CHAPTER 1

INTRODUCTION

1.1 POLYMERS

Polymers have become an indispensable part of our life and it is difficult to think of our daily life without them. Depending on its ultimate form and use, a polymer can be classified in many forms such as plastics, rubbers, fibres, foams, adhesives, surface coatings and composites.

Polymers have the advantage of easy alteration of various properties using suitable additives. The addition of inorganic fillers to a polymer matrix improves its mechanical, thermal, optical and electrical properties. To achieve the above mentioned properties, a suitable polymer mixing technique is selected to get proper dispersion and distribution of additives into the polymer matrix. There are different types of polymer mixing techniques such as melt mixing, solution mixing and physical mixing. For external incorporation of macro sized additives into the polymer matrix (Marino Xanthos 2010).

Prior to the early 1920's, chemists doubted the existence of molecules having molecular weights greater than a few thousand g/mole. This limiting view was challenged by Hermann Staudinger, a German chemist with experience in studying natural compounds such as rubber and cellulose. In contrast to the prevailing rationalization of these substances as aggregates of small molecules, Staudinger proposed that they were made up of
macromolecules composed of 10,000 or more atoms. He formulated a polymeric structure for rubber, based on a repeating isoprene unit (referred to as a monomer). For his contributions to chemistry, Staudinger was received the Nobel Prize in 1953 (Gowariker 2011).

Polymers are classified on the basis of their properties as elastomers, fibres, and plastics. An elastomer is a polymer with the property of elasticity. The term elastomer is often interchanged with the term rubber. Elastomers are amorphous polymers having low glass transition temperature ($T_g$) and the temperature existing above their glass transition temperature, so that considerable segmental motion is possible. Elastomers generally have low initial tensile modulus, but when stretched they show stiffness. Fibres are linear polymers with high symmetry and high intermolecular forces. These are characterized by high modulus, high tensile strength, and moderate extensibilities. Plastics fall between the two structural extremes such as elastomers and fibres. These have low modulus and crystalline than fibres. Based on intermolecular bonding and thermal behaviour there are two basic types of plastics such as:

(i) Thermoplastics, because of little or no intermolecular bonding, soften when heated and harden when cooled, no matter how often the process is repeated.

(ii) Thermosets, on the other hand, have strong, intermolecular bonding. Therefore, once the plastic is set into permanent shape under heat and pressure, reheating will not soften it. Both thermoplastics and thermosetting plastics are used to prepare composites by reinforcing with additives to modifying its properties as per the end user applications (Brydson 1995).
1.2 POLYMER COMPOSITES

A composite material is a macroscopic or microscopic combination of two or more distinct materials with a recognizable interface between them. A recent concept of composites is that the composite should not only be a mere combination of two materials, but the combination should have its own distinctive properties. In terms of desired characteristics, the composite must perform better than either component alone. The constituent of a composite that is continuous are presenting in greater quantity is termed as the matrix phase. The second constituent that may enhance or reinforce the mechanical properties of the matrix is referred to as the reinforcement or reinforcing phase. The effectiveness of a reinforcing phase is determined by its shape and dimensions. The reinforcing phase that may take on the form of fibres, flakes, platelets, or particulates, is usually stiffer or stronger than the matrix phase was explained by Crawford (1987). The region between the matrix and reinforcement is called the interphase. Depending upon the size of the dispersed phase, the composites are classified as macrocomposites (dispersed phase greater than millimetres), micro composites (dispersed phase in the millimetre to micrometre range), or nanocomposites (dispersed phase in the micrometre to nanometre range).

The most commonly used matrices for composites are polymeric in nature. The resins for polymer-matrix composites (PMCs) include both thermosetting and thermoplastic types; the former accounting for more than 80% of all matrices in reinforced plastics. The most widely used thermosetting resins are the polyesters, which offer a combination of low cost, versatility in many processes, and reasonably good property performance. For more demanding structural uses, epoxy resins are the preferred material because they provide a unique balance of chemical and mechanical properties combined with extreme processing versatility.
The reinforcements in PMCs have a continuous or discontinuous phase. Useful parameters for characterizing the effectiveness of reinforcing filler are:

(i) Aspect ratio that is defined as the ratio of its major to minor dimension its surface area to volume ratio, and

(ii) Compatibility and interfacial adhesion with polymer matrix

All these parameters need to be as high as possible for effective reinforcement. Compatibility and adhesion of the fillers with the polymer matrix may be improved by surface modification of filler particles through the introduction of new functional groups or the modification of existing ones by oxidation, thermal treatment, plasma treatment, vapour deposition, ion exchange, or by using additives such as coupling agents. Surface modification of the filler particles or other modifications related to increase the aspect ratio and surface to volume ratio of the filler particles may enhance and optimize not only their function as reinforcing constituent, but may also introduce or enhance additional functions. Examples include dimensional stability, thermal/thermo-oxidative stability, bioactivity, chemical/electrochemical activity, barrier characteristics, flame retardancy, scratch resistance, and modification of magnetic, electrical, optical, or other physical properties (Mallick 2007).

Recently, considerable interest has emerged among researchers in academic institutions for producing new materials through the in situ formation of nanostructured inorganic domains in the polymer matrix during processing from molecular precursors, by using sol-gel process. These materials are generally known as organic-inorganic hybrid nanocomposites (Sandra & Young 2002, Rosaria et al 2013).
1.3 ORGANIC-INORGANIC HYBRID POLYMER NANO COMPOSITES

The term "hybrid" is more often used for a material composed of an intimate mixture of both organic and inorganic components. The hybrid materials can vary from soft and flexible to hard and brittle depending on the chemical structure of the organic components and the overall composition of organic to inorganic ratio. Generally, organic polymers usually have some superior characteristics with respect to their toughness, flexibility and processability. On the other hand, inorganic materials have high heat resistance, good mechanical and optical properties. Since many of the well-established materials, i.e. metals, ceramics or plastics, cannot fulfil all technological desires, a new class of materials has to be tailored.

To develop new materials, scientists and engineers realized early that mixtures of materials could show superior properties compared with that of pure counterparts. The simplest way to realize such a composite is to incorporate, for instance, inorganic particles into a polymeric matrix, the resulting materials showing improved properties compared to neat organic ones. They combine the advantages of the inorganic material (e.g. rigidity and thermal stability) and the organic polymer (e.g. flexibility, dielectric, ductility, and process ability). Soon it became evident that decreasing the size of the inorganic units to the same level as the organic building blocks could lead to more homogeneous materials that allow a further fine tuning of materials properties on the molecular and nanoscale level, generating novel materials that either show characteristics in between the two original phases or even new properties. Nowadays, the organic-inorganic materials are regularly used for lightweight materials with advanced mechanical properties (Mammeri et al 2005).
1.3.1 Classification of Hybrid Polymer Nanocomposites

Sanchez & Ribot (1994) has classified the hybrid networks into two main classes such as:

**Class I:** Network modifiers in which the organic polymer or organic molecules are simply embedded into the inorganic matrix. No covalent bonds exist between both phases and only weak interaction such as Van der walls forces; electrostatic or hydrogen bonds are present. Figures 1.1(a) and 1.1(b) represent blends and interpenetrating networks (IPN) respectively.

**Class II:** Network formers in which the organic and inorganic parts establish covalent bonds as shown in the Figures 1.1 (c) and 1.1 (d).

![Figure 1.1 Class I and II hybrid](image)

(a) Blends (b) IPN (c) Buildings blocks covalently connected (d) Covalently connected polymers
In Figure 1.1 the black circles represent the monomer of the organic phase while the bi-pyramids represent the building blocks of the inorganic phase.

Further, Mackenzie (1993) distinguished three types of hybrid networks such as:

**Type A-Entrapped organics:** The organic molecule, such as a dye or pigment, can be mixed into the sol-gel solution. The resultant gel can be casted as film or bulk, shows good optical, mechanical and chemical properties.

**Type B-Impregnated organics:** In order to exploit the tuneable porosity of the silica gels, such as interconnecting pores, controllable size and size distribution, it is widely used as host for many materials including organics. The interaction between the organic polymer and the inorganic part is made via hydrogen bonds, which play an important role in avoiding phase separation and yielding transparent glass-like composites, to obtain hybrids with small amounts of silica that exhibit improved mechanical properties.

