CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION TO NANOSCIENCE AND NANOTEchnology

The nano world is frequently defined for materials where some dimension is on the order of 1 – 100 nm. Nature has offered nanomaterials since the beginning of time and much of the inorganic part of our soil is a nanomaterial with the ability to filter out particles often at a molecular or nanolevel.

A nanometer is one-billionth of a meter (10^{-9} m); a sheet of paper is about 100,000 nanometers thick and is about four times the diameter of an atom. The diameters of a few interesting materials are (i) a human red blood cell is 10,000 nm, (ii) a cell of the bacterium E. coli is 1000 nm, (iii) a viral cell is 100 nm, (iv) a polymer coil is 40 nm, (v) a Q-rod is 30 nm with a 10:1 aspect ratio, and (vi) a quantum dot (QD) is 7 nm in diameter. The driving force toward many of the nanomaterials is that they can offer new properties or enhanced properties which otherwise would be unobtainable with so-called traditional bulk materials. Some ubiquitous features such as small size, light weight and high strength-to-weight features, new properties may emerge because of the very high surface area to mass, where surface atomic and molecular interactions become significant.
Encompassing nanoscale science, engineering, and technology involves imaging, measuring, modeling, and manipulating matter at this length scale. At this level, the physical, chemical, and biological properties of materials differ in fundamental and valuable ways from the properties of individual atoms and molecules or bulk matter. Nanotechnology is directed towards understanding and creating improved materials, devices, and systems that exploit these new properties.

Wavelike (quantum mechanical) properties of electrons inside matter and atomic interactions are influenced by materials variations on the nanometer (nm) scale. By creating nanometer-scale structures, it is possible to control the fundamental properties of materials, such as their melting temperature, magnetic properties, charge capacity, and even their color, without changing the material’s chemical compositions. Use of this potential behaviour can lead to fabricate a very novel and high-performance products and technologies that would not possible before.

For decades researchers have been dealing with mostly macrocomposites such as fibre reinforced polymers, where the length scale of the polymer fillers is in the micrometer range. Nanophase and nanostructured materials in polymers, as a new branch of materials research have attracted a great deal of attention because of its potential applications in areas such as electronics, optics, catalysis, ceramics, magnetic data storage, and nanocomposites. Polymer nanocomposites have nanoscale structures with nanoparticles and nanolayers where the length scale of the reinforcement (nanoparticles) is in nanometer scale with ultra large interfacial area per volume, and the distances between the polymer and filler components are extremely short. Most of polymer coils and nanoparticles have diameter of the order 40nm, as a result, molecular interaction between the polymer and the nanoparticles will readily offer polymer nanocomposites with unusual
material properties which conventional polymers do not possess. The role played by particle size is comparable to the role of the particle’s chemical composition in addition to other parameter for designing and controlling particle behavior. The excitement surrounding nanoscale science and technology gives us unique opportunities to develop revolutionary materials. To fully understand the impacts of nanomaterials in nanoscale science and technology, one needs to know the significance of nanomaterials and its advantages.

1.2 NANOMATERIALS

Nanomaterials can be classified into nanostructured materials and nanophase/nanoparticles. The former usually refer to condensed bulk materials that are made of grains (agglomerates), with grain sizes in the nanometer size range, whereas the latter are usually the dispersive nanoparticles. The nanometer size covers a wide range, from 1 nm to as large as 100 to 200 nm. To distinguish nanomaterials from bulk, it is crucial to demonstrate the unique properties of nanomaterials and their prospective impacts in science and technology. The introduction of inorganic nanoparticles as additives into polymer systems has resulted in polymer nanocomposites (PNs) exhibiting multifunctional, high-performance polymer characteristics beyond what traditional filled polymeric materials possess. The development of these new materials will enable the circumvention of classic material performance trade-offs by accessing new properties and exploiting unique synergies between materials, that only occur when the length scale of morphology and the fundamental physics associated with a property coincide, i.e., on the nanoscale level. Multifunctional features attributable to polymer nanocomposites consist of improved thermal and moisture resistance, decreased permeability, charge dissipation, and chemical resistance. Through control/alteration of the additives at the nanoscale level, one is able to
maximize property enhancement of selected polymer systems to meet or exceed the requirements of current military, aerospace, and commercial applications. The technical approach involves the incorporation of nanoparticles into selected polymer matrix systems by surface-treatment of nanoparticle to provide hydrophobic characteristics and enhanced inclusion into the hydrophobic polymer matrix.

The value of polymeric nanostructured materials (PNM’s) technology which is not only based on mechanical enhancements of the neat resin but also its value addition, without sacrificing the inherent processability of the neat resin. Traditionally, the preparation of a blend or composite with multifunctionality requires a trade-off between desired performances, mechanical properties and cost. Development of multifunctional nanomaterials requires a balance in the four interdependent areas simultaneously: constituent selection, processing, fabrication, and performance. Two main PNM’s processing methodologies have been developed: 1) in situ routes and 2) exfoliation. Currently, exfoliation of layered silicates, carbon nanofiber/nanotubes, and polyhedral oligomeric silsesquioxanes (POSS) are used in commodity and high-performance resins which are also the most investigated PNM’s by government, academic, and industrial institutions all over the world.

1.3 ROLE OF POSS IN NANOTECHNOLOGY

Silsesquioxane exist in a variety of structures, including random polymers, ladders, and more ordered cage structures, but polyhedral oligomeric silsesquioxanes (POSS), with their nanosized cage structures, are widely regarded as some of the most promising and rapidly emerging nanocomposite materials. These three-dimensional organosilicon oligomers
are formed by complete hydrolytic condensation of their trifunctional monomers (Scheme 1.1).

Polyhedral oligomeric silsesquioxanes (POSS) are a class of nanofillers for polymers. POSS nanocube is also used as a nanoprecursor for the development of polymer nanocomposites due to the following properties:

- The chemical composition is a hybrid, intermediate \((RSiO_{1.5})_n\) between that of silica \((SiO_2)\) and silicone \((R_2SiO)_n\).

- POSS molecules are physically large with respect to polymer dimensions and nearly equivalent in size to most polymer segments and coils.

POSS molecules can be thought of as the smallest particles of silica possible. However unlike silica or modified clays, each POSS molecule contains covalently bonded reactive functionalities suitable for polymerization or grafting POSS monomers to polymer chains. Each POSS molecule contains nonreactive organic functionalities for solubility and compatibility of the POSS segments with the various polymer systems. The chemical diversity of POSS technology is very broad and a large number of POSS monomers and polymers are currently available or undergoing development.

POSS chemical technology is easy to use with monomers available in both liquid and solid form and they are solubie in most common solvents. Hence, POSS technology can be used in the same manner as common organics, in either monomer or polymeric (resin) form. POSS chemical feedstocks can be added to nearly all polymer types (glassy, elastomeric, rubbery, semicrystalline and crystalline).
Enhancements in the physical properties of polymers incorporating POSS segments result from POSS ability to control the motions of the chains while still maintaining the processability and mechanical properties of the base resin. This is a direct result of POSS nanoscopic size and its relationship to polymer dimensions.

A second generation of porous, high-strength, spin-on dielectrics with $k<3$ is being based on polyimide/polysilsesquioxane nanocomposites. It has been noted that POSS frameworks are strong electron-withdrawing substituents. Consequently, the nonlinear optical properties of H-POSS systems are being explored. Also, it might be fruitful to explore the incorporation of POSS frameworks as pendants to conjugated polymer chains to tune the electronic band-gap and hence the light-emitting properties of the conjugated polymer. Light emitting diodes (LEDs) based on such inorganic–organic, hybrid, light-emitting polymers could offer significant performance and lifetime advantages over polymer light emitting diodes (PLEDs). Numerous other applications of functionalized POSS frameworks are being proposed: membranes for gas separations; resists for EB lithography; and optical waveguides-leading to advances in multicomponent composite material systems.

