (HMD, functionality=4) etc. (Parthun & Johari 1992). They are highly reactive due to the unhindered polyfunctional nature and give cross-linked networks due to the short chain distances between active sites. The cured resins have excellent solvent resistance and mechanical strength but have poor flexibility. TETA is a mobile pale yellow liquid used to cure DGEBA resin at room temperature. It is used for casting, tooling and wet lay-up, laminating applications. Heat distortion temperature (HDT) of the cured system can be improved by post–curing at elevated temperature (Weatherhead 1980). Hexamethylenediamine has low viscosity and has better
chain flexibility due to long repeat distances between cross-linked sites: The long hydrocarbon chain makes them hydrophobic. Even though it has some limitations aliphatic amines are highly volatile, toxic and cured network can work up to $80^\circ$C and not above.

### 1.10.2 Aromatic Curing Agent

Aromatic amines, which require heat curing and are used for lamination applications to provide excellent mechanical, electrical and chemical resistance. Commonly used aromatic amines (Figure 1.4) are 4, 4'-diaminodiphenylmethene (DDM) (Mangion & Johari 1990) m-phenylenediamine (MPDA) and diaminodiphenylsulphone (DDS). DDM is also known as methylenedianiline (MDA). It is an off-white solid at room temperature and melts at 90°C and added to the resin. DDM is used for wet lay-up lamination, casting preparations. Major advantage of DDM over many other curing agents is the ability to cure liquid DGEBA resins down to 0°C in solution in presence of an accelerator such as phenol or salicylic acid (Ellis 1993).

![Structure of DDM](image)

**Figure 1.4 Structure of DDM** (Strehmel et al 1992)

### 1.10.3 Polyamidoamine

Polyamide resin, which has been widely used as a curing agent for epoxy resin (Ashcroft 1993), is formed by the condensation reaction between dimer acid and polyamine, and contains reactive primary and secondary amines in its molecules. They are dimerized or polymerized fatty acids that
have been co-reacted with various aliphatic amines such as ethylenediamine, diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA). Polyamide amine reacts with bisphenol-A-type epoxy resin to cure at or below normal temperature with moderate heat generation. It cures so slowly that it has a long pot life. They are user-friendly systems since tolerance on mix ratio is very broad (Goodman 1986; Ellis 1993). As polyamide has high hydrocarbon moiety in its molecules, it cures epoxy resin into a highly plasticized rigid thermosetting polymer. The cured resin features high tensile, compression, and bending strengths, while it is stiff, strong, and excellent in shock resistance.

1.10.4 Effect of Epoxide Structure on Reactivity

Cure of epoxy resins normally occurs without the formation of any by-products. The curing reactions are exothermic. Many researchers measured the heats of polymerization of liquid epoxy resins with amine curing agents. Several reviews on curing of epoxy resins with different curing agents are reported. The effect of epoxide structure on reactivity, the mechanism of curing reactions and the statistical treatment to cross-linking in the curing process are dealt with, in detail (Enns & Gillham 1983).

During the process of an amine cured thermoset, the reaction of primary amine (R-NH₂) with an epoxide group first forms a secondary amine (RNH-) which reacts with another epoxy group to form a tertiary amine (RN<). For a given amine, these two reactions occur concomitantly, with two distinct values of reaction rate constants leading to the formation of fully connected network at the gel point (Barton and Wright 1985). After gelation, the reaction become diffusion controlled and eventually leads to vitrification. The extent of reactions at the time of vitrification depends on the temperature of cure and is found to lie approximately between 80% and 100%. A typical curing reaction (Penn and Chiao 1990) is shown below (Figure 1.5).
1.11 TOUGHENING OF EPOXY RESIN

Epoxy resins are extensively used as adhesives and as matrices for fibre reinforced composites because of their outstanding mechanical and thermal properties. All these properties are attributed to their high crosslink density. Because of high crosslink density, these materials have very low resistance to crack initiation and propagation. It is very important to increase the toughness of these materials without causing major losses in other desirable properties. Of all the methods that have been considered and adopted in an attempt to alleviate the brittle characteristics of epoxy resin, elastomeric and thermoplastic modifications were found to be most successful.

1.12 POLYESTER RESINS

A large number of thermoset polyester resins are commercially available and these can be conveniently classified into alkyds, unsaturated polyesters, vinyl esters, allyl resins etc. Table 1.2 presents a few important properties of polyester (Maksimov et al 1999).
Table 1.2 Typical properties of cast thermoset polyester resins

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Gravity</td>
<td>1.1 – 1.4</td>
</tr>
<tr>
<td>Tensile strength, MPa</td>
<td>34.5 – 103.5</td>
</tr>
<tr>
<td>Tensile modulus, GPa</td>
<td>2.1 – 3.45</td>
</tr>
<tr>
<td>Elongation, %</td>
<td>1.5</td>
</tr>
<tr>
<td>HDT, °C</td>
<td>60 – 205</td>
</tr>
<tr>
<td>Cure shrinkage, %</td>
<td>5 – 12</td>
</tr>
</tbody>
</table>

1.12.1 Unsaturated Polyesters

Unsaturated polyesters are prepared by reacting a mixture of unsaturated and saturated dicarboxylic acids with diols. The condensate is then dissolved in an unsaturated co-reactant diluent like styrene, methyl methacrylate or diallyl phthalate to get a resin formulation. Styrene is the commonly used diluent. The degree of flexibility, toughness, tensile strength and hardness depend on the chemical structure of the resin. General purpose (GP) grade UP resin is prepared by the condensation of propylene glycol (PG) with a mixture of maleic anhydride (MA) and phthalic anhydride (PA). When cross-linking is initiated with the help of a catalyst and an accelerator styrene facilitates cross-linking at the sites of unsaturation in the polyester chains. The saturated acid reduces the number of cross linking sites and consequently the cross-link density and brittleness of the cured resin. Since cross-linking occurs via free radical addition mechanism across the double bonds in the polyester chain and the reactive diluent no volatiles are given off during cure.

1.12.2 Alkyd Resins

Alkyd resins are produced by reacting a polyhydric alcohol, usually glycerol, with a polybasic acid, usually phthalic acid and the fatty acids of various oils such as linseed oil, soyabean oil and tung oil. They are nowadays
employed mostly in the surface coatings field. Alkyd resins are modified by rosin, phenolic resins, epoxy resins and monomers like styrene. When the resin is applied to a substrate oxidative cross-linking via unsaturated groups in the fatty acid occurs and the resin hardens. These resins have low cost, durability, flexibility, gloss retention and heat resistance.