**Type C-Chemically bonded organic-inorganic:** In this case, the organic and inorganic are chemically bonded via covalent bonds. The stronger nature of the covalent bond improves the mechanical properties of the composites as shown in Figure 1.2. One of the best systems to obtain organic inorganic hybrid matrix (OIHM) is by this approach is the combined reaction of silanol-terminated polymer as organic component with silicon alkoxide name TEOS or tetramethyl orthosilicate (TMOS) as inorganic component.
Recently there have been intensive studies to produce polymer nanocomposites showing improved properties such as stiffness, toughness, and wear (Ming et al 2002). The term nanocomposites are used if one of the structural units, either organic or inorganic, is in a defined size range of 1-100 nm. Commonly the term nanocomposites is used if discrete structural units in the respective size regime are used and the term hybrid materials is more often used of the inorganic units are formed insitu by molecular precursors such as sol-gel process.

1.4 SOL-GEL PROCESS

The hydrolysis and condensation of silicates to form silica gels is not new. Ebelmen in 1844 first reported silica gels are common in nature, and synthesis of silica gels (Dimitriev 2008). More recently, however, it has been
demonstrated that by control of the process parameters, e.g. R, the H$_2$O/Si molar ratio, and nature and concentration of catalyst, it is possible to vary the structure and properties of sol-gel silicates over wide ranges.

The sol-gel process is a method for producing solid materials from small molecules. It involves the generation of colloidal suspensions, “sol”, which are subsequently converted to viscous gels and then to solid materials. Sol is a dispersion of colloidal particles suspended in Brownian motion within a liquid, whose dimensions, ranging between 1 and 1000 nm, are small enough to ignore the gravitational force. The interactions between the particles are dominated by short-range forces (i.e. Van der waals and superficial charges). Through the polycondensation the sol is converted into a gel, which is a continuous solid structure containing liquid phase. The method is used for the fabrication of metal oxides, especially the oxides of silicon and titanium. The process involves conversion of monomers into a colloidal solution (sol) that acts as the precursor for an integrated network (or gel) of either discrete particles or network polymers. The sol-gel process is chemically related to an organic polycondensation reaction in which small molecules form polymeric structures by the loss of substituents. The reaction results in a three-dimensional crosslinked network. The fact that small molecules are used as precursors for the formation of the crosslinked materials implies several advantages, for example a high control of the purity and composition of the final materials and the use of a solvent based chemistry, which offers many advantages for the processing of the materials formed (Livage 1999, Pomogailo 2005).

The sol-gel process and its applications are represented are represented in Figure 1.3.
In sol-gel process the precursor material used is alkoxides. The well-known alkoxide is silicon tetraethoxide, or TEOS. The chemical formula for TEOS is given by \( \text{Si (OR)}_4 \), where the alkyl group \( R = \text{C}_2\text{H}_5 \). Alkoxides are ideal chemical precursors for sol-gel synthesis because they react readily with water. The reaction is called hydrolysis, because a hydroxyl ion becomes attached to the silicon atom as follows:

\[
\text{Si (OR)}_4 + \text{H}_2\text{O} \rightarrow \text{HO-Si(OR)}_3 + \text{R-OH} \quad (1.1)
\]

Depending on the amount of water and catalyst present, hydrolysis may proceed to completion to silica:

\[
\text{Si (OR)}_4 + 2 \text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4 \text{R-OH} \quad (1.2)
\]
Complete hydrolysis requires a significant excess of water and catalysts such as acetic acid or hydrochloric acid. Intermediate species include \([(\text{RO})_2\text{Si-(OH)}_2]\) or \([(\text{RO})_3\text{Si-(OH)}]\), resulting from partial hydrolysis reactions. Early intermediates result from two partially hydrolysed monomers linked via a siloxane \([\text{Si–O–Si}]\) bond.

\[
(\text{RO})_3\text{Si-OH} + \text{HO–Si-(OR)}_3 \rightarrow [(\text{RO})_3\text{Si–O–Si(OR)}_3] + \text{H-O-H} \tag{1.3}
\]

(or)

\[
(\text{RO})_3\text{Si-OR} + \text{HO–Si-(OR)}_3 \rightarrow [(\text{RO})_3\text{Si–O–Si(OR)}_3] + \text{R-OH} \tag{1.4}
\]

Thus, polymerization is associated with the formation of a 1-2- or 3-dimensional network of siloxane \([\text{Si–O–Si}]\) bonds accompanied by the production of H-O-H and R-O-H species.

The three main stages of sol-gel process for the formation of nanosilica from the precursor are presented in Figure 1.4.

**Figure 1.4 Three main stages in the sol-gel process**
In the first stage, the hydrolysis process will occur by mixing of a metal alkoxide with water to form an immiscible phase. Since alkoxides $\text{Si(OR)}_4$ are not miscible with water, a common solvent (alcohol) is added to enhance the miscibility and favours the hydrolysis reaction.

$$\text{Si (OR)}_4 + \text{H}_2\text{O} \rightarrow \text{HO-Si(OR)}_3 + \text{R-OH}$$  \hspace{1cm} (1.5)

In the second stage, the condensation reaction proceeds through the mediation of a silanol group. The result in both cases is a dimer in which two silicon atoms are linked by a siloxane bond. The dimer may be involved in condensation reactions that lead to the formation of a trimer, then tetramer, and so on. However, the processing does not go beyond the production of oligomers (Wright & Sommerdijk 2001).

$$\text{Si (OR)}_4 + 2 \text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4 \text{R-OH}$$  \hspace{1cm} (1.6)

The third stage, in which the sol-gel transition takes place, consists of the linkage of particles. This proceeds through their cross-linking by the condensation reactions. To promote this a catalyst is introduced.

$$\text{Si(OR)}_4 \rightarrow \text{Si-O-Si}$$  \hspace{1cm} (1.7)

The reactions involve a nucleophilic attack on the electrophilic silicon atom both in acid and basic catalysis. Since the sol stability to the coagulation is caused by the negative charge that is dependent on the pH, the processing is often triggered by the addition of acid or alkali in the solution (Brinker & Scherrer 1990).
The hydrolysis reaction involves a nucleophilic attack of the water molecule to the central silicon atom of the alkoxy silane, followed by a proton transfer from H$_2$O to an alkoxy group OR, and the exit of an alcohol molecule, which is substituted by the OH group. Often acid or basic catalysis is necessary because of the slow reaction rate of the hydrolysis process.

The hydrolysis mechanisms related to the action of acidic and basic catalysts for tetraethoxysilane were suggested by (Aeliona et al 1950) and successively elaborated by Keefer (1984).

In the basic mechanism, the reaction proceeds through a nucleophilic substitution.

![Chemical reaction diagram](image)

Equation (1.8) represents the mechanism of base-catalysed hydrolysis by nucleophilic substitution ($R = \text{H, Et or Si} \,(\text{OR})_3$)

The hydroxide nucleophile coordinates with the silicon, forming a transient trigonal-bipyramid intermediate; the alkoxide group positioned at the opposite site leaves the intermediate and reacting with water leads to the renewal of the catalyst.

In the acidic catalyzed mechanism the hydrolysis reaction takes place as an electrophilic reaction. The hydronium ion approaches the alkoxy silane molecule to form an activated complex. Afterwards the water molecule becomes the entering specie while one alkoxide group positioned at the opposite side becomes the leaving groups as alcohol.
Equation (1.9) represents the mechanism of acid-catalysed hydrolysis by electrophilic reaction.

The condensation reaction takes place as soon as some hydrolysed precursor molecules are present in the solution and it occurs at the same time and with the same reaction path as the hydrolysis, depending on the quantity of water and catalyst present in solution.

Equation (1.10) represents the mechanism of condensation by nucleophilic substitution.

Condensation in the pH range 3-12 firstly proposed by Iler (1979) is a nucleophilic substitution reaction, where a protonated silanol is attacked by a deprotonated silanol (the nucleophile), forming a $\equiv$Si-O-Si$\equiv$ bond and displacing a hydroxyl in the process.