The nanosized synthetic platforms can be modified to contain groups for copolymerization, adhesion, light sensitization, binding catalysts, and liquid crystalline properties. The chemistry of the apex silicon atoms particularly, organic transformations at one of the eight apices in the octasilsesquioxane ($T_8$) structures, has been extensively reported, yielding 1 where $R'\neq R$. If $R'$ is a reactive functional group, while the other seven functional groups ($R$) are nonreactive, the resulting monofunctional POSS monomer can be copolymerized with standard organic monomers to yield nanocomposite copolymer alternatives to silica-reinforced plastics, allowing
single-phase composite processing. The $T_{8}$ structure has been suggested as a model for silica surfaces. Polysilsesquioxane foams, which cannot be prepared directly because of low $T_{g}$’s, have been prepared by a base-catalyzed disproportionation reaction of polyhydridosiloxanes that also generated a chemical blowing agent.

1.4 DEVELOPMENT OF POSS AND SILICA BASED HYBRID MATERIALS

Organic-inorganic hybrid nanocomposites with well defined architectures have attracted increasing attention because of their potential to provide materials with controlled morphology at nanometer scale. These organic-inorganic hybrid nanocomposites exhibit many unique multifunctionality arising from the organic and inorganic components. Polyhedral oligomeric silsesquioxane have emerged as a new class of organic-inorganic hybrid materials that possess a synergistic combination of the constituent properties. Recently, it has been demonstrated that octafunctional cubic silsesquioxane (a derivative of POSS), regarded as nanobuilding blocks, offers an efficient route in developing novel hybrid nanocomposites (Scheme 1.2). The cubic silsesquioxane has a well-defined nanometer-sized structure with high surface area, controlled porosity, and various functionalities. It consists of a rigid, hollow silica-like core with 0.53 nm body diagonal and the eight equally reactive functional groups that link covalently to its eight vertices. Due to the stable silica structure and controllable functionalities, polyhedral oligomeric silsesquioxane (POSS) has been widely utilized to fabricate hybrid materials with enhanced thermomechanical properties, good thermal stability, chemical resistance, oxidation resistance, resistance to atomic oxygen in low earth orbit (LEO), abrasion resistance, glass transition temperature, mechanical properties, dielectric behaviour, optical properties, weather resistance and low water uptake.
POSS cube offer potential access to numerous nanostructures for a wide variety of applications including the development of:

- Core-shell architectures,
- Dendrimers and hyperbranched materials
- Janus (two faced) particles
- Porous materials for
  - Low-k dielectrics
  - Encapsulants for drug delivery
  - Confined space catalytic studies
  - Hydrogen storage
  - Gas and liquid separations
  - Pollutant trapping
  - Analytical applications (for column chromatography, concentrations, etc.)
- Highly polyfunctional materials
- Novel functional coating systems.

Hybrid materials (Scheme 1.3) (Clement et al 2005) are developed by using POSS nano precursor by melt-intercalation, solvent method or in situ polymerisation method. These POSS nanocubes are incorporated into the
polymeric materials through physical interactions, covalent bonding and without any bonding simply acts as fillers are purely depends on the organic moiety attached to the POSS units. Thus POSS based polymer hybrid nanocomposites can be prepared by grafting, blending, copolymerization and sol-gel methods.

Another type of development of hybrid organic-inorganic materials is mainly due to the development of soft inorganic chemistry processes, especially sol-gel processes, where mild synthetic conditions allow versatile access to chemically designed combinations of inorganic domains.

Organic-inorganic hybrids exhibiting specific properties are easily prepared by incorporation of organic fragments in an inorganic network. The increasing attention is being paid to hybrid silsesquioxane gels, which are prepared by sol-gel hydrolysis condensation of organic molecules containing two or more trialkoxysilyl substituents. These hybrids consist of a mixed three-dimensional network, where the organic fragment, cross-linking siloxane chains, is part of the framework. Owing to the presence of a strong Si-C bond between the organic and the inorganic fragments, highly stable hybrid network are produced in this way. A variety of materials can be
produced according to the intrinsic properties of the organic polymers. Hence sol-gel technique is a convenient method for the synthesis of nano-ordered composite materials consisting of organic polymers and inorganic compounds.

Scheme 1.3 Scheme of the main chemical routes for the synthesis of organic-inorganic hybrids

1.5 SOL-GEL PROCESS

The sol-gel process in general is based on the transition of a system from a liquid solution "sol" (mostly a colloidal suspension of particles) into a gelatinous network "gel" phase. It is a long-established industrial process and is very cost-effective and versatile.
With this, it is possible to create at low temperature ceramic or glass materials in a wide variety of forms. It has been further developed in the recent past for the production of:

1) advanced nanomaterials and coatings
2) oxide nanoparticles
3) composite nanopowders
4) organic-inorganic materials.

The advantage of the sol-gel technique for the preparation of composite materials is the fact that the reactions can be carried out at ambient temperature, while the conventional melt fusion technique for silica glasses requires high temperature. Further its versatility and the possibility to obtain high purity materials (shaped as monolithic blocks, powders or thin layers), the composition of which is perfectly controlled.

The sol-gel reaction of metal alkoxide is the most practical technique for the synthesis of these hybrid materials. The method comprises initial hydrolysis of the metal alkoxides and subsequent condensation and removal of the solvent, resulting in metal oxides. This process makes it attractive for application in the formation of organic-inorganic hybrid composite materials with molecular domain size.
The sol-gel technique is mainly based on hydrolysis of liquid precursors and formation of colloidal sols. The precursors are usually organosilicates (e.g. TEOS - tetraethoxysilane) yielding silicate sol-gel materials. However, the method is not restricted to the silicon compounds - for example compounds of zirconium, vanadium etc. can also be used as precursors leading to materials possessing different physico-chemical properties. Furthermore, it is possible to obtain modified organosilicate precursors with direct Si-C bonds (which do not undergo hydrolysis) and possessing terminal functional groups (e.g. -NH_2, -SH_2 etc.). Such precursors, either pure or mixed with the conventional ones, yield organic-inorganic materials with improved mechanical (e.g. elasticity) and physico-chemical properties. The functional groups can be also used for covalent bonding of various chemicals (including biomolecules) giving specifically modified glassy materials.

In order to obtain waveguide or a bulk glass, various routes may be used. Among the available techniques, the sol-gel process is undoubtedly the simplest and the cheapest one. The method is based on the phase transformation of a sol obtained from metallic alkoxides or organometallic precursors. This sol, which is a solution containing particles in suspension, is polymerized at low temperature to form a wet gel. This one is going to be
densified through a thermal annealing to give an inorganic product like a glass, polycrystals or a dry gel.

The hybridization of different materials accomplishes the creation of new materials. Especially, it has been found that the obtained hybrid materials show unique properties compared with the microscale composites when different materials hybridize under nanomaterials scale. From the viewpoints of versatility of synthesis, properties, and broadness of the scope of application, these materials have raised a great deal of scientific, technological, and industrial interests and have led the research in materials science in a new direction. The obtained sol-gel based hybrid materials show not only organic and inorganic properties but also attractive novel properties resulted from hybridization at the nanometer level. Thus, they are considered as innovative advanced materials and promingly applied for many fields such as optics, coatings, electronics, mechanics, sensors, biomedical and membranes.

1.6 APPLICATIONS OF ORGANIC-INORGANIC HYBRID POLYMERS

Organic-inorganic polymer hybrids show both organic and inorganic properties. The properties of organic polymer include high flexibility, versatility in design of functionality and film-forming property, and so on. The inorganic compounds provide the potential for high tensile strength, good gas barrier property, high thermal and mechanical stabilities, Bulk properties of polymer hybrids depend on ratio of organic polymer and inorganic materials. Therefore, the properties of polymer hybrids can be easily controlled. Organic-inorganic polymer hybrids can be applied as adhesive between organic and inorganic materials because of high compatibility with both class of materials. Furthermore, nano-scale hybrid
materials offer different chemical and physical properties, which are different from those of single materials. Transparency of polymer hybrids is one of the most striking feature of the hybrid materials. Scattering loss is avoided because of the dispersion of components in the order of nanometers. Gas barrier property of polymer hybrid also increases when compared with that of silica gel (without organic polymer). Usually, silica gel prepared from sol-gel method is low density and high roughness on the nano-meter scale because of the shrinking derived from removing molecules such as water and alcohol. On the other hand, polymer hybrids form high density and smooth surface at the molecular scale due to molecular level dispersion of organic polymer in silica gel matrix. In addition, the surface hardness and abrasion-resistance of silica gel also increase by hybridization with organic polymer at the nano-meter level.