1.12.3 Vinyl Ester Resins

Vinyl esters are chemically the reaction products of epoxy resin and ethylenically unsaturated monocarboxylic acids like methacrylic acid with styrene added as a coreactant. They are similar to unsaturated polyesters in the sense that they are reasonably priced, cure rapidly and have processability. But their mechanical properties are akin to epoxy resins. The vinyl groups present at the ends of the molecule impart high reactivity, low residual unsaturation and high tensile elongation. The terminal ester groups are protected by pendant methyl groups which give chemical resistance to the resin. The unreacted hydroxyl groups derived from the epoxide moiety are partly responsible for their excellent adhesion to glass. Vinyl ester resins are widely used for reinforced plastic chemical plant equipment such as scrubbers, pipes and tanks and chemically resistant coatings such as tank and flue stack linings. A wide variety of resins can be prepared by simply altering the choice of epoxy resin and for monocarboxylic acid. The most widely used cross-linking monomer is styrene.

1.12.4 Phenolic Resins

Phenolic resins were the first polymeric resins produced commercially from simple low molecular weight compounds. Phenol formaldehyde (PF) resins are prepared by the polycondensation between phenol and formaldehyde in the presence of either an acid or a base catalyst. The nature of the product is dependent on the type of catalyst and the mole
ratio of reactants. The initial phenol formaldehyde reaction products may be of two types, novolacs and resols. Novolacs are prepared by reacting formaldehyde and a molar excess of phenol under acidic conditions. Initially these reactants slowly react to form polyhydroxy methyl phenols.

1.13 REINFORCEMENT

Reinforcements are used with resin systems primarily to improve the mechanical properties of the cured resins. The reinforcement normally used with matrix resins in fibre-reinforced composites is glass, carbon nanotubes, metal nano powders. The choice of reinforcement depends on many parameters such as strength, stiffness, environment stability. The reinforcement of metal nanoparticles in polymer matrix yields polymer nanocomposites. Polymer nanocomposites consisting of metal nanoparticles of 1 - 100 nm are exhibiting specific characteristics. The metal nanoparticles-based materials have been commonly used for coloring glasses since the Medieval Ages, such as stained glasses in Cathedrals. The metal nanoparticles materials show nonlinear electronic transport (single-electron transport of Coulomb blockade) and nonlinear/ultrafast optical response due to the surface plasmon resonance. The nonlinear optical properties are to be applied for optical switching and optical logic elements, etc. in photonic fields.

1.14 FIBRE REINFORCED COMPOSITES

Fibre reinforced composites (FRC) contain reinforcements having lengths much higher than their cross-sectional dimensions. Fibres are the load-carrying members, while the surrounding matrix keeps them in the desired location and orientation. Further, the matrix acts as a load transfer medium and protects the fibres from environmental damage due to elevated temperature and humidity. Fibre reinforced composites have a low specific
gravity and high strength weight and modulus-weight ratios, which have tremendous potential, and consequently possess a distinct advantage over conventional, materials. Nowadays fibre reinforced composites have emerged as a major class of structural materials with an increasing application in weight-critical components for industry, particularly the aerospace, marine, and automotive sectors. Fibre reinforced plastic (FRP) composites form a major class of composites. The versatility, strength and non-corrosive properties of plastics in combination with fibres have helped to establish this class of composites as a potential and viable alternative in several applications.

1.14.1 Glass Fibres

Glass fibres are the most common of all reinforcing fibres for polymer matrix composites. Glass fibres are amorphous solids. Chemically, glass is primarily composed of silica (SiO₂) backbone in the form of “(-SiO₄⁻)” tetrahedral. Modifier ions are added for their contribution to glass properties and manufacturing capability. Glass fiber reinforced composites offer the most reliable engineering materials compared with other composites.

1. It is easily drawn into high-strength fibres from the molten state.

2. It is readily available and may be fabricated into a glass-reinforced plastic economically using a wide variety of composite-manufacturing techniques.

3. As a fiber it is relatively strong, and when embedded in a plastic matrix, it produces a composite having a very high specific strength.
When coupled with the various plastics, it possesses a chemical inertness that renders the composite useful in a variety of corrosive environments.

Glass fibres in the form of woven fabric are most commonly used for composite laminates because of the high fracture toughness, ease of handling and their balanced in-plane properties. In addition, the transverse tensile strength of woven fabric composites is much higher than that of unidirectional composites. Table 1.3 presents typical properties of glass fibres (Seena Joseph et al 2002).

<table>
<thead>
<tr>
<th>Property</th>
<th>E-glass</th>
<th>S-glass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Gravity</td>
<td>2-6</td>
<td>2.5</td>
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<tr>
<td>Young’s Modulus, GPa</td>
<td>72</td>
<td>87</td>
</tr>
<tr>
<td>Tensile Strength, MPa</td>
<td>3450</td>
<td>4310</td>
</tr>
<tr>
<td>Tensile elongation, %</td>
<td>4.8</td>
<td>5.0</td>
</tr>
<tr>
<td>Coefficient of Thermal Expansion, µm/m°C</td>
<td>5.0</td>
<td>5.6</td>
</tr>
</tbody>
</table>

### 1.14.2 Aramid Fibres

The aramid fibres are very important reinforcement for advanced composites. The aramid-fibre-forming polymers is the aromatic polyamides, are believed to be made of solution-polycondensation of diamines and diacid halides at low temperatures. Their high degree of toughness, associated with the failure mechanism of aramids, and damage tolerance promotes good impact/ballistic performance. When aramid fibres break, they do not fail by brittle cracking, as do glass or carbon fibres. Instead, the aramid fibres fail by a series of small fibril failures, where the fibrils are molecular strands that
make up each aramid fibre and are oriented in the same direction as the fibre itself. Tensile strength and modulus are substantially higher and fibre elongation is significantly lower for Kevlar fibres than for other organic fibres. Kevlar fibres have poor characteristics in compression, with compressive strength being only one-eighth of the tensile strength. This is a result of the anisotropic structure, which permits the relative ease of local yielding, buckling, and kinking of the fibre in compression. Table 1.4 shows the important properties of Kevlar fibres (Young et al 1992).