Equation (1.11) represents the mechanism of condensation by electrophilic substitution.
In acidic condition, (pH < 3) the mechanism for condensation changes from nucleophilic to electrophilic. The Si-OH group available is protonated and becomes the electrophile. All the hydrolysis and condensation reaction showed are reversible.

**Acid Catalysis**

![Acid catalysed reaction of sol-gel process](image)

Equation (1.12) Acid catalysed reaction of sol-gel process.

**Base Catalysis**

![Base catalysed reaction of sol-gel process](image)

Equation (1.13) Base catalysed reaction of sol-gel process.

**1.4.1 Factors Affecting Sol-gel Process**

**i) Nature and concentration of catalyst**

The nature of the catalyst determines the relative rates of hydrolysis and condensation reactions and therefore it affects the typology of gel in terms of open network structure or dense network structure. Aelion et al (1950) reported that the rate and extent of alkoxide hydrolysis are greatly influenced by the dissociation constant and concentration of the acid or base catalyst. In the presence of HCl the hydrolysis rate is proportional to the concentration of the acid. These authors have reported that the low rates of reaction with weak acids.
The hydrolysis under basic conditions with NaOH catalyst, (Aeliona et al 1950) reported a first order kinetics with respect to TEOS in dilute solution, although at higher concentrations of monomer the reaction was complicated by the formation of insoluble polysilicates. Weaker bases such as NH$_4$OH and pyridine were only effective as catalysts at higher concentrations. Also, in comparison to acid catalysed hydrolysis, their results revealed a more pronounced dependence of the base catalyzed hydrolysis on solvent nature.

Matejka et al (1998) have studied the effect of catalysts belonging to three different classes of catalysts: acid, neutral and basic, p-toluene sulphonic acid monohydrate (PTSA), dibutyltin dilaurate (DBTDL) and benzyldimethylamine on the condensation of silanes. The catalysed TEOS polymeric structures were studied with SAXS. Basic catalysts lead to typical compact structures, while catalysis by PTSA and DBTDL (pH neutral) lead to more homogeneous structures and more optically transparent gels, similar to those produced under acid catalysis. This effect is a result of a relatively slower hydrolysis and monomer consumption with respect to the condensation. The monomer is available for condensation even at a late stage, in contrast to the acid catalysis, where it is consumed very quickly.

**ii) pH**

The reaction under basic conditions, the hydrolysis steps successive to the first one are faster, since the silanols [(RO)$_3$ SiOH] obtained replacing the alkoxy groups on the silicon with hydroxyl group are more acidic and so more prone to be attacked by hydroxide ions Keefer (1984). The overall kinetics of the basic catalysed process is ruled by the formation of the first silanol because this is the slower step. The silanols were generated immediately used up by fast condensation, leaving no intermediates in the reaction medium (Assink & Kay 1991). The result of basic catalysis is an
aggregation (monomer-cluster) of highly cross-linked sol particles to form gels with large pores between the interconnected particles.

Under acid-catalyzed conditions the hydrolysis reaction is speed up more efficiently than the condensation reaction producing weakly cross-linked or linear polymers. Condensation involves the attack of silicon atoms carrying protonated silanol species by neutral SiOH nucleophiles. The most basic silanol species are those contained in monomers or weakly branched oligomers so condensation is limited and a bushy network of weakly branched polymers can be obtained as shown in Figure 1.5 (Goutam et al 2000, Jones & Fishbach 1987).

Zhihai et al (2012) reported under neutral condition the hydrolysis reaction is slow than the condensation reaction. Chetan et al (2013) reported that enzyme silicatein α was shown to be the template for the formation of silica from TEOS in neutral pH and ambient temperature. Jian Liu et al (2008) reported the hydrolysis of TEOS in neutral condition with mild buffer to form tunable silica structure.

iii) $\text{H}_2\text{O/TEOS molar ratio } [\text{H}_2\text{O/TEOS}]$

According to the theoretical models proposed by (Jaec & Jae 1991) the minimum molar ratio water/TEOS (R-value) required for hydrolysis to completion is R2. This ratio assures the formation of silicate network and completely void of hydroxyl groups. Yoldas (1986) showed that with R4 orthosilicic acid is formed, which has a very large intermolecular separation, and therefore is unable to polymerize. In practical terms, excess of water (R > 2) is expected to cause an increase in the rate of hydrolysis compared to condensation (Brinker et al 1990). In acidic conditions, hydrolysis predominates and goes to completion, leading to a decrease in the content of intermediates and to the development of a more cross-linked polymer
(Sanchez et al 2005). This behaviour justifies the formation of chain-like aggregates because under low water conditions the condensation of hydrolysed monomer (whose product is water) is inhibited by a shift of the condensation equilibrium in favour of the reverse reaction, consequently encouraging further hydrolysis (Sakka et al 1980). The effects of water in basic conditions are similar to those for acidic conditions. An excess of water affects hydrolysis more than condensation.

iv) Solvents

An important factor in sol-gel reaction is the type of solvent used. It affects the rates of hydrolysis and condensation and, consequently, also the structural development of the polysiloxane domains. Several types of solvents have also been used such as polar protic solvents (H$_2$O, methanol and formamide), polar aprotic solvents (DMF, THF and acetonitrile) and non-polar aprotic solvent (dioxane). The polar aprotic solvents inhibit the condensation reactions by deactivating the nucleophile through H-bonding and salvation (Atraki et al 1986). The non-polar aprotic solvents, on the other hand, cannot impede the condensation process because they offer no possibilities of either H-bonding or solvation on the negatively charged ions. Alcoholic solvents, such as ethanol (EtOH) and propanol (PrOH) form azeotropic mixtures with water. The azeotrope, which has a higher vapour pressure than each single component, evaporates first and leaves behind either water or alcohol (depending on their initial amount). If the alcohol is in excess, silanols re-esterify and the water produced is readily removed as part of the azeotrope, thus driving the reverse alkoxylation reaction to completion. Therefore, because the hydrolysis reaction is thermodynamically favourable, the composition of the sol-gel solution should be optimized in order to ensure that water (and not the alcohol) evaporates last Cihlar (1993).
The gelation occurs when the repulsive charges located on the surface of siloxane aggregates are low enough to allow aggregation and growth. This condition depends on the pH level. As a result of aggregation into three-dimensional networks, an increasing fraction of the sol becomes occupied by micro gel regions Iler (1979). These regions have the same refractive index and density as the surrounding sol, which explains the transparency of the system. Before the gelation point and under acidic conditions, the precursor of the gel consists of linear or randomly branched polymers, while, under basic conditions this is made up of individual highly branched clusters. At the gelation point, linear chains become entangled while branched clusters impinge on each other (Brinker & Scherer 1990).
viscosity at this stage increases asymptotically and a transparent gel is formed.

v) Ageing and drying

Although the increase in viscosity which accompanies the gelation freezes the systems in a particular structure, after the gel point this frozen-in structure may change appreciably with time depending on the temperature, solvent and pH conditions. The effect of this process, known as ageing Yoldas (1986), consists of shrinkage and stiffening of the material. The changes in gel structure which can originate from the early stages of its formation are:

- Gel separation into regions of high and low density because, as the gel point is approached, fluctuations in density grow larger and larger throughout the system;

- Promotion of additional cross-linking as un-reacted terminal groups (OH and OR) come in contact in regions of higher density;

- Acceleration of the phase separation process and creation of liquid-solid interfaces (synergises); Starting with polymer gels it is expected that the removal of solvent brings shrinkage due to additional cross-linking as un-reacted hydroxyl and alkoxy groups come in contact. The drying process is very important and many of the structural properties of the resulting solid material (i.e. density, elastic properties) depend on the evolution of the system during this phase.

The evaporation of the liquid from the gel surface, in fact, increases the vapour/solid interface, which has even a greater energy. For this reason the liquid flows from the bulk of the gel to the surface, to cover the dried
surface. Because of the evaporation the liquid cannot cover the whole surface without the creation of a meniscus on the pore surface.