One of the novel properties of organic polymer by hybridization with silica gel on the nano-meter scale is flame-resistance. Inorganic materials, which are mixed with organic polymer on the nano-meter scale, inhibit the flame spreading between organic polymer chains. As mentioned above, the density of hybrid materials is so high that the solvent resistance property of polymer hybrids also increases. The novel properties of organic-inorganic polymer hybrids can be improved by controlling the polymer hybrid structure. Formation of organic polymer gel in silica gel matrix can be achieved. One is stepwise IPN method; after preparation of semi-IPN structure converted to IPN by crosslinking between polymer chains. The simultaneous IPN procedure is formation of organic polymer gel during the sol-gel reaction of alkoxysilane. The obtained IPN structured polymer hybrid show as excellent solvent resistance compared with semi-IPN structured polymer hybrids due to strong interpenetration between the organic polymer gel and silica gel. Polysilane-silica hybrid thin films displayed higher
durability to photo-degradation when compared with non-hybrid polysilane films (Matsuura et al 2003).

1.7 TYPE OF INTERACTION IN SOL-GEL HYBRIDS

The physical interactions normally exist between organic polymer and inorganic solid phases are hydrogen bonding, ionic, and \( \pi-\pi \) interactions. The physical interactions such as ionic, electron donor acceptor, CH-\( \pi \) interactions between organic polymer and silica also exist in various kinds of transparent polymer hybrids involving covalent bond were previously reported (Schmidt 1994). Bridging between organic polymer and inorganic phases through covalent bonding is one of the useful preparative methods.

In-situ method for preparation of organic-inorganic polymer hybrids: To overcome the phase separation between organic and inorganic phases, in-situ method is one of the useful and convenient techniques. One of the in-situ methods is simultaneous polymerization of organic monomer during the formation of silica gel from hydrolysis and condensation hydrolysis and condensation of metal alkoxides.

Application of polymer hybrids for biomaterials has also been reported (Clement 2005). It’s already known that biocompatibility of artificial bone or dental materials were increased by covering its surface with hydroxyl carbonate apatite. To form the hydroxyl carbonate apatite on the surface of these materials, calcium salts (source of hydroxyl carbonate apatite) and nucleation site are necessary. Polymer hybrids with poly(methacryloxypropyl trimethoxysilane-co-2-hydroxyethyl methacrylate) containing calcium salts formed perfectly hydroxyl carbonate apatite on the surface of polymer hybrids by soaking the hybrid in simulated body fluid for 1 week. The silanol moieties
resulted from hydrolysis of alkoxy silane acted as a nucleation site for hydroxyl carbonate apatite (Ruben 2006).

1.8 RESIN MATRICES

1.8.1 Epoxy resin

In the late 1930s Piere Castan of Switzerland and Sylvian Greenlee from the United States independently synthesized the first bisphenol-A epichlorohydrin-based resin material. A few years later in 1946, the first industrially-produced epoxy resins were introduced to the market. Since then, the use of thermosetting polymers has steadily increased. The wide variety of epoxy resin applications include: coatings, electrical, automotive, marine, aerospace and civil infrastructure as well as tool fraction and pipes and vessels in the chemical industry. Due to their low density of around 1.3g/cm$^3$ and good adhesive and mechanical properties, epoxy resins became a promising material for high performance applications in the transportation industry, usually in the form of composite materials such as fibre composites or in honeycomb structures. In the aerospace industry, epoxy-composite materials can be found in various parts of the body and structure of military and civil aircrafts, with the number of applications on the rise. A recent approach to improve and diversify the polymer properties in the aerospace industry is through the dispersion of nanometer-scaled fillers in the polymer matrix. A significant number of academic and industrial projects have been investigated to improve the properties of epoxy resins through the strategy of producing nanocomposites.

The term ‘epoxy resin’ refers to both the prepolymer and its cured resin/hardener system. The former is a low molecular weight oligomer that contains one or more epoxy groups per molecule (more than one unit per
molecule is required if the resultant material is to be cross linked). The characteristic group, a three-membered ring known as the epoxy, epoxide, oxirane or glycidyl group is highly strained and therefore very reactive. Epoxy resins can be cross-linked through a polymerization reaction with a hardener at room temperature or at elevated temperatures. Curing agents used for room temperature cure are usually aliphatic amines, whilst commonly used higher temperature, higher performance hardeners are aromatic amines and acid anhydrides. However, an increasing number of specialized curing agents, such as polyfunctional amines, polybasic carboxylic acids, mercaptans and inorganic hardeners are also used. All of these result in different, tailored properties of the final polymer matrix. In general, the higher temperature cured resin systems have improved properties, such as higher glass transition temperatures, strength and stiffness, compared to those cured at room temperature.

1.8.2 Cyanate ester

Cyanate esters are a potential candidate for high temperature adhesives and composites matrices. The cyanate esters are crosslinked thermosetting material which has good adhesive nature along with good thermal and mechanical properties.

Cyanate esters have evinced a lot of interest in high-performance applications in view of their attractive physical, high thermal stability, excellent mechanical and electronical properties. These resins are high temperature thermosets and in widespread use including structural aerospace, electronic and microwave-transparent composites. Thus, they have been used in high performance electronic devices and aerospace applications. A large variety of cyanate ester resins with different backbone structures and properties are available. Among them, bisphenol A dicyanate (BACY) is very
versatile and is an ideal thermoset resin possesses most of the above properties. Since the typical preparation method of cyanate (CE) resin, synthesized by phenol and cyanogen halide, was reported by Grigat on a patent in 1964, it is widely used everywhere.

Cyanate esters are remarkable in that they polymerize via a cyclotrimerisation reaction to form a high degree of efficiency, the use of metallic or amine catalyst can reportedly achieve conversions greater than 98%. In practice, cyanate ester resins are usually cured by a transition metal carboxylate, or chelate catalyst, in the presence of an active hydrogen co-catalyst such as nonylphenol. Despite the importance of cyclotrimerisation, the mechanism of the reaction is uncertain, it is from cyclotrimerisation of a species where three cyanates are co-ordinated to a metal ion in sufficiently close proximity to allow ring closure to occur by either a step-growth or anion-initiated ionic mechanism. Most of the research into cyanate cyclotrimerisation has centered on the search for dimeric intermediates.

The attractive range of properties of cyanate esters makes them prime candidate for use in a variety of applications from microelectronics to aerospace. Aerospace applications include high temperature adhesives and matrix resins for structural components. Electronic applications include printed wiring circuit boards, multichip laminates, and chip encapsulates. Their transparency to microwave and radar energy makes them suitable for the conical radome nose cones that house radar antennas of military and weather reconnaissance planes. Micro crack resistance and impact resistance characteristics of cyanate ester find useful for communication satellites, aircrafts structures and engine pistons. Cyanate ester resins and composites find their way mainly into high-value applications where performance at whatever cost is critical. Cyanate ester (CE) resins have been widely used in high signal speed printed circuit boards, high performance electromagnetic
wave penetrated structural components and aerospace structural composites due to their many excellent performances, such as low dielectric losses, good adhesive and mechanical properties, resistance to hot/wet conditions, and processability. However, they have the fatal drawback of brittleness caused by the highly crosslinked three-dimensional structures in the cured CE resins. Hence, toughness behaviour of cyanate esters needs improvement using appropriate polymeric modifiers to utilize them for improved longevity and high performance applications.

1.8.3 Unsaturated polyester

The actual preparation of the first polyester resin is accredited to both Berzelius in 1847 and Gay-Lussac and Pelouze in 1883. The unsaturated polyester (UP) resins used in today’s reinforced plastics (RP) are combinations of a number of reactive monomers. Carleton Ellis discovered that unsaturated polyester resins made by reacting glycols with maleic anhydride could be cured to insoluble solids by adding a peroxide catalyst. Later it was discovered by combining the unsaturated polyester alkyd with reactive monomers as vinyl acetate (or) styrene, which makes it easier to add the catalyst and apply the resin. Polyester resins are typically reaction products of a dicarboxylic acid, acid halide (or) anhydride, with a polyhydric alcohol. The unsaturated polyester is made using diols and mixture of saturated and unsaturated diacids. Such acids include maleic acid (or) anhydride, terephthalic acid, hexahydrophthalic acid (or) anhydride, adipic acid, isophthalic acid etc., Maleic acid or anhydride and fumaric acid are the most widely used.