Table 1.4 Typical properties of kevlar fibres

<table>
<thead>
<tr>
<th>Property</th>
<th>Kevlar 149</th>
<th>Kevlar 49</th>
<th>Kevlar 129</th>
<th>Kevlar 29</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Gravity</td>
<td>1.44</td>
<td>1.44</td>
<td>1.44</td>
<td>1.44</td>
</tr>
<tr>
<td>Young’s Modulus, GPa</td>
<td>186</td>
<td>124</td>
<td>96</td>
<td>68</td>
</tr>
<tr>
<td>Tensile Strength, MPa</td>
<td>3440</td>
<td>3700</td>
<td>3380</td>
<td>2930</td>
</tr>
<tr>
<td>Tensile elongation, %</td>
<td>2.5</td>
<td>2.8</td>
<td>3.3</td>
<td>3.6</td>
</tr>
<tr>
<td>Coefficient of thermal expansion, μm/m°C</td>
<td>-2.0</td>
<td>-2.0</td>
<td>-2.0</td>
<td>-2.0</td>
</tr>
</tbody>
</table>

1.14.3 Carbon and Graphite Fibres

Graphite fibres are the predominant high-strength, high-modulus reinforcement used in the fabrication of high-performance resin matrix composites. The term 'graphite fibre' is used to describe fibres that have a carbon content in excess of 99% whereas the term 'carbon fibre' describes fibres that have a carbon content of 80-95%. The carbon content is a function of the heat treatment temperature.

1. Carbon fibres have the highest specific modulus and specific strength of all reinforcing fiber materials.
2. They retain their high tensile modulus and high strength at elevated temperatures; high-temperature oxidation, however, may be a problem.

3. At room temperature, carbon fibres are not affected by moisture or a wide variety of solvents, acids, and bases.

These fibres exhibit a diversity of physical and mechanical characteristics, allowing composites incorporating these fibres to have specific engineered properties (Margaret et al 1987) (Table 1.5).

**Table 1.5 Typical properties of commercially available graphite fibres**

<table>
<thead>
<tr>
<th>Property</th>
<th>Low modulus</th>
<th>Intermediate modulus</th>
<th>Ultrahigh modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Gravity</td>
<td>1.8</td>
<td>1.9</td>
<td>2.2</td>
</tr>
<tr>
<td>Young’s Modulus, GPa</td>
<td>230</td>
<td>370</td>
<td>900</td>
</tr>
<tr>
<td>Tensile Strength, MPa</td>
<td>3450</td>
<td>2480</td>
<td>3800</td>
</tr>
<tr>
<td>Tensile elongation, %</td>
<td>1.1</td>
<td>0.5</td>
<td>0.4</td>
</tr>
<tr>
<td>Coefficient of thermal expansion μm/m°C</td>
<td>-0.4</td>
<td>-0.5</td>
<td>-0.5</td>
</tr>
</tbody>
</table>

**1.14.4 Boron Fibres**

Boron filaments are produced by the chemical vapour deposition, from the reduction of boron trichloride (BCl$_3$) with hydrogen, on a tungsten or carbon monofilament substrate. Currently boron filaments are produced with diameters of 100, 140 and 200 pm, in descending order of production quantity; however, both smaller and larger diameter fibres have been produced in experimental quantities.
1.15 FABRICATION OF FIBRE REINFORCED COMPOSITES

The fabrication and shaping of composites into finished products are often combined with the formation of the material itself. The formation of the composite involves the combination of the matrix and fibre such that the matrix impregnates, surrounds, and wets the fibres. The important processing methods for thermosetting polymers include hand lay-up, bag moulding process; filament winding, pultrusion, bulk moulding, sheet moulding, resin transfer moulding etc.

1.15.1 Hand Lay-Up

The hand lay-up technique is the oldest, simplest and most commonly used method for the manufacture of both small and large fibre reinforced plastic products. The random chopped strand glass mat or woven roving is cut to fit the open mould contour and impregnated with the catalysed resin using a brush in successive plies. The quality of the product depends on the skill of the personnel in removing air bubbles and voids. The hand lay-up method is labour intensive and is suitable for low rate of production.

1.15.2 Spray-Up Technique

Spray-up technique is the principal fabrication process used by the FRP industry. The catalysed resin and chopped glass fibre are laid down simultaneously on the mould surface with specialised spray equipment. The chopped fibre, 3.8-5.0 cm long is produced by feeding continuous glass fibre roving into a rotating chopper at the head of the spray gun. The technique requires skilled operators to get uniform products and to prevent excessive scrap by over spraying.
1.15.3 Bag Moulding Process

Bag moulding is one of the oldest and most versatile of the processes used in manufacturing composite parts. The lamina is laid up in a mould and resin is spread or coated, covered with a flexible diaphragm or bag and cured with heat and pressure. After the required curing cycle, the materials become an integrated moulded part shaped to the desired configuration. The general process of bag moulding can be divided into three basic moulding methods: pressure bag, vacuum bag, and autoclave. Vacuum bag and autoclave methods are used to produce most bag-moulded parts.

1.15.4 Filament Winding

The strength of FRP products is enhanced by the concentration and length of the glass fibre reinforcement. The winding of continuous glass roving that have been impregnated with catalysed resin over a rotating mandrel gives maximum structural performance. However this technique is limited to articles with axial symmetry such as cylindrical products. The winding of the glass roving follows a reciprocating helical pattern using a bias angle suitable for the structural requirement. Filament winding is used for the manufacture of pipes, tubes, cylinders, and spheres and is frequently used for the construction of large tanks and pipe work for the chemical industry.

1.15.5 Resin Transfer Moulding (RTM)

Resin transfer moulding is unique in that it permits the manufacture of high performance composite parts of essentially unrestricted geometry with fast cycle times. A dry reinforcement preform is placed in the mould and the mould is closed. The preform is impregnated with a thermoset liquid resin which is injected into the mould. During the infiltration process, the resin wets out the reinforcement and polymerises (Potter 1997).
1.15.6 Liquid Composite Moulding

A series of processes has emerged in which the reinforcement is placed in the mould and the resin matrix is injected. These are called collectively Liquid Composite Moulding (LCM). At its simplest, this involves placing the glass in the mould in a prescribed pattern, followed by injection of resin. Manual placement of glass is slow and skill-dependent, and preforms are widely used.

1.16 NANOPARTICLES REINFORCED COMPOSITES

The properties of composites mostly depend on size of filler particles, their concentration, as well as the type of interaction with polymer matrix. Also, polymer composites take advantage of desired properties of host polymers such as possibility to be designed in various shapes, long-term stability and reprocess ability (Godovsky et al 2000; Rozenberg et al 2008). Hence, an effective approach to enhance mechanical and thermal properties of polymer is introducing various nanofiller such as inorganic nanoparticles, carbon nanotube and organoclay into the polymer matrix (Zabihi et al 2011; Zanetti et al 2009; Manfredi et al 2008; Kathi et al 2009). The nanoparticles used provide improved interfacial surface area and smaller interparticle distances, which are believed to contribute to improved mechanical properties (Jordon et al 2005; Gotro et al 2004).