1.4.2 Non-hydrolytic Sol-gel Process

The non-hydrolytic sol gel method (without participation of water) is also promising, especially with respect to transition metal oxides. This concerns mainly reactions associated to chloride hydrolysis with metal alkoxides.

1.4.3 Advantages of Sol-gel Process

i) The main benefits of sol–gel processes are the high purity and uniform nanostructure achievable at low temperatures.

ii) Produces thin bond-coating to provide excellent adhesion between the metallic substrate and the top coat.

iii) Produces thick coating to provide corrosion protection performance.

iv) It can easily shape materials into complex geometries in a gel state.

v) Sol-gel process can produce high purity products because the organo-metallic precursor of the desired ceramic oxides can be mixed, dissolved in a specified solvent and hydrolysed into a sol, and subsequently a gel, the composition can be highly controllable.

vi) Sol-gel product has low temperature sintering capability, usually 200-600°C.
vii) Sol-gel derived materials have diverse applications in optics, electronics, energy, space, biosensors, medicine (e.g. controlled drug release) and separation (e.g. chromatography) technology. One of the more important applications of sol-gel processing is to carry out zeolite synthesis.

viii) It can be used in ceramics manufacturing processes, as an investment casting material, or as a means of producing very thin films of metal oxides for various purposes. Other elements (metals, metal oxides) can be easily incorporated into the final product and the silicalite sol formed by this method is very stable.

ix) Other products fabricated with this process include various ceramic membranes for microfiltration, ultrafiltration, nanofiltration, per evaporation and reverse osmosis.

1.5 MATERIAL SELECTION

Polymer nanocomposites consist of matrix and reinforcement. In sol-gel process, epoxy is selected as polymer matrix and the precursor is used for the insitu generation of nanosilica as reinforcement. The precursor used is TEOS.

1.5.1 Epoxy

Epoxy resins are an important class of polymeric materials, characterized by the presence of more than one three-membered ring known as the epoxy, epoxide, oxirane, or ethoxy line group as shown in Figure 1.6.
The word “epoxy” is derived from the Greek prefix “ep”, which means over and between, and “oxy,” the combining form of oxygen. By the definition, epoxy resins refer only to uncross-linked monomers or oligomers containing epoxy groups. However, in practice, the term epoxy resin is loosely used to include cured epoxy systems. It should be noted that very high molecular weight epoxy resins and cured epoxy resins contain very little or no epoxide groups. The vast majority of industrially important epoxy resins are bi- or multifunctional epoxides. The mono-functional epoxides are primarily used as reactive diluents, viscosity modifiers, or adhesion promoters, but they are included here because of their relevance in the field of epoxy polymers (Bhatnagar 1996).

Epoxies are one of the most versatile classes of polymers with diverse applications such as metal coatings, automotive primer, printed circuit boards, semiconductor encapsulates, adhesives, and aerospace composites. Most cured epoxy resins provide amorphous thermosets with excellent mechanical strength and toughness; outstanding chemical, moisture, and corrosion resistance; good thermal, adhesive, and electrical properties; no volatiles emission and low shrinkage upon cure; and dimensional stability—a unique combination of properties generally not found in any other plastic material. These superior performance characteristics, coupled with outstanding formulating versatility and reasonable cost, have gained epoxy resins wide acceptance as materials of choice for a multitude of bonding, structural, and protective coatings applications (Ellis 1993).
Commercial epoxy resins contain aliphatic, cycloaliphatic, or aromatic backbones and are available in a wide range of molecular weights from several hundreds to tens of thousands. The most widely used epoxies are the glycidyl ether derivatives of bisphenol-A (>75% of resin sales volume). The capability of the highly strained epoxy ring to react with a wide variety of curing agents under diverse conditions and temperatures imparts additional versatility to the epoxies. The major industrial utility of epoxy resins is in thermosetting applications. Treatment with curing agents gives insoluble and intractable thermoset polymers. In order to facilitate processing and to modify cured resin properties, other constituents may be included in the compositions: fillers, solvents, diluents, plasticizers, catalysts, accelerators, and tougheners (Lee & Neville 1967).

Most commercially important epoxy resins are prepared by the coupling reaction of compounds containing at least two active hydrogen atoms with epichlorohydrin followed by dehydrohalogenation. These included polyphenolic compounds, mono and diamines, amino phenols, heterocyclic imides and amides, aliphatic diols and polyols, and dimeric fatty acids. Epoxy resins derived from epichlorohydrin are termed glycidyl based resins. Alternatively, epoxy resins based on epoxidized aliphatic or cycloaliphatic dienes are produced by direct epoxidation of olefins by per acids. Approximately 75% of the epoxy resins currently used worldwide is derived from the diglycidylether of bisphenol-A (DGEBA). This market dominance of bisphenol-A based epoxy resins is a result of a combination of their relatively low cost and adequate-to superior performance in many applications.

The first epoxy resin used in coatings, and still by far the largest in volume, are bisphenol-A (BPA) epoxies made by reaction BPA and epichlorohydrin (ECH). Under basic condition the initial reaction is formation of BPA anion, which attacks ECH and results in the formation of new oxirane ring with elimination of chloride anion.
Reaction Scheme 1: Preparation of bisphenol-A

\[
\text{CH}_2\text{==CH + Cl}_2 \rightarrow \text{CH}_2\text{==CH} + \text{HCl}
\]

Propylene

\[
\text{Cl--CH}_2\text{--CH(OH)--CH}_2\text{--Cl + NaOH \xtrem{Elev. Temp.} \rightarrow CH}_2\text{--CH}--\text{CH}_2\text{--Cl}
\]

Reaction Scheme 2: Preparation of epichlorohydrin

\[
\text{Cl--CH}_2\text{--CH--CH}_3 + \text{HO}--\text{C--CH}_2\text{--CH--CH}_3 \rightarrow \text{OH} + \text{Cl--CH}_2\text{--CH--CH}_2\text{--Cl}
\]

\[
\text{NaOH} \rightarrow \text{Cl--CH}_2\text{--CH--CH}_2\text{--O}--\text{C--CH}_2\text{--CH--CH}_2\text{--Cl}
\]

Reaction Scheme 3: Preparation of the diglycidyl ether of bisphenol-A

\[
\text{NaOH} \rightarrow \text{CH}_2\text{--CH--CH}_2\text{--O}--\text{C--CH}_2\text{--CH--CH}_2\text{--Cl} + 2\text{HCl}
\]
Bisphenol-A can also be replaced with other phenols such as bisphenol-F and bisphenol-S to improve the properties. The illustrations of following phenols are given below in Figure 1.7.

![Figure 1.7 Structure of bisphenol-A and bisphenol-F](image)

The molecular weight of the polymer is controlled by the ratio of ECH / BPA with a large excess of ECH, it is possible to make a resin that is dominantly DGEBPA, where n=0 in the general formula. The pure n=0 compound is a crystalline solid but commercial grades of low molecular weight resin are liquid with n values of 0.11 to 0.15 (so called standard liquid resin).

As the ratio of ECH/BPA is reduced, that is, as ECH/BPA approaches 1:1, the molecular weight and the n value of the epoxy resin increase. Viscosity also increases with molecular weight. Above an average n value of 1, the resin is largely amorphous solid. As molecular weight increases, epoxy equivalent weight and average hydroxyl functionality also increases (Hadad 1988).

### 1.5.2 Structure and Applications of Epoxy

The oxirane ring and bisphenol-A determine the important properties of DGEBA. The thermoset behaviour of epoxy is due to the presence of oxirane ring, which gets cross linked with curatives. Good corrosion and thermal properties are due to the presence of bulky aromatic rings in the backbone. Good adhesion of epoxy is mainly due to the presence of secondary alcohol. Despite of these properties, it is flexible and has poor
UV stability due to the presence of bulky group. Compared to other resins epoxy has its unique properties which has been illustrated in the Figures 1.8 and 1.9.