UP represent one of the most commercially important thermoset matrices used to fabricate composites employed for engineering and industrial applications. Unsaturated copolyesters, also called polyester resins, are based
on macromolecules with a polyester backbone in which both a saturated acid and unsaturated acid are condensed with a dihydric alcohol. UP resin is a thermoset capable of being cured from a liquid or solid state when subjected to the set of conditions. Styrene is the most commonly used diluent that links the polyester chains to form strong three dimensional polymer networks. The addition of styrene in amounts of up to 50% helps to make the resin easier to handle by reducing its viscosity. The styrene also performs the vital function of enabling the resin to cure from a liquid to a solid by ‘cross-linking’ the molecular chains of the polyester, without the evolution of any by-products when cured with accelerator and catalyst. Polyester resins have a limited storage life as they will set or ‘gel’ on their own over a long period of time. Often small quantities of inhibitor are added during the resin manufacture to slow this gelling action. There are two types of polyester resin used in composite industry. Orthophthalic polyester resin is the most commonly used standard economic resin and isophthalic polyester resin is the preferred material in industries such as marine where its superior water resistance is desirable.

UP resins may be cured by means of an initiator and low viscosity cross-linking monomer. Monomers have ethylenic unsaturation such as monostyrene, alkyl acrylates and methacrylates, substituted styrenes such as α-methyl styrene, α-chloro styrene, 4-methyl styrene, acrylonitrile etc. Styrene is the preferred monomer for commercial use. Initiators include t-butyl hydroperoxide, t-butylperbenzoate, benzoylperoxide, methyl ethyl ketone (MEK) peroxide etc. The polymerization initiator is employed in a catalytically effective amount, such as from about 0.3 to about 2 to 3 weight percent, based on the weight of polystyrene and the crosslinking monomer.

The curing of a polyester resin can be considered to take place in three stages.
1. Gelation - where the resin changes from a free-flowing liquid to a soft gel
2. Hardening - where the resin cures from a soft gel to a hard material
3. Final curing - where the resin achieves its full mechanical and chemical properties.

Catalysts or initiators for unsaturated polyester resin system consist of organic peroxides. Organic peroxides are of two types - the true peroxides such as benzoyl peroxide and the hydroperoxides such as cumene peroxides. The most commonly used peroxides at room temperature cure are MEK peroxide; cyclohexanone peroxide and acetylacetone benzoyl peroxide. For elevated temperature cure, benzoyl peroxide is frequently used.

1.8.4 Polystyrene

**General Purpose Polystyrene (GPPS)** is water clear polystyrene with generally higher melt flow for optimum injection molding. Typical applications include disposables such as cutlery, plates and cups as well as medical and laboratory parts, jewel boxes, CD cases, electronic packaging and office accessories.

Polystyrene is an important commodity thermoplastic and finds wide range of applications because of its superior properties like easy processability, transparency, good electrical properties and low cost. However its application is limited because of its brittleness, low heat distortion temperature and poor weathering resistance. To improve impact properties of polystyrene, high impact polystyrene (HIPS) was developed by using polybutadiene and styrene. HIPS possess improved impact strength with limited thermal stability and weathering resistance. In order to achieve further
improvement in weathering resistance, nanofillers have been introduced into the polystyrene matrices.

1.9 REVIEW OF LITERATURE

Voronkov and coworkers (1982) reviewed the methods for synthesizing different types of POSS compounds and their characterization.

Feher and Newman (1989) have reported the synthesis of silsesquioxanes by the controlled hydrolysis and condensation of commercially available organotrichlorosilanes and characterized them through spectral studies.

Adam Chaplin et al (1994) synthesized a range of allyl-functionalized cyanate ester oligomers (and their precursors) containing four and six phenylene groups in the backbone and characterized using nuclear magnetic resonance (NMR) spectroscopy and microanalysis. Thermal analysis of these oligomers was performed using DSC, and they obeyed first-order kinetics. Thermo-oxidative stability studies demonstrated that the incorporation of functionalized and cyanate esters into BMI networks possess better stability than unfunctionalised cyanate esters.

Mascia and Kioul (1995) evaluated the influence of siloxane composition and morphology on properties of polyimide-silica hybrids. Compatibilization of the two components was achieved with the addition of small amounts of $\gamma$-glycidyloxy-propyltrimethoxysilane, and the evolution of the morphology was controlled by the partial substitution of tetraethoxysilane with dimethylethoxysilane.
Sellinger et al (1996) synthesized Pt-catalyzed hydrosilylation of alkenes or alkynes with (HSiO\textsubscript{1.5})\textsubscript{8} and (HMe\textsubscript{2}SiOSiO\textsubscript{1.5})\textsubscript{8} cages which is used a nano precursor for the preparation of nanocomposites.

Andre Lee and Joseph D. Lichtenhan (1998) studied the thermal and viscoelastic property enhancements of epoxy resins using monofunctional POSS-epoxy macromers. It was observed that the glass transition temperature \(T_g\) was increased with increasing weight fraction of the monofunctional POSS-epoxy due to the influence of polymer chain motions.

Leno Mascia and Tao Tang (1998) reported the curing and morphology of epoxy resin–silica hybrids. Hybrids of epoxy resin and silica were cured using methyl nadic anhydride (MNA) and 4,4-diaminodiphenyl sulfone (DDS). The control of morphology was achieved through the fictionalization of a diglycidyl ether resin with monofunctional and difunctional secondary amine trialkoxysilanes. Tetraethoxysilane (TEOS) and DDS were used as silica matrix and hardener respectively.

Xenopoulos (1998) studied the effect of formulation variables on the gelation behaviour of alkoxysilane solutions based on tetraethoxysilane (TEOS) and that of corresponding polyimide-based hybrid solutions compatibilised by means of organofunctional trialkoxysilane coupling agents.

Fasce et al (1999) have reported the synthesis of multifunctional POSS derivatives using the simple hydrolytic condensation of modified aminosilanes.

Ryo Tamaki and Yoshiki Chujo (1999) investigated the synthesis of nanometer scale homogeneous polystyrene and silica gel polymer hybrids
utilizing ionic interactions. The partially sulfonated polystyrene (10 mol%) was used as a starting organic polymer and ($\gamma$-aminopropyl)trimethoxysilane ($\gamma$-APS) was used as a countercation as well as the precursor to the inorganic phase. The content of silica gel was controlled by the further addition of tetramethoxysilane (TMOS). The level of dispersity of the organic and the inorganic phase was found to be dependent on the amount of $\gamma$-APS.

Feher et al (2000) published a review article covering a comprehensive detail of synthetic routes for POSS and derivatives of POSS. In addition Li et al (2000) have also reviewed the synthesis of monofunctional and multifunctional POSS monomers and polymers.

Ashok Kumar et al (2000) synthesized the siliconized epoxy-bismaleimide intercross linked matrix materials. Data obtained from mechanical studies 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 into epoxy improved both tensile strength and thermal behaviour. However, the introduction of both siloxane and bismaleimide into epoxy enhances both mechanical and thermal properties according to their percentage content.

Benjamin D. Fitz and Jovan Mijovic (2000) studied molecular dynamics via broad-band dielectric relaxation spectroscopy (DRS) to assess the in situ network formation in cyanate esters.

Suh (2000) studied the properties of unsaturated polyester (UP)/montmorillonite (MMT) nanocomposites. They reported that the physicochemical properties of resulting nanocomposites were depend on the nature of the interaction between polymer and MMT clay.
Bartolomeo et al (2001) studied the curing of cyanate ester resin using FTIR spectroscopy and also compared the data resulted from other techniques.

Choi et al (2001) reported that there was an increase in thermal stability of octakis (glycidyldimethylsiloxy) octasilsesquioxane (OG)/DDM system than DGEBA/DDM with varying DDM ratios. The effect of curing conditions on nanostructural organization and mechanical properties was studied. The diglycidyl ether of bisphenol A (DGEBA) epoxy resin was used as a reference material.