1.17 METAL OXIDE NANOPARTICLES

1.17.1 Silica

The hydrolysis and polymerization of tetraalkoxysilanes (TEOS) in ethanol solution containing water and ammonia allows preparation of monodispersed silica powders. The final particle size diameter was determined as a function of initial reagent concentrations over the range
studied 0.170.5 M TEOS, 0.53 M NH₃, 0.514 M H₂O (at 25°C). It was
possible to obtain SiO₂ particles with average diameters between 15 and 700
nm. The solgel method provides means for modifying glasses and crystalline
ceramics with organic polymers, promising materials displaying unique and
varied mechanical, electrical and optical properties.

1.17.2  Zinc Oxide

ZnO nanowires were successfully synthesized by simply heating
the desired metal powder to a temperature above its melting point in a flow of
mixed faces (20% O₂, 80% Ar, with the 120 flow rate). Transmission
electron microscopy observations show that as-synthesized products are
exclusively nanowires, structurally uniform and single crystalline. The same
technique was used to fabricate arrays of ZnO nanowires on silicon substrates,
which would be particular interest for direct integration in the current silicon-
technology-based optoelectronic devices (Ruoyu Hong et al 2006). Sigma-
Aldrich is marketing the zinc oxide powder of 50-70 nm.

1.17.3  Iron Oxide

Magnetic nanoparticles have been proposed for use as biomedical
purposes to a large extent. In recent years, nanotechnology has developed to
a stage that makes it possible to produce, characterize and specifically tailor
the functional properties of nanoparticles for clinical applications. Generally
nanosized iron oxide has been prepared by the gas-phase-synthesis.

Highly crystallized iron oxide nanorods were fabricated by
hydrothermal synthesis in the cavity of carbon-coated nanochannels with a
diameter of 25 nm. The carboned nanochannels were prepared by uniform
carbon coating on the inner walls of the straight nanochannels of an anodic
aluminium oxide film. Iron nitrate was loaded in the nanochannels by
impregnation method and then subjected to hydrothermal treatment with NaOH aqueous solution in an autoclave. Upon the treatment, the aluminium oxide template was dissolved to leave carbon nanotubes, in which highly crystallized nanorods of $\text{Fe}_2\text{O}_3$ were formed. Then, the carbon nanotubes were completely removed by high temperature oxidation and the nanorods were liberated from carbon nanotubes as a result. Isolated, magnetically decoupled single-domain centers of nano-scaled iron oxide were embedded in an amorphous silica matrix were prepared by flame synthesis providing superparamagnetic behavior.

1.17.4 Titania

Titanium Dioxide is an important catalyst for oxidation of hazardous compounds in air and water particularly for photo-catalysis. Although it is traditionally used for photo-catalyst with UV light, when its energy band gap is reduced, it is effective with sun light. This can be achieved through making particles nano size thus changing the crystalline structure. The synthesis of $\text{TiO}_2$ is carried out by sol-gel route with the carboxylic acid groups. This gel solution was deposited on the pyrex glass by the dip-coating processes in order to obtain thin layer of titanium dioxide. $\text{TiO}_2$ has good crystallinity at 400$^\circ$C, and has accepted conductivity. Titanium (IV) oxide nanoparticles with 5 and 10% dispersion in water having dimensions of $\sim$ 40 nm are being marketed by Sigma-Aldrich. In the powder form also titanium oxide is available with dimensions ranging from 5-10 nm (99.7% purity) and 60-100 nm (99.9% purity).

Among various nanomaterials, those based on nano-$\text{Fe}_2\text{O}_3$ are promising candidates for practical applications because these $\text{Fe}_2\text{O}_3$ particles are readily available and also exhibit multi-functional properties. For example, the nanocrystalline $\text{Fe}_2\text{O}_3$ would have potential applications in the fields (Kupovich et al 2001, Patil et al 2006) materials, solar energy
conversion, and electrochromism are used in iron (III) oxide nanoparticles. Also the iron (III) oxide nanoparticles are used in ferrofluids, magnetic storage, magnetic refrigeration and color imaging (Marinovic-Cincovic et al 2006; Oh et al 2011).

Introducing good linkages between the fillers and the polymer matrix is still a challenge for specific composite fabrication. However, appropriate chemical engineering treatment of the nanofiller surface by introducing proper functional groups could improve both the strength and toughness of the subsequent composites with improved compatibility between the nanofillers and the polymer matrix, and make the nanocomposites stable in harsh environments as well (Gao et al 2002). Thus, surface functionalization of nanoparticles with a surfactant or a coupling agent is important not only to stabilize the nanoparticles (Shenhar et al 2005) during processing but also to render them compatible with the polymer matrix.

1.18 LITERATURE REVIEW

1.18.1 Polyester Modified Epoxy Matrix

Yeng-Fong Shih et al (2002) studied the effect of carbon black as flame retardants to improve the flame resistance of the interpenetrating polymer networks (IPNs) based on unsaturated polyester/epoxy at elevated temperatures. The results of DSC reveal that the $T_g$ of the IPN became indistinct as the carbon black was added. It was also found from adiabatic calorimeter studies that the heat of combustion of the IPN sample was decreased by the addition of carbon black. The results shows that the degradation process of IPN was inhibited as the carbon black was added to the IPN which lower molecular weight compounds and also produces fewer species of degradation products.

Tsotras et al (2004) prepared electrically conductive blends by
mixing a Polyaniline –dodecybenzenesulfonic acid (PANI-DBSA) salt with epoxy resin (EP). The thermal, mechanical, and electrical properties of blends containing different amounts of PANI-DBSA were studied. The flexural properties were not significantly influenced by concentrations smaller than 7 wt.% PANI-DBSA, but after this content they were decreasing sharply. The electrical conductivity of the samples increased with the addition of PANI-DBSA, reaching a value higher than $10^{-7}$ S/cm with 10 wt.% of PANI-DBSA.

Lapprand et al (2003) studied miscibility and curing behavior of blends of poly(vinyl acetate) (PVAc) and diglycidyl ether of bisphenol A (DGEBA) resin using 4,4’-diaminodiphenylsulphone (DDS) as curing agent. The PVAc component was used as a potential toughness modifier. Binary mixtures DGEBA + PVAc show complete miscibility over the whole composition range. It was also found that phase separation occurs in DGEBA, DDS and PVAc blends. In the final cured material has two phases: an epoxy phase and a PVAc phase separately. It was also found a slow down of the reaction when PVAc was present.