**Figure 1.8 Unique properties of epoxy influenced by its structure**

**Figure 1.9 Illustrates the unique properties of epoxy**

### 1.5.3 Curing of Epoxy Resin

The chemical chosen to react with the epoxides is referred to as the curing agent (or hardener), and it typically has active hydrogen attached to nitrogen, oxygen, or sulphur. Epoxy resins can be cured or cross linked by a large variety of chemical compounds such as aliphatic and aromatic amines,
acid anhydrides, and latent curing agents or catalysts. Other types of curing agents used in significant quantities in commercial applications are the phenols, carboxylic acids, urea, inorganic acids and bases, and mercaptan. The high molecular weight epoxy resins are cured through the hydroxyl groups with phenols or ureas (Bruins 1968).

The selection of the curing agent depends on many parameters and will determine, to a large extent, the performance of the final epoxy thermoset. Amine curing agents are the most common and can be primary or secondary, aliphatic or aromatic, or cycloaliphatic. The amines typically have three reactive sites per molecule that facilitate the formation of a three-dimensional polymer network when mixed with the epoxy resin (Barton et al. 1967, Tanaka & Bauer 1988).

The epoxide group reacts with several substance classes. Only a few of the possible reactions are used for curing in practice. Curing agents of epoxy resins can be subdivided into three classes:

i) Compounds with active hydrogen,

ii) Ionic initiators, and

iii) Hydroxyl coupling agents.

The most commonly used curing reaction is based on the polyaddition reaction, thereby opening the epoxide ring. The glycidyl group can be cured by amines and other nitrogen-containing compounds such as polyamides. Many of the amines effect curing at room temperature. This type of curing is called a ‘cold curing’.

The reactivity of an epoxy compound with an amine depends on the structure of the compounds. The relative reaction rates of the secondary amine
to the primary amine can be explained in terms of substitution effects. Anhydrides are active only at elevated temperatures. This type of curing is addressed as ‘hot curing’. The oxygen’s extra pair of electrons swipes hydrogen from the ammonium nitrogen for making an alcohol group and amine group. Then two more epoxide group adds to the amine at other end of diamines. In this manner, all the diamine molecules and all the diepoxy molecules become tied together in one big molecule as shown in Figure 1.10.

![Figure 1.10 Epoxy - amine reaction](image)

Aliphatic polyamines such as diethylenetriamine, triethylenetetramine and other aliphatic hydrocarbon-based amines have been used for ambient-cure temperature epoxy resin systems in applications such as civil engineering, adhesives and architectural and maintenance coatings (Nazanin et al 2005). Aromatic diamines such as 4, 4’ diaminodiphenylmethane have been used as heat or ambient-curing hardeners after chemical modification.
In addition to the above types of curing agents there are also non-
amine based curing agents. Either aromatic or aliphatic isocyanates may also
be used as curing agents for epoxy resins. The isocyanates react through the
hydroxyl groups of the epoxy resin and provide very good low temperature
curing, good flexibility, good impact and abrasion resistance as well as good
adhesion (Keefer 1984). Epoxy resins contain secondary hydroxyl groups as
reactive groups only or secondary hydroxyl plus amine diffuses into the
epoxy resin forming an interphase with a thickness of some micrometres.
Depending on the functional groups available in the epoxy resin, urethane and
urea groups are formed in the interphase.

The hybrid network can be prepared by two procedures such as:

i) In the two-step procedure, where sol-gel of TEOS is carried in
the epoxy matrix followed by curing (Dae-Geun et al 2003).

ii) In the three-step procedure, TEOS is hydrolysed in the first
step, then in the second step mixed with the epoxy matrix and
polymerized under the formation of silica and epoxide
networks (Ki Do Kim & Hee Taik Kim 2002).

Large compact silica aggregates, with 100 to 300 nm diameter, are
formed by the two-stage process of polymerization. In the two-stage process
the partial hydrolysis of TEOS effects an acceleration of the gelation. This
results in somewhat smaller silica structures. The most homogeneous hybrid
morphology with the smallest silica domains of size 10 to 20 nm can be
achieved in a two-step preparation of the interpenetrating network (Matejka

An increase in modulus by two orders of magnitude was achieved
at silica content below 10%. Phenolic novolac/silica and cresol novolac
epoxy/silica hybrids can be prepared in a similar manner with TEOS (Jian et al 2003).

1.5.4 **Liquid Silicone Rubber (ACS)**

Modified epoxy is a silicone rubbery polymer is ethoxy terminated poly [dimethyl siloxane-co-(3-amino propyl) methyl siloxane] has a strong Si-O chemical structure that gives the elastomer unique properties. Liquid silicone rubber with amine pendant groups may be added to impart toughness to the epoxy resin, for a few special applications. The amine groups can react with epoxy resin at above 50°C and hence compatibilisation of this blend is easy. The following may be the advantage of modifying epoxy with silicone rubber (Abdullah et al 2011).

1. High and low temperature stability,
2. Inertness (no odour),
3. Translucent and easy to colour,
4. Surface finish,
5. Easy release of solidified plastic from the mould cavity.

1.6 **REINFORCEMENT**

Nano particles are small clusters of atoms about 1 to 100 nanometres in size. 'Nano' derives from the Greek word "Nanos", which means dwarf or extremely small. Studies on the effect of solid nano fillers on polymers are of much importance from the scientific and engineering points of view. Nano fillers, mostly based on clay and silica, impart enhanced physical and chemical properties of polymers even at low concentration. Understanding the interaction between nano filler and a polymer matrix is a
1.6.1 Nano Silica

The various types of silica used as reinforcement are classified as

- Precipitated silica
- Fumed silica
- Insitu generated silica

1.6.1.1 Precipitated silica

Silica is precipitated by acidification of alkali silicate solutions under controlled conditions. The precipitated silicic acid is washed and dried. Depending on the conditions of preparation, the silica filler is more or less active. The products with the highest activity are pure silicic acids with large specific surfaces. Ca- silicates are a little less active but easier to process. Al-silicates have in this series the low reactivity. Physically observable single filler particles of precipitated silica have a particle diameter of approx. 15-20 µm. The silanol content on the particle surface can reach values as high as 6 or more than 10 Si-OH per 1 nm².

1.6.1.2 Fumed silica

Silica produced by a thermal method is frequently called fumed silica. The original process was developed by the Degussa Company in Germany in the 1940s and the product marketed, as it still is under the brand name Aerosil. This silica is made by flame hydrolysis of readily volatile silicon tetrachloride. Silicon tetrachloride, hydrogen, and oxygen are burned in a cooled combustion chamber.
\[ \text{SiCl}_4 + 2\text{H}_2 + \text{O}_2 \rightarrow \text{SiO}_2 + 4\text{HCl} \]

The reaction products are quenched immediately after coming out of the burner. Pyrogenic silica is too active and expensive. Physically observable single filler particles of precipitated silica have a particle diameter of approx. 15µm. (Maryanne & Collinsel 1998).

### 1.6.1.3 Insitu generated silica

The sol-gel reaction of silicon alkoxides generated silica insitu in the polymer matrix. The dispersion of silica generated insitu was better than conventionally added silica due to its formation in place. The diameter distribution of insitu silica was monodispersed. Better filler-polymer interaction is achieved leading to good reinforcement. The amount of silanol groups on the insitu generated silica was smaller than that of the conventional silica surface. The wettability of polymer on to insitu silica, was higher than that on to conventional silica, the fewer silanol groups on the insitu silica would increase the wettability between the polymer molecules and silica due to the lower hydrophilicity of insitu generated silica than conventional silica at room temperature as reported by (Hui et al 2006).

### 1.6.2 Silica Precursor

Sakka & Kamiya (1980) reported conventional organo-functional silanes (metal alkoxide) are first hydrolysed in the presence of water and then condenses to produce metal oxide. Sol-gel synthesis of silica is based on the hydrolysis of alkoxy silanes like tetraethoxysilane or tetramethoxysilane on condensation leads to the formation of insitu generated nano silica in rubber matrix (in the presence of solvent and catalyst). Silicon alkoxide (tetraethoxysilane (TEOS)) is the most commonly used metal alkoxide due to its mild reaction condition as shown in Figure 1.11.
Figure 1.11 Examples of silica precursor (TEOS)

Matejka (2000) presented his work on rubbery cross-linked epoxide was reinforced with silica–siloxane structures formed in situ by sol–gel process from tetraethoxysilane (TEOS). The increase in modulus by two orders of magnitudes was achieved at a low silica content (10 volume %).