Eva M. Maya (2001) synthesized and characterized a series of dimethylsiloxane (DMS) linked cyanate ester monomers (NCOC₆H₄(CH₂)₃(Si(CH₃)₂O)ₙSi-(CH₂)₃C₆H₄OCN, n = 1, 2, 3). The incorporation of 2, 3, and 4 DMS units results in a large depression of the glass transition (15 to -43 °C). The dielectric constant of the resin series displays a strong dependence on frequency and small dependence on siloxane chain length which correlates with siloxane composition. The loss tangent of the resin series increased with increasing siloxane chain length.

Gui Zhi Li et al (2001) reported the preparation of aliphatic epoxy composites with multifunctional polyhedral oligomeric silsesquioxane (POSS) ((C₆H₅CHCHO)₄(Si₈O₁₂)(CH₂CHC₆H₃)₄) nanophases (epoxy/POSS 95/5 and 75/25) and epoxy blends with the prepolymer of ladderlike polyphenylsilsesquioxane (PPSQ) (95/5, 90/10, and 85/15) by solution casting. The Tₕ of epoxy/PPSQ 85/15 is lower than that of neat epoxy probably due to the hindrance of epoxy resin cross-linking caused by hard PPSQ-rich particles resulting from phase separation. The flexural modulus and hardness of epoxy resins are improved by incorporating either the
multifunctional POSS or PPSQ. The flexural strengths of both epoxy/POSS composites and epoxy/PPSQ blends are lower than that of neat epoxy resin.

Jeffrey and Richard (2001) reported the use of layered-silicate (clay) into resin systems. Montmorillonite clay was dispersed at the nanometer level in cyanate ester resins (PT-15) for improving flammability. The use of treated MMT clay in CE resin yields exfoliated and intercalated MMT in cured CE nanocomposites.

Jiwon Choi et al (2001) prepared epoxy nanocomposites with completely defined organic/inorganic phases by reacting octakis (glycidyldimethylsiloxyl) octasilsesquioxane (glycidyl Me₂SiOSiO₁.₅)₈] (OG) with diaminodiphenylmethane (DDM) at various compositional ratios. The effects of reaction curing conditions on nanostructural organization and mechanical properties were explored and compared with DGEBA. OG/DDM composites possess comparable tensile moduli and fracture toughness to, and better thermal stabilities than, DGEBA/DDM cured under similar conditions.

Laine et al (2001) studied the dispersion of multifunctional POSS into epoxy matrix probably on the molecular level, even at POSS weight percent 25%. The epoxy/POSS composite having 75/25 composition shows lower $T_g$ than neat epoxy resin, which has been ascertained to the possible incomplete curing reaction of epoxy due to the inclusion of POSS cages.

Lee and Lichtenhan (2001) have investigated the effects of influence of POSS reinforcement on epoxy resin and compared the results of thermal and viscoelastic properties of neat epoxy resins.

Reghunadhnan Nair et al (2001) developed maleimide modified novolac cyanate esters from the corresponding maleimide containing novolac
resins. They observed that the cyanate resins underwent two-stage independent curing due to the cyclotrimerisation of the cyanate groups and polymerization of maleimide group through FTIR and DSC studies.

Dinakar et al (2002) developed the epoxy-cyanate ester interpenetrating network matrices/organoclay nanocomposites. Data obtained from mechanical studies and thermal characterization indicates that the introduction of cyanate ester into epoxy improves the toughness and thermal stability with reduction in strength and modulus values. The prepared organophilic montmorillonite clay-epoxy and cyanate ester-epoxy nanocomposites were evaluated by X-ray diffraction (XRD), dynamic mechanical analysis (DMA) and SEM. The results showed the formation of nanocomposites.

Ian Hamerton et al (2002) studied the synthesis and polymerization of the cyanate ester monomers and characterization of the polymer blends using thermal and mechanical methods.

Lee and Lichtenhan (2002) studied thermal behaviour of DGEBA incorporated with monofunctional epoxy POSS. It was found that the $T_g$ broadened with increasing incorporation of POSS upto 10 wt %.

Sunil et al (2002) studied are reported the moisture absorption behaviour of cyanate ester modified epoxy resin matrices.

Ste´phane Reculusa et al (2002) synthesized raspberry like silica-polymer nanoparticles through emulsion polymerization. Well-defined silica spheres were first prepared via a base-catalyzed sol-gel process. Then the adsorption of a PEG methacrylate derivative was achieved on the silica surface to provide double bonds for reaction with the monomer. Finally,
Emulsion polymerization of styrene was performed with the help of a surfactant and sodium persulfate as an initiator.

Triantafillidis et al. (2002) reported a new approach to the preparation of epoxy-clay nanocomposites based on the intercalation and exfoliation of homostructured mixed inorganic/organic cation exchanged forms of a commercially available montmorillonite (MMT) and a synthetic fluorohectorite (FH) clay. The amount of organic modifier needed to transform smectite clay into a derivative suitable for nanocomposite formation was dramatically reduced by converting the clay into a mixed-ion homostructure in which inorganic and organic cations mixtures co-occupy the gallery regions between nanolayers.

Wenhua Zhang (2002) synthesized random copolymers of methyl methacrylate with polyhedral oligomeric silsesquioxane (POSS) and blended with PS and PMMA homopolymer thin films. The effects of the POSS on phase segregation were studied using a variety of complementary techniques. The results showed that these copolymers were efficient at compatibilizing immiscible polymer blends. The compatibilization is due to the increased site functionality provided by the POSS molecule without the entropic penalty associated with introducing functionalities via grafting directly onto the polymer chains.

Zhang et al. (2002) prepared random copolymers of methyl methacrylate with polyhedral oligomeric silsesquioxane (POSS) and blended with PS and PMMA homopolymer to form thin films. The effects of the propylmethacrylheptacyclopentyl POSS on phase segregation were studied.

Choi et al. (2003) reported the comparison of octaglycidyldimethylsiloxyl octasilsesquioxane (OG) cured with DDM and
octa(ethylcyclohexylepoxide)dimethyl siloxy silsesquioxane (OC) cured with DDM, which results an increase of 2-fold elastic modulus for OC/DDM and well defined network architecture.

Dinakaran et al (2003) prepared an intercross linked network of cyanate ester (CE)–bismaleimide (BMI) modified epoxy matrix system was made by using epoxy resin, 1,3-dicyanato benzene and bismaleimide (N,N'-bismaleimido-4,4'-diphenyl methane) with diaminodiphenylmethane as curing agent. BMI-CE-epoxy matrices were characterised using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and heat deflection temperature (HDT) analysis.

Hanan Sertchook and David Avnir (2003) described a convenient, one-step sol-gel route to composite polymeric organic-inorganic particles. The synthesis is based on performing the sol-gel polycondensation within a surfactant-stabilized emulsion of a solution of polystyrene of various molecular weights in tetraethoxysilane, with or without toluene, all dispersed in a basic ethanolic medium. Three useful applications of these particles were demonstrated: as a source for the formation of mesoporous silica particles; as a source for core-shell architecture, and as leach-proof carriers for dyes.

Sabyasachi Ganguli et al (2003) prepared nanocomposites of cyanate esters by dispersing organically modified layered silicates (OLS) into the resin. The inclusion of about 2.5% by weight of OLS led to a marked improvement in physical and thermal properties (Coefficient of thermal expansion, $T_g$ and effective thermal stability). Most impressively, a 30% increase in both the modulus and toughness was obtained.

Yu-Wen Wang et al (2003) synthesized photosensitive polyimide/silica hybrid optical materials and studied the properties. In this
study, the volume shrinkage of photosensitive poly(4,4′-(hexafluoro isopropylidene diphthalic anhydride)-co-oxy dianiline) (6FDA-ODA)/MDAE was largely reduced by photocrosslinking MDAE with a coupling agent and the silica domain in the hybrid materials.

Ian Hamerton et al (2004) reported the studies on a dicyanate containing four phenylene rings and polycyanurate copolymers. Applications of mathematical models have been used to determine the kinetics of the thermal degradation processes.