Chinnakkannu Karikal Chozhan et al (2007) studied the thermo mechanical behaviour of unsaturated polyester toughened epoxy–clay hybrid nanocomposites. The reduction in the values of Tg for unsaturated polyester toughened epoxy system is due to the flexibility imparted by unsaturated polyester to the epoxy matrix. The mechanical studies inferred that the incorporation of unsaturated polyester into epoxy resin enhanced the values of impact strength. The fractured surfaces of the unsaturated polyester toughened epoxy system indicated the presence of homogeneous microstructure. The incorporation of organoclay into UP–epoxy greatly improved the values of Tg, HDT, tensile, flexural and impact strength and thermal stability. The UP toughened epoxy–clay nanocomposites exhibited better thermo-mechanical
properties and good resistant to water absorption properties than that of unmodified epoxy resin system.

Benny cherian et al (2007) studied the physical, electrical and thermal properties of the cured blends epoxy and unsaturated polyester resins (UPR). Epoxy resins show good miscibility and compatibility with the UPR resin on blending and the co-cured resin showed substantial improvement in the toughness and impact resistance. Considerable enhancement of tensile strength and toughness are noticed at very low loading of epoxy. Differential scanning calorimetry (DSC) were employed to study the thermal properties of the toughened epoxy resin.

Varada Rajulu et al (2003) prepared untreated and 2% aqueous NaOH treated bamboo fibres with epoxy, unsaturated polyester (UP) and their blends. The chemical resistance of these fibres to acetic acid, nitric acid, hydrochloric acid, sodium hydroxide, ammonium hydroxide, sodium carbonate, benzene, toluene, carbon tetrachloride and water were studied. The blend coated fibres showed better chemical resistance than uncoated bamboo fibres. The blend coated fibres had higher tensile strength which was attributed to the hydrogen bonding between the unsaturated polyester and epoxides group.

Cicala et al (2008) reported the thermo-mechanical and rheological properties of epoxy blends modified with different percentages of a hyperbranched polyester. The cryo-fractured surfaces of the cured samples were analyzed by scanning electron microscopy which showed that the blends did not have phase separation. This result was further supported by dynamic mechanical testing (DMTA) indicating a single relaxation peak for all the formulations studied.
1.18.2 Epoxy Nanocomposites

Fothergill et al (1996) studied the effect of dielectric spectroscopy and space charge measurements on epoxy resin filled with 10% w/w micro and nano sized particles of TiO$_2$, Al$_2$O$_3$ and ZnO. The result obtained shows that the nanoparticles are significantly influencing the dielectric properties than micro particles. It also suggested that the dielectric properties of such nano-filled composites are controlled by Stern-Gouy-Chapman layers (“interaction zones”) around the particles.

Chantarasiri et al (2000) developed new epoxy polymers containing copper, cobalt and nickel ions by curing diglycidylether of bisphenol A (DGEBA) with Schiff base complexes of these metal ions. The experimental data revealed that the introduction of metal ions, especially the copper ion, into the polymer matrices gave polymers with good thermal stability and mechanical properties.

Punchaipetch et al (2001) studied the cure kinetics of epoxy and liquid crystalline epoxy co-reacted networks. The study reveals that the liquid crystalline epoxy affect the curing kinetics of the epoxy resin (DGEBP-F) and network exhibits single $T_g$.

Ashok Kumar et al (2002) synthesized the siliconized epoxy–bismaleimide intercrosslinked matrix materials. Data obtained from mechanical and thermal characterization indicate that the introduction of siloxane into epoxy improves the toughness and thermal stability with reduction in strength and modulus values. Similarly the incorporation of bismaleimide in to epoxy resin improved both tensile strength and thermal behavior. However the introduction of both siloxane and bismaleimide into epoxy enhances both mechanical and thermal properties according to their percentage content.
Su et al (2002) found the rigid rod epoxies of azomethine (AM), bisphenol (BP) and tetramethyl biphenol (TMBP) exhibit higher $T_g$ and weight retention at high temperature than the flexible DGEBA epoxy due to the low molecular motion and high thermal stability of rigid rod structure. The AM epoxy has the best thermal properties among the rigid rod epoxies because of its longest rigid rod chain and possible intermolecular chain formation in the cured network. The DDS-cured epoxies have a better thermal stability than Dicy-cured epoxies because of the high functionality and rigid structure of DDS.

Allaoui et al (2002) has observed the intrinsic potential of the CNT (Carbon Nano Tubes). Small quantity addition can modify considerably the mechanical and electrical behavior of a soft polymer matrix, the addition of 1 and 4 wt. % of CNT into the epoxy matrix has a remarkable effect on the mechanical properties.

Puglia et al (2003) observed that the rate of reaction and thermal degradation increases with increasing SWNT concentration, these being effect already appreciable at the lower nanotube concentration analyzed (5%). A further increase of the SWNT does not produce a proportional effect, suggesting a saturation of the nanotube incorporation.

Park et al (2003) used an ultrasonic method to disperse iron oxide particles of two different sizes in an epoxy vinyl ester resin. Dispersion is most effective in the early stage of sonication and becomes more difficult to improve later. Once separated, however, the particles do not come into direct contact with one another because of the steric hindrance. The nano-size (29 nm) particles delay curing whereas the larger (200 nm) particles do not. The results indicate a strong interaction between nanoparticles and the resin.
Gojny et al (2004) observed that the addition of only small amounts of carbon nanotubes leads to improve mechanical properties. In comparison to a carbon black filled epoxy, the nanotube/epoxy composites showed an increased tensile strength and Young’s modulus under retention of the ductility.

Levchik et al (2004) prepared phosphorus-containing epoxy as reactive flame retardants. They also discussed the physical properties of the new reactive organo phosphorus epoxy resin, specially designed for electrical and electronic applications.

Yoon Jin Kim et al (2005) studied electrical conductivity of modified multi walled carbon nano tube/epoxy composites. This study reveals that the amount of damage to the MWNTs has much influence on the electrical properties of the MWNTs composites, causing the electrical conductivity to be lowered and the percolation threshold to be raised. But the oxidation of MWNT with the mixture of H₂O₂ and NH₄OH endows the MWNT composite with high conductivity and a relatively low percolation threshold to. In order to improve the electrical properties of the MWNT/polymer composites, the wet processes of the MWNTs should be carried out under condition in which no damaged processes.