Kohjiya et al (2005) reported that the average diameter of the silica particles was close to 10 nm. When the TEOS concentration is increased to 30 weight% with respect to alkyl acrylic copolymer (ACM), the same silica particles grow much bigger in size, displaying an average diameter of 70 nm. This trend is still continuing at 50 weight % of TEOS concentration, where the average diameter of the in situ-generated silica particles reaches almost 100 nm.

Concentration of TEOS in all these cases has been restricted up to 50 weight % with respect to the rubber. Beyond 50 weight %, all the hybrids show phase separation which may be due to higher amount of water condensate that is continuously generated and acts as a non-solvent for the rubbers. This is easily understood from the visual appearance of the samples; phase-separated composites slowly turn opaque in the course of gelation (Bandyopadhyay et al 2006).

1.7 SYNTHESIS OF NANO SILICA

The synthesis of nano scale silica is currently of great interest as silica has higher thermal tolerance and lower thermal conductivity, refractive index, dielectric constant and Young’s modulus.
Jal et al (2004) have synthesized nanosilica by precipitation method and characterized it by various analytical tools. From transmission electron micrograph, the silica particles were found to have an almost spherical shape with a dimension of 50 nm. The surface area was found to be of 560 m$^2$ g$^{-1}$ and density 2.2 g cm$^{-3}$. From thermogravimetric analysis the total silanol density in the silica was found to be 7.68 nm$^{-2}$. The number of reactive silanols that formed a hydrogen bond with water molecules was found to be 2.48. The infrared spectral data supported the presence of the hydrogen bonded silanol group and the siloxane groups in silica.

Nanosilica can also be produced in a form of a dry powder by pyrolysis of tetraalkoxysilanes or tetrachlorosilane in the presence of water as well as by direct hydrolysis of sodium meta-silicate or tetraalkoxysilanes

1.7.1 Synthetic Strategies towards Hybrid Materials

In principle two different approaches can be used for the formation of hybrid materials:

- The building block approach,
- Insitu formation of the components.

1.7.1.1 Building block approach

At least partially keeping their molecular integrity throughout the material formation, which means that structural units that are present in these sources for materials formation can also be found in the final material. Representative examples are modified inorganic clusters or nanoparticles with attached reactive organic groups. Inorganic cluster consist of at least one functional group that allows an interaction with an organic matrix. The building block approach has one large advantage compared with the insitu
formation of the inorganic or organic entities: because at least one building block unit will not undergo significant structural changes during the matrix formation, better structure-property predictions are possible.

1.7.1.2  **Insitu formation of the components**

It is based on the chemical transformation of the precursors used throughout materials preparation. The sol-gel process is applied to produce the inorganic component, well-defined discrete molecules are transformed to multidimensional structures, which often show totally different properties from the original precursors. The internal structure of the final material is determined by the composition of these precursors but also by the reaction conditions. Therefore control over the latter is a crucial step in this process. Changing one parameter can often lead to two very different materials. For example, the inorganic species are a silica derivative formed by the sol-gel process, the change from base to acid catalysis makes a large difference because base catalysis lead to a more particle-like microstructure, while acid catalysis leads to a polymer-like microstructure. Hence, the final performance of the derived materials is strongly dependent on their processing and its optimization.

1.8  **LITERATURE REVIEW**

The research area involving organic-inorganic hybrid network materials prepared by the sol-gel technique has gained more significance in the recent years. The silica particles extracted from natural resources contain metal impurities and not favourable for advanced scientific and industrial applications. Thus focus is given to synthesis of silica (colloidal silica, silica gel, pyrogenic silica and precipitated silica, which is pure and produced mostly in amorphous powder forms compared to natural silica (quartz, tridymite, cristobalite), which are in crystalline form. The present research
focus on the incorporation of nano silica into epoxy matrix by sol-gel process is to improve the dispersion and distribution of nano silica in epoxy matrix and to enhance its mechanical and thermal properties. A detailed literature survey on epoxy, precursor, sol-gel process, epoxy-silica nanocomposites, characterization, testing and its applications is presented.

1.8.1 Sol-gel Process and its Applications

Mahasweta & Bhaumik (2004) have presented a review that a number of inorganic solid state materials are formed using solid precursors and high temperature processes, which are not compatible with the presence of organic groups, because they are decomposed at elevated temperatures and sol-gel process is a suitable alternative technique.

Ismail & Vejayakumaran (2012) presented a review article emphasizing on the synthesis of silica nanoparticles, characterization on size-dependent properties and surface modification for the preparation of homogeneous nanocomposites generally by sol-gel technique.

Brinker & Scherer (1990) related the sol-gel process to an organic polycondensation reaction in which small molecules form polymeric structures by the loss of a substituent. The sol-gel processes are a synthesis route consisting in the preparation of a sol and successive gelation and solvent removal. The precursor used is metal-organic alkoxides especially silica, since they can form an oxide network in organic matrices. The most common silica precursor is TEOS because it is readily purified and has a relatively slow and controllable rate of reaction (Chen & Iroh 1999).

Stober et al (1968) have synthesised spherical silica particles with size ranging from 5 to 2000 nm from aqueous alcohol solutions of silica alkoxides in the presence of ammonia as catalyst. The main advantage of
Stober method is the ability to form monodispersed spherical silica particles compared to the acid catalysed systems which usually results in gel structures.

Cabane et al (1987) dissolved TEOS monomers in water-ethanol mixture in the presence of acid catalysis, which undergoes hydrolysis and condensation of TEOS to form aggregates of branched siloxane network polymers and within a few hours the polymer builds a gel throughout the solution to form a spatial pattern.

Brinker (1988) reviewed the hydrolysis and condensation of monomeric alkoxysilanes and organylalkoxy siliane utilized in sol – gel process. Both reactions are carried out in acid and basic medium. It was observed that acid-catalysed mechanism are preceded by protonation of OH or OR substituents attached to Si, whereas under basic conditions hydroxyl or silanolate anions attack Si directly. Many of the observed structural trends are understood on the basis of the pH and [H$_2$O] dependence of the hydrolysis, condensation, and dissolution reaction.

Vander Vis et al (1993) studied the thermodynamic properties and thermal decomposition of TEOS by insitu IR spectroscopy. During pyrolysis only ethanol and methanol are observed and this shows that the initiating step is the formation of oxygen free radical followed by oxygen-TEOS intermediate, which decompose to ethanol.

Rubio et al (1998) studied the hydrolysis and polymerization of non-catalyst TEOS by Fourier Transform Infrared (FTIR) Spectroscopy. It was observed that the hydrolysis was followed by the decrease in the 1168 and 812 cm$^{-1}$ band as the time increases which shows the hydrolysis. At the same time the 1200 and 1147 cm$^{-1}$ increases with time showing the formation of Si-OH and Si-O-Si bonds. Also it was reported that at 960 and 920 cm$^{-1}$ band are responsible for Si-OH and Si-O free broken bonds.
Hajji et al (1999) investigated the use of acid catalysed results in faster hydrolysis of TEOS and open weak polymer structure is formed. In contrast, slower hydrolysis and faster polycondensation were observed in the case of base catalysed leading to compact colloidal particles. Larger spherical particles are expected in the base catalysed reactions, while linear chain growth is expected via acid catalysis. It has been observed that base catalysis usually yields opaque composites with phase dimensions well above 100 nm and more generally in the micrometre range. The transparent nanocomposites with morphology less than 100 nm can be achieved by using acid catalyses. Therefore the polymer-silica nanocomposites prepared by sol-gel process are generally obtained by acid catalysis.

Goutam et al (2000) have generated dense silica microspheres from the hydrolysis and condensation of TEOS in the presence of fixed concentration of acetic acid and water as catalyst. The formation of dense silica microspheres was monitored by FTIR. The particle size was analysed by dynamic light scattering and transmission electron microscopy. The study confirmed the generation of nano silica of dimension about 50 nm, which gradually grow to 2000 to 3000 nm at the end of the reaction.