Jiwon Choi (2004) studied epoxy-functionalized cube nanocomposites and were prepared from octa(aminophenyl)silsesquioxane (OAPS), poly(aminophenyl)silsesquioxane (PAPS), octa(dimethyl siloxypropylglycidyl ether) silsesquioxane (OG), diglycidyl ether of bisphenol A (DGEBA) and dianinodiphenylmethane (DDM). They find that (i) tethers with aromatic components increased the char yields and decomposition temperatures, (ii) cube loadings are important in thermal stabilities, and (iii) aromatic tether structure, short lengths and high cross-link densities reduce tether segmental relaxation motions which in turn stiffen the network and minimize macroscopic glass transitions. Finally, nanocomposites prepared from OAPS and PAPS exhibit nearly identical thermomechanical properties with PAPS offering a low cost alternative to OAPS.

Jiwon Choi et al (2004) prepared nanocomposites by reacting octa (dimethylsiloxylethylcyclohexyl epoxide) silsesquioxane (OC, 1.3 nm diameter) with dianinodiphenylmethane (DDM). The resulting nanocomposites offer excellent elastic moduli and thermal stabilities at the expense of poor fracture toughness. OC/DDM is a “single phase” hybrid nanocomposite that was used as a matrix for about 100 nm diameter core shell rubber (CSR) reinforcing particles. Composites showed that the fracture
toughness was improved significantly on inclusion of CSR particles with little effect on elastic moduli and thermal stability. Stress and strain at failure also improved, indicating better fracture toughness. SEM studies suggested that the shear yielding and CSR pull-out are the sources of toughening.

Kopesky et al (2004) have characterized poly(methyl methacrylate)s containing both tethered and untethered polyhedral oligomeric silsesquioxanes (POSS) by wide-angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC), and rheological measurements. The presence of tethered-POSS in entangled copolymers led to a decrease in the plateau modulus compared with the PMMA homopolymer. Octacyclohexyl-POSS and octaisobutyl-POSS were used as untethered-POSS fillers and blended with PMMA homopolymer.

Edward et al (2004) reported that poly(methyl methacrylate) (PMMA) containing both tethered and untethered polyhedral oligomeric silsesquioxanes (POSS) were examined through the use of wide-angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC), and rheological characterization. The presence of tethered-POSS in entangled copolymers leads to a decrease in the plateau modulus when compared with PMMA homopolymer. Isobutyl-POSS was also blended with a POSS-PMMA copolymer containing 25 wt % tethered isobutyl-POSS distributed randomly along the chain. Blends of untethered-POSS with copolymer show a significant increase in zero-shear-rate viscosity ($\eta_0$) for all loadings, greater than that expected for traditional hard-sphere fillers.

Litenhan et al (2004) incorporated octafuncational POSS into the vinylester and studied the viscoelastic properties of VE/POSS nanocomposites. Dynamic thermal analysis confirmed the reduced thermomechanical behaviour for the VE resin system on incorporation of POSS.
Min Chen et al (2004) prepared waterborne raspberry-like PMMA/SiO$_2$ nanocomposite particles through a free radical copolymerization of methyl methacrylate (MMA) with 1-vinylimidazole (1-VID) in the presence of ultrafine aqueous silica sols. These particles had a reasonably narrow size distribution, and average particle sizes were in the range of 120-350 nm and silica contents were up to 47% by varying the initial silica charge, reaction temperature, pH value of the system, and 1-VID charge.

Phillips et al (2004) studied the use of octa functional POSS enhanced the cross linking density many fold as well as, it act as nano reinforcing material, which satisfied the requirement for high performance applications. The POSS nanocomposites also possessed high thermal stability due to high dimensional stability of the POSS as well as high bond energy of Si-O-Si skeleton.

Tamaki et al (2004) studied the morphological and thermal behaviour of the polystyrene silica hybrids prepared by \pi-\pi interaction through insitu sol-gel method.

Yong Ni et al (2004) prepared the organic–inorganic hybrids involving epoxy resin and polyhedral oligomeric silsesquioxanes (POSS) via in situ polymerization of diglycidyl ether of bisphenol A (DGEBA) and 4,4′-diaminodiphenylmethane (DDM) in the presence of the two structurally similar POSS monomers. The organic groups on silsesquioxane cage are aminophenyl and nitrophenyl groups, respectively. The curing reactions were started from the initially homogeneous mixture of DGEBA, DDM and the POSS cages. The inorganic–organic hybrids containing up to 20 wt% of POSS were obtained. The morphologies of the resulting hybrids were quite dependent on the types of organic groups in the POSS monomers.
Ashok Kumar et al (2005) prepared stereo regular polystyrene silica hybrid through stereoregular complex formation by insitu sol-gel method.

Cuiming Wu (2005) studied the synthesis and characterizations of novel, positively charged poly(methyl acrylate)-SiO$_2$ nanocomposites. The nanocomposites were prepared through the sol–gel process of positively charged alkoxy silane-containing polymer precursors. The precursors were synthesized by coupling different amounts of N-[3-(trimethoxysilyl) propyl] ethylene diamine (A-1120) to poly(methyl acrylate) (PMA), followed by a quaternization reaction.

Ogasi et al (2005) prepared polystyrene silica hybrid by ionic interaction through an coupling agent in the presence of tetraethoxysilane TEOS.

Ruben Kannan (2005) developed octafunctional POSS methacrylate which is blended with aliphatic methacrylate and studied the composites for dental applicatons.

Tim J. Wooster et al (2005) reported the rheological properties and mechanical properties of percolated cyanate ester monomer/layered silicate mixtures. A number of different cation exchanged montmorillonites were examined in an effort to achieve maximal montmorillonite delamination. The dispersion throughout the cyanate ester of a montmorillonite with phenylated ammonium cations (2MBHT MMT) results in the formation of a percolated network. The rheology of this percolated network undergoes a viscous liquid to elastic solid transition at 4 wt% montmorillonite. The percolation of the montmorillonite in the cyanate ester results in a significant improvement in crack resistance (80%) without a sacrifice of flexural strength.
Yonghong Liu et al (2005) prepared POSS-containing nanocomposites of epoxy resin via the co-curing reaction between octa(propylglycidyl ether) polyhedral oligomeric silsesquioxane (POSS) and the precursors of epoxy resin. The glass transition temperatures ($T_g$) of the nanocomposites almost remained invariant whereas the nanocomposites containing POSS more than 40 wt% displayed the lower $T_g$ than the control epoxy resin. The improved thermal stability could be ascribed to the nanoscaled dispersion of POSS cages and the formation of tether structure of POSS cages with epoxy matrix.

Ni et al (2005) studied the effect of POSS-NO$_2$ and POSS-NH$_2$ on DGEBA system, and confirmed that the amine POSS containing system possessed better thermal stability compared to DGEBA/DDM system.

Hongzhi Liu (2005) reported the incorporation of phenyltrisilanol POSS [Ph$_7$Si$_7$O$_9$(OH)$_3$, POSS-triol] with diameter ranging from 0.3 to 0.5 µm into the epoxy networks with the content up to 30 wt %. The phase separated composites possessed the higher glass transition temperatures ($T_g$’s) while the nanocomposites displayed the higher storage modulus of glassy states and it displayed a higher initial thermal decomposition temperatures ($T_d$’s). The improvement in thermomechanical properties has been ascribed to the nanoscaled dispersion of POSS blocks in the materials.

Krishnan et al (2005) developed the octamaelimidePOSS incorporated polymaleimide resin exhibited higher thermal behaviour. Morphology characterization was confirmed by XRD and calculated the crosslink density of the nanocomposites.

Kyoungmoo Koh et al (2005) reported a new POSS-holding initiator for ATRP was designed and used to synthesize a tadpole-shaped
hybrid polymer with an “inorganic head” of fluorinated POSS and an “organic tail” of well-defined PMMA. Neutron reflectometric, XPS, and contact angle measurements for an annealed blend film composed of the hybrid polymer and PMMA showed that the POSS moieties in the film were highly populated on the outermost surface of the film. Because of this unique structure, the blend film exhibited strong resistance against Ar+ ion etching.

Liang et al (2005) reported that the trisilanolphenyl POSS has been molecularly dispersed into epoxy/cyanate ester copolymers. The molecular dispersion of POSS, octaaminophenyl POSS and trisilanolphenyl - POSS, into cyanate ester resins or epoxy/cyanate ester copolymer increased the use temperature of cyanate ester resins and epoxy/cyanate ester copolymer.