Kin-tak Lau et al (2005) studied thermal and mechanical properties of single-walled carbon nanotube bundle-reinforced epoxy nanocomposites: the role of solvent for nanotube dispersion such as acetone, ethanol, DMF. DMF dispersion can make the composites possess a peculiar endothermic behavior and extremely low hardness and flexural strength compared to the pure epoxy and other solvents treated SWNT bundle /epoxy composites. They found solvent effects are in the order of their boiling points.
Ragosta et al (2005) studied epoxy-silica nanocomposites by dispersing silica-organosol particles in TGDDM/DDS resin mixtures. The resulting materials were investigated in terms of chemical interactions, curing behavior and electrical properties. A reaction between epoxy groups and silanol groups present on the surface of the silica phase was detected, leading to an increased interfacial adhesion. The curing behavior of the epoxy matrix was not affected by the inorganic phase. A continuous increase of modulus and yield strength was found by increasing the silica content.

Gonon et al (2005) studied the effect of water absorption on the dielectric properties of a mica/glass/epoxy composites used for high-voltage insulation. They found clearly distinguish between two regimes. The regime of ‘low water uptake’ (M<0.3 wt% in their case) where the resistivity drops by several orders of magnitude when the water content increases by a few tenths of a percent, and the regime of ‘high water uptake’ (M>0.3 wt %) for which the conductivity almost saturates.

Erik Thostenson et al (2006) studied processing-structure-multi-functional property relationship in carbon nanotube/epoxy composites. In this work they found as-processed nanocomposites exhibited significantly enhanced fracture toughness at low nano tube concentrations. The high aspect ratio of the carbon nano tubes in the processed composites enabled the formation of a conductive percolating network at concentrations below 0.1% by weight. The thermal conductivity increased linearly with nano tube concentration to maximum increases of 60% at 5wt. % carbon nanotubes.

Ananda Kumar et al (2006) studied the siloxane moiety incorporated epoxy resin, cured with phosphorus containing diamine (BAPP) curative exhibited higher LOI values than unmodified epoxy indicating the flame-retardant behaviour imparted improved by both siloxane and
phosphorus to epoxy resin. Siliconization of epoxy resin enhanced the moisture resistant behaviour and decreased the heat distortion temperature due to its inherent hydrophobic nature and flexibility.

Zheng Yaping et al (2006) studied functionalized effect on carbon nanotube/epoxy nanocomposites. This study reveals when the content of the MWNTs-NH2 is 0.6%, the bending strength and flexural modulus can be increased 100% and 58% respectively.

Peng Cheng Ma et al (2007) observed composites containing silane-CNTs exhibited better thermal stability flexural modulus and strength, fracture resistance than those containing untreated-CNTs and the electrical conductivity of the nanocomposites were decreased due to the wrapping of non-conductive silane onto CNT surface and well dispersed CNTs.

Jianfeng Shen (2007) observed the reinforcement role of different amino-functionalized multi-walled carbon nanotubes in epoxy nanocomposites. They confirmed that different amino groups on surfaces of the MWNTs have a great effect on the thermal and mechanical properties of the composites. The composites have been greatly affected by the amino groups, which will also have effect on the Tg and onset decomposing temperature of the resulting composites.

Guo Yang et al (2007) studied mechanical properties of modified epoxy resins with flexible diamines. This study provided valuable information for improvement of the mechanical performance of epoxy resins modified with flexible diamines especially at 77 K and hence could help for choosing proper epoxy compositions for cryogenic engineering applications.

Marco Sangermano et al (2007) studied functionalized iron-oxide nanoparticles with epoxy groups and were dispersed into a dicyclo-aliphatic
epoxy resin to obtain organic - inorganic hybrid coatings via cationic ring - opening photo polymerization. Increasing the iron oxide nano-filler in the photo curable resin induced an increase in the Tg values. By controlling the phase separation it was possible to obtain transparent iron-oxide nanostructured coatings, characterized by improved hardnes.

Zhou et al (2008) found that ultrasonic cavitation is an efficient method of infusing carbon nanotubes into epoxy resin when CNT weight fractions are lower than 0.3wt%. Above the 0.3 wt%, agglomerated. The resistivity of epoxy decreased with CNT content, and permittivity increased with increasing of CNT. Flexural modulus steadily increases with a higher CNT weight percent.

Xianhong Chen et al (2008) studied the mechanical and thermal properties of epoxy nanocomposites reinforced with amino-functionalized multi-walled carbon nano tubes and they found that amino functionalized carbon nano tubes act as a curing agent and it increases the mechanical properties such as tensile and impact strength significantly more over it increases thermal properties of the epoxy composites.

Santanu Singha et al (2008) investigated the dielectric properties of epoxy nanocomposites using TiO$_2$, ZnO and Al$_2$O$_3$ as nanofillers. The effect of different experimental parameters like frequency, filler size, and filler concentration was studied. The increasing dielectric characteristics of epoxy based nano dielectric systems were obtained due to large volume fraction of interfaces in the bulk of the material and the ensuing interactions between the charged nanoparticle surface and the epoxy chains.

Meng-Kao Yeh et al (2008) studied fabrication and mechanical properties of multi walled carbon nano tubes /epoxy nanocomposites. In this study they observed the addition of MWNTs in the epoxy matrix increases the
Young’s modulus of MWNTs/epoxy nanocomposites 51.8% for the nanocomposites with 5 wt. % of MWNTs when compared with the neat epoxy matrix. The tensile strength of the MWNTs/epoxy nano composites increase of Young’s modulus becomes slow, while the tensile strength decreases due to non-uniform dispersion for higher volume of MWNTs in epoxy.

Kortaberria et al (2008) analyzed nanocomposites of photo curable epoxy resin and epoxy-modified iron oxide magnetic nanoparticles by dielectric relaxation spectroscopy. Relaxation times did not change with the nanoparticle content, but they noticed that the relaxation strength increased. The increase could not be explained when they take account of the molecular origin of the relaxation. The presence of ferromagnetic nanoparticles enhanced the internal field and increased the relaxation strengths.

Pinho et al (2009) developed a novel composite structure by combining chitosan nanofibres in polymeric matrix using electrospinning technique. The reinforced microfibres were analysed by scanning electron microscopy and showed a considerable alignment of the chitosan nanofibres along the longitudinal main axis of the microfibre composite structure. The tensile mechanical properties revealed that the introduction of the nanofibre reinforcement in the particulate microfibre composite increased the tensile modulus by up to 70 %. The combination of good mechanical properties and enhanced degradability of the developed structures is believed to have great potential for various biomedical applications.