Sungtack Kang et al (2001) prepared uniform sized silica particles (S) by sol-gel reaction and then modified either by substituting surface silanol groups into epoxide ring (S-epoxide), amine (S-NH$_2$) or isocyanate (S-NCO) groups or by calcinating them to remove surface silanol groups (CS). The modified particles are identified by Infrared and Raman spectroscopy, differential scanning calorimetry (DSC), and particle size analyser. It was found that surface modified particles can be chemically reacted with epoxy matrix, which is confirmed by exothermic peaks in DSC thermograms. In scanning electron micrographs of fractured composites, it is observed that the particle dispersion and interface are considerably affected by functional
groups of fillers. Weak interfaces and aggregation of particles are observed for composites filled with silanol groups or S-NCO. However, the aggregation of fillers is highly suppressed in composites filled with S-epoxide and S-NH$_2$ particles. Generally, the coefficients of thermal expansion (CTE) of composites are reduced with an increase of filler contents. Moreover, composites with strong interface exhibit an additional reduction of CTEs. Composites with weak interface show essentially no change in glass transition temperature ($T_g$) and damping with filler contents, while composites with strong interface show an increase of $T_g$ and a decrease of damping with filler content.

Ki Do Kim & Hee Taik Kim (2002) adopted a new method for formation of silica nano particles which consists of a two stage semi-batch / batch hydrolysis reaction of TEOS using base catalyst. A slow rate of hydrolysis was reported in semi-batch method compare to the batch method. The silica particle produced has a size was 106 nm in semi-batch method and the size was 23 nm in the batch method.

Green et al (2003) used $^{29}$Si NMR, small-angle X-ray scattering (SAXS), and dynamic light scattering (DLS) to monitor the synthesis of silica nanoparticles from the base-catalysed hydrolysis of TEOS in methanol and ethanol. The silica particle size was 10.3 nm in methanol and 20.7 nm in ethanol.

Xuefeng Ding et al (2004) synthesised hollow silica nanoparticles with incorporation of silanol groups (SiOH) onto polymer particles in dispersion polymerization and the polycondensation reaction of TEOS exclusively took place at the particles surface in the presence of ammonia following the so-called Stober process and the silica-coated polymer powers were calcined at 800 °C. The diameters of hollow silica spheres are found to be very close to the original diameter and the average pore diameter is less
than 100 nm. Moreover, the hollow silica nanoparticles have uniform aperture, do not agglomerate and collapse.

Rahman et al (2006) produced monodispersed silica particles in the range 20 nm to 34 nm by small additions of anion electrolyte (ammonium salts of Br, I and Cl). It was found that all anions were able to reduce the particle size by 73 to 78 %, among them Br and I have the highest than Cl. The synthesised silica powder was free from cation impurities. Rahman et al (2007) produced homogeneous and stable silica nanoparticles with mean particles size of 7.1 to 1.9 nm in ethanol, under the influence of low frequency ultrasound.

Anna & Johan (2004) synthesised organically modified silica (ORMOSIL) particles by using both the hydrolytic and non-hydrolytic sol-gel routes. The hybrid (nano) composites are organically modified with an alkyl or aryl group covalently bonded to silicon.

Kota et al (2005) used a sequential process to prepare monodispersed and uniform-size silica nanoparticles using ultra sonication by sol–gel process. The silica particles were obtained by hydrolysis of TEOS in ethanol medium and a detailed study was carried out on the effect of different reagents on particle sizes. Various-sized particles in the range 20–460 nm were synthesized.

Keifeng et al (2005) employed a novel approach for the fabrication of silica nanocubes with controlled size and shape. The silica nanocubes were highly dispersed with width of about 30 nm and product with high purity. A small amount of tartaric acid was introduced in the TEOS hydrolysis process. In this work tartaric acid as the organic template, was formed on the surface of hydrous silica colloidal particles. The organic template ordered by
carboxyl, led to the self-assembly of amorphous silica sol encapsulated into cubic matrixes, and the organic template was packed into 3D structure.

Xin et al (2007) prepared an organic-inorganic hybrid SiO$_2$–matrix composite through sol–gel process using TEOS and MEMO ($\beta$-methoxyethoxy methyl ortho silicate) as precursors. The structures and thermal stability of the composites were investigated by various complementary techniques. The results indicate that both TEOS and MEMO hydrolyse and polymerize in sols to gelatinize and form silica–matrix materials after being baked at 60 °C. Increase of the MEMO concentration in the sols results in reduction of low-molecular compounds (such as H$_2$O, CH$_3$OH, etc.) incorporated in baked gels, thus significantly decreasing the thermal weight-loss at temperature lower than 400°C. On the other hand, the organic functional groups bonded with –Si–O in MEMO polymerize and gelatinize to change the atomic structures and chemical states of Si in the composites. The sol–gel composites induced by the TEOS/MEMO gelatinization process become pure silica after thermal treatment over 500°C, due to decomposition and evaporation of the incorporated organic groups. It is interesting to note that from the sol containing TEOS and MEMO precursors, hydrolysed product from then MEMO precursor preferably dip-deposits compared with that from TEOS.

Dimitriev et al (2008) reviewed the of sol-gel process and has the potential in producing important materials synthesis of bulk materials, fibre, sheet, coating and particle at low temperature, it also produce materials with new composition, with high purity and high homogeneity. It also emphasised on the role starting precursor.

Guskos et al (2009) reported the use of nonhydrolytic sol-gel process by reacting metal halides and alkoxides. Chetan et al (2013) investigated the formation of silica from TEOS by a non-peptide block
copolymer enzyme mimic under neutral condition. The bio-inspired polymer combines the features of neutral pH, low temperature and structure control in silica formation.

### 1.8.2 Epoxy-silica Nanocomposites

Sadanand et al (2011) discussed a review on organic-inorganic hybrid materials by sol–gel approach. The explosion of activity in this area in the past decade has made tremendous progress in both the fundamental understanding of the sol–gel process and the development and applications of new organic-inorganic hybrid materials.

Francesca et al (2013) produced an epoxy–silica hybrid from a mixture of an amine-siliane functionalized bisphenol-A resin and a siloxane precursor derived from tetraethoxysilane with small amounts of glycidoxypropyltrimethoxysilane coupling agent. They compared the plain epoxy with those of two epoxy controls. Thermal properties and characterisation were carried out by DSC, dynamic mechanical analysis (DMA), electron microscopy, thermogravimetric analysis (TGA), UV–Vis spectroscopy, SAXS and densitometry. Mechanical properties such as modulus, strength and ductility were measured in 3-point bending mode at 23°C and 50°C. The siloxane hybridization of the original epoxy resin was found to increase the glass transition temperature ($T_g$) of cold cured systems by more than 10$^\circ$ $T_g$ and to produce large improvements in mechanical properties.

Matejka et al (1998) examined the evolution of heterogeneous structure during polymerization in the epoxy–silica hybrid was followed by small-angle X-ray scattering using a position-sensitive detector. The organic–inorganic hybrid was composed of an epoxide–amine system and the silica formed by the sol–gel process from tetraethoxysilane (TEOS). Silica structure
evolution is determined by catalytic conditions and the way of preparation: one- or two-stage process. The one-stage polymerization was base-catalysed by an amine used as a cross-linker of the epoxide. The reaction results in formation of large overlapping polysiloxane clusters from the very beginning of the reaction. During polymerization more branched domains gradually appear within the structure. The polymer shows a compact structure with fractal dimension increasing during the polymerization to \( D_{s2.5} \). The two-stage procedure consisting in acid pre-hydrolysis of TEOS and basic catalysis in the second step leads to an acceleration of gelation. Primary particles are formed in the first step followed by aggregation into clusters in the second step. The inner structure of the clusters described by a fractal dimension does not change during the polymerization. The diffusion-limited cluster–cluster reaction may be responsible for a more open structure with a fractal dimension \( D_{s1.7} \).