Kaiwen Liang et al (2006) developed cyanate ester (PT-15, Lonza Corp.) composites containing the blended polyhedral oligomeric silsesquioxane (POSS), and trisilanolphenyl-POSS \((C_{42}H_{38}O_{12}Si_{7})\), with composition of PT-15/POSS 99/1, 97/3, 95/5, 90/10, and 85/15 w/w ratios. The storage bending moduli, \(E'\), and the glass transition temperatures, \(T_g\), of PT-15/POSS 99/1, 97/3, and 95/5 composites are higher than those of the pure PT-15 over the temperature range from 35 to 350 °C.

Liang et al (2006) prepared cyanate ester POSS nanocomposites using multifunctional octaaminophenyl POSS and mono functional cyanopropylheptacyclopentyl POSS into the PT-15 cyanate ester resin network by thermal (250 °C) curing. Thermal properties were improved with the incorporation of POSS.

Michael E. Wright et al (2006) prepared a series of four new end-capped and hydroxymethyl-functionalized polyimides through a two-step chemical modification process (3-aminopropyl) (hepta-\(i\)-butyl) polyhedral
oligomeric silsesquioxane (POSS) by covalently attached to the polymer backbone. POSS loading levels as high as 36 wt % could be obtained while maintaining excellent processability and optical clarity of thin films. Concurrent attachment of either a cyanate ester or hydroxyethyl methacrylate (HEMA) group afforded processable POSSpolyimides that underwent thermal curing to yield solvent-resistant films, both having final $T_g$’s of 251°C. Kinetic analysis of the cure reactions yielded energy of activations of 93 kJ/mol (cyanate ester) and 103 kJ/mol HEMA. Exposure of a POSS-polyimide containing 31 wt % POSS to atomic oxygen displayed no measurable level of erosion relative to a Kapton H standard.

Mya and He (2006) reported thermomechanical properties of octafunctional POSS epoxy (OB) and (OG) with tetruglycidyl oxides results no $T_g$ was observed by adding 20 mol %. The storage modulus increased at higher temperatures.

Dhakal et al (2006) studied the nanoindentation behaviour of layered silicate reinforced unsaturated polyester nanocomposites. The experimental results showed that there was a strong correlation between nanomechanical properties and inter layer d-spacing of clay particles in the nanocomposite system. The incorporation of 1%, 3% and 5% by weight nanoclay into the polyester resin results an improvement in hardness of 29%, 24% and 14%, respectively.

Andrew J. Guenthner (2006) synthesised a new cyanate ester monomer from bis(4-cyanatophenyl)dimethylsilane (SiMCy) and it was found to have a melting point about 20°C lower than that of the commercial bis(4-cyanatophenyl) dimethylmethane (BADCy) with similar melt viscosity, curing kinetics, and postcure glass transition temperature. The combination of improved thermooxidative stability and reduced moisture absorption without
significant loss in ease of processing or mechanical properties makes SiMCy an important potential “drop in” replacement for BADCy and demonstrated the power of the molecular level approach to designing new high-temperature polymer materials.

Ruben Kannan (2006) developed POSS methacrylate nanocomposites and its use as artificial bone and also made an attempt for use as cardiovascular valves.

Shuwang Duo et al (2006) prepared polyimide/silica (PI/SiO2) hybrid films by the sol–gel process to improve the erosion resistance of polyimide materials in atomic oxygen (AO) environments. The p-aminophenyltrimethoxysilane (APTMOS) was used as a coupling agent to enhance the compatibility between the PI and SiO2. The effect of addition of APTMOS on morphological properties of PI/SiO2 hybrids were investigated using UV–Vis spectrophotometer, FTIR spectroscopy and SEM. The addition of APTMOS remarkably reduced the size of the silica particles, the PI/SiO2 hybrid films became transparent, and the compatibility between the PI and SiO2 and the thermal stability of the hybrids were significantly improved. During AO exposure, a passive inorganic SiO2 layer was formed on the PI/SiO2 hybrid films, causing the hybrid films to possess excellent AO resistance. The optical properties of the PI/SiO2 hybrid films were not altered a significant extent after AO exposure.

Jiaqiang Qin et al (2007) observed the phase separation process of the polyimide/silica hybrid films made from polyamic acid (PAA) and precursor (TEOS-A) hydrolyzed tetraethoxysilane under acidic condition in N-methyl-2-pyrrolidone (NMP) through sol–gel method was investigated by the scanning electron microscope (SEM).
Michael E. Wrigh et al (2007) synthesized a new monotethered-POSS molecule which will form micellar aggregates that undergo a thermally induced polymerization/cure reaction to afford very stable and discrete nanosized macromolecular structures.

Ning Hao et al (2007) prepared nanocomposites by blending polyhedral oligomeric silsesquioxane with phenethyl substituents into polystyrene by a well-adapted solution casting method. Homogeneous transparent films are obtained for a reasonable concentration range of PhenethylPOSS from 0 to 40 wt %. The different behavior of PhenethylPOSS in polystyrene and polycarbonate is interpreted in terms of the different interaction of the phenyl rings within the POSS substituents with the phenyl rings of the polymers. For polystyrene, the interaction is stronger than for polycarbonate which probably leads to the enhanced miscibility of PhenethylPOSS into polystyrene. A detailed analysis of the temperature dependence of the dielectric relaxation strengths points also to additional interactions in the nanocomposites when compared to pure polystyrene. Therefore the broadening of the loss peak with increasing concentration of POSS is interpreted by composition fluctuations on the scale of a few nanometers.

Qingxiu Li and Sindee L. Simon (2007) reported the shear response of polycyanurate networks with different cross-link densities, varied by changing the ratio of difunctional to monofunctional cyanate ester, by measuring shear stress relaxation and dynamic experiments.

Yong Ni and Sixun Zheng (2007) synthesized Polyhedral oligomeric silsesquioxane (POSS)-capped PCL via ring-opening polymerization of caprolactone with 3-hydroxypropylheptaphenyl POSS as the initiator. The formation of the nanostructures in the epoxy thermosets was
addressed on the basis of miscibility and phase behavior of the subcomponents (viz. POSS and PCL chains) of the organic-inorganic amphiphilic macromolecule with epoxy resin after and before curing reaction. It is judged that the formation of the nanostructures in the organic-inorganic hybrid composites follows the mechanism of self-assembly. The static contact angle measurements indicated that the organic-inorganic nanocomposites displayed a significant enhancement in surface hydrophobicity as well as reduction in surface free energy. The improvement in surface properties was ascribed to the enrichment of POSS moiety on the surface of the nanostructured thermosets, which was evidenced by X-ray photoelectron spectroscopy.

Zhang et al (2007) reported the use of Octa(aminopropyl)silsesquioxane \( (\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2)_8\text{Si}_8\text{O}_{12} \) (POSS-NH\(_2\)), containing eight amino groups on the vertexes, as the curing agent for epoxy resin [diglycidyl ether of bisphenol A (DGEBA)] in order to improve the overall performance of epoxy resins, such as mechanical properties, thermal resistance and dielectric properties. The disappearance of epoxy groups on the FT-IR spectra at the end of the curing process indicated that epoxy groups reacted with POSS to form a three-dimensional crosslinking network, and the epoxy resin was completely cured. Properties of the cured DGEBA/POSS nanocomposite containing 30wt% of POSS-NH\(_2\) were studied. The SEM images of the flexural fractures of epoxy/POSS system indicated that the inorganic-organic materials possessed excellent toughness. TGA analysis revealed that the cured network showed an enhanced thermal stability with respect to the cured DGEBA/DDS system.

Zengping Zhang et al (2007) prepared a series of polyhedral oligomeric silsesquioxane / epoxy nanocomposites (POSS/EP) containing 0 wt%, 5 wt%, 10 wt% and 15 wt% content of POSS. Mechanical properties
were used as the index to show the effect of POSS on the thermo-oxygen degradation resistance of epoxy resin. The incorporation of POSS into epoxy networks enhanced the thermo-oxygen resistance of epoxy. The presence of POSS led to the formation of inert layer on the surface of materials which could protect the internal structure from decomposition. As a result, the retention of mechanical properties of EP/POSS hybrids increased with increasing POSS content.