Sridhar Alapati et al (2008) studied electrical treeing phenomena of epoxy resin as the base polymer and silica as the nano filler. Treeing experiments were conducted at a constant AC voltage of 20 kV, 50 Hz on epoxy samples without any filler and with 1% by weight of nano silica fillers.
Time for tree inception as well as tree growth patterns were studied. The results showed that addition of small amount (1% by weight) of nano silica particles in epoxy resin improves the treeing resistance by delaying the tree inception time as well as the time required by the tree to reach the opposite electrode.

Perrin et al (2009) observed water transport in epoxy–aliphatic amine networks – Influence of curing cycles. The fully crosslinked network was found to absorb slightly more water and at a greater rate than a slightly less crosslinked network (conversion around 0.98).

Gautam Das, Niranjan Karak (2009) prepared the epoxy/clay nanocomposites at different clay loadings by using mechanical shearing and ultrasonication. Significant improvement in performance characteristics like curing, mechanical, thermal and chemical resistance of the nanocomposites was observed over the pristine polymer.

Yoshino Sugita et al (2010) studied that experimental investigation of degradation of woven carbon/epoxy lap joints, carbon/epoxy monolithic and structural adhesive specimens due to different fluids: water, jet fuel, hydraulic fluid, anti-icing fuel additive. The results from this study indicate that the fuel additive and hydraulic fluid irreversibly damage the adhesive, with a catastrophic effect on the adhesives hardness and tensile strength at temperatures higher than room temperature.

Abdul Khalil (2010) et al were prepared and characterized epoxy composites containing 5% carbon black (CBs) obtained from agricultural waste materials namely bamboo stem, coconut shell and oil palm empty fruit bunch. The flexural strength and flexural modulus of the carbon black composites values are slightly higher than the value obtained for neat epoxy
polymer and the thermal stability of epoxy composites were enhanced by the addition of 5 wt. % CBs from agricultural waste biomass.

Patankara et al (2011) studied that EPON 862 MWNT nanocomposite was fabricated by dispersing MWNT via sonication. They observed the addition of MWNT has a positive impact on the glass transition temperature, tensile as well as the thermomechanical behavior of EPON 862 resin.

Shree Meenakshi, Pradeep Jaya Sudhan (2011) developed high functionality epoxy resin namely TGDDM (Tetra Glycidylether of Diamino Diphenyl Methane). These epoxies were cured with DDM (Diamino Diphenyl Methane) and BAPPO respectively, with and without the incorporation of nanoclay (Nanomer 1.30 E) and nano reinforcement (POSS-amine) to get matrix materials to be utilized for high performance applications. The developed materials were characterized by spectral studies to ascertain their structures. They found novel organic–inorganic nano hybrid composites having improved mechanical, thermal properties being self extinguishable, heat resistant at the same time with excellent dielectric properties.

Isik et al (2003) prepared modified epoxy/montmorillonite nanocomposites. They observed that the polyol modified epoxy (with no montmorillonite) the impact strength increases as the polyether polyol content increases. However, in the epoxy–montmorillonite binary systems (with no polyol), impact strength shows a maximum at 1 wt % montmorillonite content. In epoxy–montmorillonite–polyether polyol ternary systems, the impact strength, in general, decreases with respect to increasing amount of montmorillonite. DSC analyses indicate that $T_g$ increases with the addition of montmorillonite, and exhibits a maximum with respect to the polyether polyol content.
Chena et al (2003) prepared epoxy layered-silicate nanocomposites. They found the disappearance of the ordered structure of the layered silicate in the beginning of the curing process, and reappearance of the ordered structure of the silicate later, is related to the epoxy resin curing process surrounding the silicate nanosheets. The solvent uptake for the nanocomposites is significantly low compared with the pristine polymer.

Becker et al (2004) studied the thermal stability and water uptake of high performance epoxy layered silicate nanocomposites. They observed the nanocomposites of thermal stability were decreased, as indicated by a decreased onset in thermal degradation in the order of 5–10° C at a clay concentration of 10 %. The final char concentration was increased with increasing organoclay concentrations. The cone calorimetry indicates that significant decreases in heat release rate occur upon addition of nanoclays.

Sue et al (2004) studied the fracture behaviors of a-zirconium phosphate (a-ZrP) based epoxy nanocomposites, with and without core-shell rubber (CSR) toughening. The fracture process in epoxy nanocomposite is dominated by preferred crack propagation along the weak intercalated a-ZrP interfaces, and the presence of a-ZrP does not alter the fracture toughness of the epoxy matrix. However, the toughening using CSR can significantly improve the fracture toughness of the nanocomposite. The fracture mechanisms responsible for such a toughening effect in CSR toughened epoxy nanocomposite are rubber particle cavitation, followed by shear banding of epoxy matrix.

Aidah Jumahata et al (2012) studied the compressive properties of nanoclay/epoxy nanocomposites. The performance of the nanocomposites was evaluated via static uniaxial compression tests. They found that the nanocomposites offer higher compressive stiffness when compared to the neat polymer. This mainly contributed by the high stiffness nanoclay. However,
the presence of clusters of intercalated nanomer and nanovoids reduced the compressive strength of the epoxy system. A weak interfacial adhesion between nanofillers and the matrix and the presence of nanovoids may initiate the premature failure of the system.

Barabanov et al (2012) observed the epoxy/silica nanocomposites increased glass transition temperatures as compared to cured epoxy. These results can be explained by the plasticizing effect of the epoxy homopolymer.

Alamri et al (2013) studied the effect of water absorption on the mechanical properties of nanoclay filled recycled cellulose fibre (RCF) reinforced epoxy hybrid nanocomposites. They found water absorption of RCF/epoxy composites was increase dramatically due to the presence of hydrophilic cellulose fibre. However water uptake decreased progressively due the incorporation of nanoclay. Exposure to moisture for long term resulted in significant reduction in flexural strength, flexural modulus and fracture toughness due to the degradation of the fibre–matrix interface. Comparing to dry composites, impact strength and impact toughness of wet composites surprisingly increased due to the plasticization effect of adsorbed water. The presence of nanoclay platelet was found to slightly minimize the effect of moisture on the mechanical properties of the composites by improving the flexural strength, flexural modulus and fracture toughness properties of the composites.

Yuqi Li et al (2013) prepared graphene oxide nanosheets (GONS) reinforced PU/EP composites by in situ polymerization. With the incorporation of 0.066 wt% of GONS, the tensile strength, tensile modulus of nanocomposites was increased. This revealed that strong interfacial interaction with the polymer matrix with GONS.
1.18.3 Kevlar/Glass Fibre Reinforced Epoxy Nanocomposites

Kazuto Tanaka et al (2002) investigated the influence of water absorption on the interfacial properties of aramid/epoxy composite. They observed that the interfacial strength of aramid/epoxy composite was decreased by 26% after 7 week immersion time in deionized water at 80°C. The change of the interfacial strength with immersion time did not correspond with that of the water gain in pullout specimens, because the water gain did not reflect the one in the fiber/matrix interface.