Byung-Wan Jo (2008) reported that the compressive strength, elastic modulus, and splitting tensile strength and thermal stability of the polymer concrete based on MMT-UP nanocomposites are higher than those of UP polymer concrete prepared in absence of MMT.

Jiri Brus et al (2008) prepared epoxy networks based on poly(propylene oxide) chains cross-linked by diglycidyl ether of bisphenol-A and reinforced by polyhedral oligomeric silsesquioxane (POSS) in order to develop a polymer nanocomposites with hierarchical architecture. The network structure of epoxy-POSS composites, was characterized using solid-state NMR spectroscopy.

1.10 SCOPE OF THE PRESENT INVESTIGATION

Research and development in the field of polymer nanocomposites has led to the synthesis of different kinds of hybrid nanocomposites. Several investigations have been carried out in the area of nanocomposites utilizing different polymer matrices and varying types of nanofillers. However a detailed study is required for the development and characterization of hybrid organic-inorganic nanocomposites to propose them for suitable applications. Hence the present study is undertaken to develop organic-inorganic hybrid nanocomposites by involving industrially versatile polymers i.e., epoxy
resin, unsaturated polyester, cyanate ester and polystyrene, using octaaminophenyl silsesquioxane (OAPS) and octamaleimidophenyl silsesquioxane (OAPS) as nanocrosslinkers and nanosized silica particles obtained from tetraethoxysilane through sol-gel technique.

Epoxy-POSS nanocomposites were prepared by in situ polymerization of diglycidylether of bisphenol-A (DGEBA) and 4,4’-diaminodiphenylmethane in the presence of octamaleimidophenyl silsesquioxane in order to get transparent, thermally stable and improved mechanical properties of the nanocomposites. Unsaturated polyester (UP)/Octamaleimidophenylsilsesquioxane (OMPS) nanocomposite was prepared using radical polymerization in order to obtain a high crosslink density, low shrinkage and enhanced thermal stability.

Cyanate ester/POSS nanocomposite was prepared by thermal curing in order to improve the flame retardancy, low water absorption and dynamic mechanical behaviour.

Polystyrene/silica and cyanate ester/silica hybrid nanocomposites were prepared through a novel method of molecular level synthesis by sol-gel process.

In the present investigation an attempt is made:

- To synthesize functionalized polyhedral oligomeric silsesquioxane (POSS) namely octaaminophenyl silsesquioxane (OAPS) and octamaleimidophenyl silsesquioxane (OMPS).
• To develop epoxy / octamaleimidophenylsilsesquioxane nanocomposites and to study their physicochemical properties by fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) spectra.

• To synthesize unsaturated polyester (UP)/octamaleimido phenylsilsesquioxane nanocomposites using radical polymerization, and to study the effect of incorporation of OMPS into UP resin on the physicochemical, thermal, mechanical, wide angle X-ray diffraction (WAXRD), morphological properties and water absorption behaviour.

• To synthesize a novel type of cyanate ester/ octamaleimidophenylsilsesquioxane (CE/OMPS) nanocomposites and to characterize them by physico-chemical, thermal properties like differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA), morphological studies and WAXRD analysis.

• To synthesize polystyrene/silica hybrid nanocomposites by Michael-addition reaction utilizing insitu sol-gel method and to study their physicochemical, morphological, thermal, solvent resistance behaviour including nitrogen porosimetry analysis.

• To prepare a transparent cyanate ester silica hybrid nanocomposite at molecular level by in situ sol-gel method using bisphenol-A cyanate ester and TEOS by changing the physical parameters like temperature, gelation time, solvent, catalyst, cross linking agent and the concentration of silica.
• To study the physico-chemical, thermal, morphological and solvent resistant properties of cyanate ester silica (CE/SiO$_2$) nanocomposites.

All these form the subject matter of the thesis and are divided into eight chapters. **Chapter one** describes the introduction to nanocomposites and reviews the literature concerning a variety of organic-inorganic polymer hybrid nanocomposites and their preparation, the method of preparation of nanoparticles, type of interaction between the polymer and the nanoparticles, effect of incorporation of nanoparticles, and the variation of properties due to incorporation of POSS into different type of resin systems like epoxy, cyanate ester, unsaturated polyester and polymethylmethacrylate (PMMA). In addition, the introduction and the literature reviews about the development of polymer silica hybrids namely polystyrene, epoxy, PMMA and polyimide through sol-gel method including the properties and applications of the polymer/silica hybrid nanocomposites, and the commercial importance and the role of epoxy resin, cyanate ester resin, unsaturated polyester resin and polystyrene towards high performance applications are also included in this chapter.

**Chapter two** describes the synthesis of octafunctionalised POSS nanoprecursor namely octaaminophenylsilsesquioxane (OAPS) and octamaleimidophenylsilsesquioxane (OMPS, Scheme 1.4).
Scheme 1.4 Synthesis of octamaleimidophenylsilsesquioxane

Synthesis of cyanate ester monomers, synthesis of N-chloromethylmaleimide and synthesis of maleimide substituted polystyrene (PS-s-Ma) are also included in this chapter.

Chapter three presents the physico-chemical properties of POSS nanoprecursor namely octaaminophenylsilsesquioxane (OAPS) and octamaleimidophenylsilsesquioxane (OMPS), cyanate ester monomers, N-chloromethylmaleimide and maleimide substituted polystyrene by FTIR, $^1$H, $^{13}$C and $^{29}$Si NMR spectroscopy. In addition, the determination of molecular weight of the OAPS and OMPS by using gel permeation chromatography (GPC), the conformation of nanocubic structure of octaphenylsilsesquioxane by powder X-ray diffraction analysis (XRD) and analysis of curing temperature and melting point of the cyanate ester
monomer by differential scanning calorimetry thermograms are also included in this chapter.

**Chapter four** explains the formation of molecular structure of epoxy/POSS nanocomposites (Scheme 1.5).

![Network structure](image)

**Scheme 1.5 Schematic representation of OMPS reinforced epoxy nanocomposites**

The effect of incorporation of varying percentages (5, 10, and 15 wt%) of POSS nanoprecursor into epoxy resin on thermal (DSC), dynamic mechanical properties (DMA), flexural and tensile strength and water absorption behaviour including morphology of the nanocomposites studied using WAXRD and scanning electron microscope (SEM) are presented in this chapter.
Chapter five illustrates the formation of UP/POSS nanocomposites between unsaturated polyester and OMPS through radical polymerization (Scheme 1.6).

![Scheme 1.6 Network structure of OMPS incorporated UP resin](image)

The formation of homogeneous hybrid and nanoreinforcement of POSS into UP resin studied using FTIR, WAXRD and SEM, thermal, mechanical and water absorption properties of varying percentages (1, 3, 5 and 10 wt %) of POSS incorporated UP/POSS hybrid nanocomposite are also presented in this chapter.

Chapter Six describes the thermal characterization of CE/POSS nanocomposites with different weight percentages (1, 3, 5 and 10 wt %) of POSS. Cure reaction behaviour and the interaction of POSS into the cyanate ester resin studied using FTIR analysis, water absorption behaviour, and the morphology of fractured surface of CE/POSS studied by SEM and XRD analysis are presented in this chapter. Char yield and thermal degradation temperature of different CE/POSS loaded system and neat CE resin studied and compared are also included in this chapter.
Chapter Seven describes the importance and preparation of polymer-silica hybrids through sol-gel method.

Scheme 1.7 Schematic representation of PS/silica hybrid nanocomposites

The physico-chemical properties of polystyrene/silica hybrids utilizing Michael-addition reaction and comparison of thermal properties and thermal degradation temperature of different hybrids with unmodified polystyrene are explained in this chapter. The cyanate ester/silica hybrids prepared by the addition reaction between cyanate ester and amino group of $\gamma$-aminopropyltriethoxysilane confirmed by FTIR analysis, the solvent resistant behaviour of the organic-inorganic hybrids observed from TGA thermograms, nanolevel dispersion of organic-inorganic hybrids confirmed by nitrogen porosimetry studies and surface morphology of the hybrids studied by SEM are also presented in this chapter.

Chapter eight presents the summary and conclusions of the preceding chapters including the utility of these materials as coatings for satellites, ablative materials, wave guide materials and solar cells, contact lenses and microelectronic and optical applications.