Szabo et al (2004) studied the effect of fibre surface treatment on the mechanical response of ceramic fibre mat-reinforced interpenetrating vinylester/epoxy resins. They found the fibre surface treatment strongly affects stiffness, strength and fracture toughness of composites. This was traced to chemical reactions between the functional groups of the coupling agents and matrix constituents (vinyl or epoxy resins), which control the interface (phase) properties.

Srivastava et al (2005) studied the effects of flyash filler, impingement angle and particle velocity on the solid particle erosion behaviour of E-glass fibre reinforced epoxy (GFRP) composites. They found the inclusion of flyash filler in the GFRP composite decreases the hardness, the tensile strength as well as the density. The erosive wear of 4 g flyash filled GFRP gives the lower value as it restricts fibre–matrix debonding. GFRP without any filler showed the highest erosion rate due to weak bonding strength.

Lin et al (2006) layered silicate/glass fiber/epoxy hybrid composites were prepared using a vacuum-assisted resin transfer molding (VARTM) process. The epoxy/clay hybrids showed good impregnation when unidirectional glass fibres were aligned in the longitudinal direction. When
the glass fibres were placed in the transverse direction, air bubbles were readily entrapped during resin flow, negatively affecting the properties of the hybrid. However, fairly uniform distributions of clay were observed for both directions of resin flow, that is, along and perpendicular to the fiber direction. XRD and TEM revealed the intercalation structure of the clays in the epoxy resin, which greatly influenced the molecular mobility of the epoxy.

Chaowasakoo et al (2007) studied the Mechanical and morphological properties of fly ash/epoxy composites using conventional thermal and microwave curing methods. The conventional thermal curing was performed at 70° C for 80 min while microwave curing was carried out at 240 W for 18 min in order to achieve the optimum cure of the composites. They found that tensile and flexural moduli of the fly ash/epoxy composites were observed to increase with increasing fly ash content whereas the mechanical (tensile, flexural and impact) strengths, and tensile strain at break of the composites progressively reduced with fly ash content. It was recommended that 0.5 wt% coupling agent be added into of the fly ash/epoxy composites for optimization of the mechanical properties.

Gang et al (2008) prepared phosphoric acid (PA) functionalized Kevlar fiber and epoxy matrix for filament winding composites. They found the amount of surface oxygen and hydroxyl groups of Kevlar fiber can be much increased by 20 wt% phosphorus acid fictionalization. The monofilament tensile strength of Kevlar fiber was constant until the fictionalizations of 40 wt% PA, while it linearly increased as PA concentration was over 40 wt%. Owing to the increase of polar functional groups on the fiber surface, the compatibility between resin matrix and PA-functionalized Kevlar fiber can be improved greatly.

composites. They observed that the air–plasma treatment of Kevlar fabric increases the antiwear, friction-reducing abilities and load-carrying capacity of Kevlar fabric/phenolic composites. Some active groups were introduced on the surface of Kevlar fabric and the roughness of the fiber surface increased, which enhances the adhesion between the Kevlar fabric and phenolic adhesive. As a result, the tribological performance of the Kevlar fabric/phenolic composites with air–plasma-treated Kevlar fabrics has been improved significantly.

Fang Guo et al (2010) studied the tribological behavior of spun kevlar fabric composites filled with fluorinated compounds. They found that tribological behavior of spun Kevlar depends on the concentration of on the content and distribution of the filler, and is best as composites contain 15 wt% PFW (polyfluo wax) and 5 wt% LaF$_3$, respectively. Because of the low melting temperature and self-lubrication of the PFW filler, the transfer film of the spun Kevlar fabric composite filled with 15wt% PFW is compact, uniform and smooth, corresponding to the best friction and wear abilities of the composite.

Manjunatha et al (2010) studied the tensile fatigue behaviour of silica nanoparticle-modified glass fibre reinforced epoxy composites. They observed that the fatigue life of 10 wt.% silica nanoparticle-modified bulk epoxy is about three to four times higher than that of neat epoxy. Silica nanoparticle debonding and subsequent plastic void growth absorb energy and contribute towards the enhanced fatigue life for the nanoparticle-modified epoxy.

Reis et al (2012) studied the impact response of Kevlar composites with cork powder and nanoclays Cloisite 30B filled epoxy matrix. They found that adding clays damaged area increases relatively to the control samples around 29 %. In opposite the cork powder promotes small damage area
around 20%. The filler increases the residual strength and the better results were obtained when nanoclays added.

Ramesh et al (2013) studied the comparative evaluation on properties of hybrid glass fiber- sisal/jute reinforced epoxy composites. They found that the sisal/GFRP composite samples possess good tensile strength and can withstand the strength up to 68.55 MPa. The jute/GFRP composite specimen is holding the maximum flexural load of 1.03 kN slightly higher than the sisal/GFRP composite sample. From the results, it can be concluded that sisal-GFRP composites performing better for tensile loading and jute-GFRP composites perform better for flexural loading.

1.19 SCOPE OF THE PRESENT INVESTIGATION

Though these studies result more useful information but still it requires more modification and systematic approach to evaluate the overall performance of the modified systems. A detailed work is needed to develop the unsaturated polyester modified epoxy hybrid matrix systems in order to obtain matrix systems with high tensile and flexural properties, hardness and good thermal stability.

- To develop unsaturated polyester modified epoxy hybrid matrix system
- To prepare siliconized iron (III) oxide nanoparticles.
- To prepare siliconized iron (III) oxide nanoparticles reinforced UP toughened epoxy nanocomposites.
- To prepare glass and Kevlar fibre reinforced epoxy filled siliconized iron (III) oxide nanocomposites.
- To study the structural characteristics of unsaturated polyester toughened epoxy matrix using FT-IR spectroscopy

- To study the mechanical properties of siliconized iron (III) oxide nanoparticles reinforced UP toughened epoxy nanocomposites and glass/Kevlar fibre reinforced nanocomposites with SEM images.

- To study the thermal behavior of siliconized iron (III) oxide nanoparticles in unsaturated polyester toughened epoxy matrices.

- To study the effect of siliconized iron (III) oxide nanoparticles content in UP toughened epoxy matrix on the electrical properties.

- To study wear behavior and water absorption studies of siliconized iron (III) oxide nanoparticles in UP toughened epoxy nanocomposites.