Steven et al (2003) prepared epoxy-based inorganic–organic hybrid polymers, for coatings applications, from 3-glycidoxypropyltrimethoxysilane by a sol–gel process. The precursor molecule possesses both epoxy and silicon alkoxides functionality and so interlinked inorganic–organic networks can be formed. Diethylenetriamine was used to open the epoxy rings and form the organic network to an extent determined by the initial ratio of amine to epoxy groups. The materials were cured either at room temperature or with an additional heat treatment at 150°C. Structural characterisation of the cured hybrid materials was performed using a combination of Raman, and \(^{29}\)Si and \(^{13}\)C MAS NMR spectroscopies. It was observed that the formation of the two networks does not occur independently and the rate or extent of organic cross-linking has a direct effect on the extent of the inorganic network formation, and vice versa.
Masahiro Fujiwara et al (2004) prepared nanocomposites based on epoxy resin and silica using a simple procedure wherein diglycidyl ethers of bisphenol-A (DGEBA) as the prepolymer of epoxy resin, tetraethoxysilane (TEOS) as silica source, and hexahydrophthalic anhydride (HHPA) were mixed together and heated at 170 °C in a sealed autoclave. HHPA played two roles in this reaction system: one role is as a well-known curing reagent of epoxy resin; the other is as the condensation reagent of alkoxysilane, since transesterification promotes this reaction. These two reactions occurred simultaneously in homogeneous solution, and organic–inorganic composite materials were readily obtained. Field emission SEM/EDX images showed that silica particles of nano size (below 50 nm) were included in the epoxy resin matrix. Some of these epoxy resin/silica nanocomposites materials displayed high thermal stability. When DGEBA bearing about three bisphenol-A units and five molar equivalents of TEOS were reacted, the obtained composite displayed no T_g point below 300°C in the DSC thermogram. This high thermal stability is likely to be derived from the interaction of hydroxyl groups of DGEBA with silica.

Shaorong Lu et al (2006) prepared a new type of inorganic-polymer hybrid materials of epoxy/silica-titania by incorporating grafted epoxy, which had been synthesized by epoxy and tetraethoxysilane (TEOS), with highly reactive TEOS and tetrabutyltitanate (TBT) by using the insitu sol–gel process. The grafted epoxy was confirmed by FTIR and ^1H-NMR spectroscopic technique. Analytical results using FTIR spectroscopy and atomic force microscopy (AFM) demonstrated that epoxy chains have been covalently bonded to the surface of the SiO_2-TiO_2 particles. The particles size of SiO_2-TiO_2 are about 20–50 nm, as characterized by AFM. The experimental results showed that the glass-transition temperatures and the modulus of the modified systems were higher than that of the unmodified
system, and the impact strength was enhanced by two to three times compared with that of the plain epoxy.

Shaorong Lu et al (2005) synthesised a transparent organic-inorganic epoxy/silica hybrid material by using epoxy resin, functionalized-epoxy resin, which was partially functionalized by 3-aminopropyl triethoxysilane (APTES), and highly reactive polysilicic acid (PSA), which was prepared through hydrolysis and condensation of meta-silicate salt. The properties of hybrid materials such as impact strength, tensile strength, glass transition temperature ($T_g$), thermogravimetric temperature (TGA), and thermal effect of the hybrid materials were studied. The size of PSA particles in THF, measured by dynamic light scattering technique ranges between 10-28 nm. The results of experiment indicated that modified epoxy resin posed better roughness than that of the pure epoxy resin. The structure of the hybrid materials was characterized by FTIR spectroscopy and $^{29}$SiNMR spectroscopy.

Federica Bondioli et al (2011) prepared the insitu generation of silica, zirconia, or titania within epoxy resins based on bisphenol-A diglycidyl ether and Jeffamine VR by means of the aqueous sol–gel process. The morphology of the prepared hybrids varied from a particulate dispersed phase to a co-continuous morphology. Silica and zirconia filled epoxies were characterized by a significant increase in thermal stability, attributable to the high thermal stability of silica and zirconia phases. On the contrary, the introduction of titania induced a strong decrease in thermal stability of the epoxy/titania hybrids compared with the pure epoxy resin, attributable to metal-catalyzed oxidative decomposition mechanism in the polymer/titania composite. Hybrids were much more transparent than unfilled epoxy. The transmittance of silica- and titania-based hybrids showed a slight decrease by increasing the content of filler, while the transparency of zirconia-based
hybrids was very high and almost constant independently by the nominal content of filler. The presence of insitu generated fillers significantly enhanced the scratch resistance of the epoxy resin as indicated by the marked increase of critical load for all the hybrids.

Nazanin Farhadyar et al (2005) reported the organic-inorganic hybrid coating based on epoxy resin. The hybrid networks possess excellent optical transparency and nano scale micro phase separation. The hybrid materials can be used for coating aluminium alloy (AA) substrates. The morphology of the fractured surface was observed by scanning electron microscopy (SEM). It was found that the average diameter of particles is 167 nm, which indicates the transparency of the hybrid system. TGA results show that cross-linking between the epoxy resin and silica increases the thermal stability of the system.

Sungtack Kanga et al (2001) investigated on the preparation and characterization of epoxy composites filled with functionalized nano silica particles obtained via sol-gel process. The modified particles were identified by infrared and Raman spectroscopy, differential scanning calorimetry (DSC), and particle size analyser. It was found that surface modified particles can be chemically reacted with epoxy matrix, which was confirmed by exothermic peaks in DSC thermograms. In SEM of fractured composites, it was observed that the particle dispersion and interface are considerably affected by functional groups of fillers. Composites with weak interface show essentially no change in glass transition temperature ($T_g$) and damping with filler contents, while composites with strong interface show an increase of $T_g$ and a decrease of damping with filler content.

Federica Bondioli et al (2005) investigated on the preparation, characterization, and modelling of silica nanoparticles having different sizes was obtained by the sol-gel process. The nanoparticles were subsequently
used as reinforcing fillers to prepare epoxy-based composites with a silica content ranging from 1 to 5 weight %. SEM analysis and tensile tests carried out on the silica-epoxy nanocomposites indicated the absence of particle aggregation and a reinforcing effect in terms of increased elastic modulus. Mechanical properties were also modelled by using a finite element code able to construct a numerical model from a microstructural image of the material. A more reliable model was prepared by considering the presence of an interphase layer surrounding the particles with intermediate elastic properties between the epoxy and the inclusions and a characteristic size proportional to the particle radius.

Ragostaa et al (2005) produced epoxy-silica nanocomposites by dispersing silica-organosol particles in TGDDM/DDS resin mixtures. The resulting materials were investigated in terms of chemical interactions, curing behaviour and mechanical and fracture 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 behaviour of the epoxy matrix was not adversely affected by the inorganic phase. A conspicuous increase of modulus and yield strength was found by increasing the silica content. Fracture mechanics tests showed that the addition of silica nanoparticles up to 10 weight % brings about a considerable enhancement in fracture toughness and an increase in the critical crack length for the onset of crack propagation. This enhancement in toughness is larger than that achieved until now with micro-sized particles.

Liu et al (2003) prepared epoxy-silica nanocomposites from directly blending diglycidylether of bisphenol-A and nanoscale colloidal silica and then curing with 4, 4’-diaminodiphenylmethane. The epoxy-silica nanocomposites showed good transparency and miscibility observed with AFM, SEM, and TEM. The thermal stability of the epoxy resins was
improved with the incorporation of the colloidal silica. However, a depression on the glass transition temperature of the resins was observed, owing to the plasticizing effect of the colloidal silica. Moreover, the nanoscale colloidal silica did not show effectively synergistic effect on char formation and flame retardance with phosphorus.

Johnsen et al (2007) prepared epoxy resin, cured with an anhydride, and modified by the addition of silica nanoparticles. The particles were introduced through a sol–gel technique which gave a very well-dispersed phase of nanosilica particles which were about 20 nm in diameter. Atomic force and electron microscopies showed that the nanoparticles were well-dispersed throughout the epoxy matrix. The glass transition temperature was unchanged by the addition of the nanoparticles, but both the modulus and toughness were increased. The measured modulus was compared to theoretical models, and good agreement was found. The fracture energy increased from 100 J/m² for the unmodified epoxy polymer to 460 J/m² for the epoxy polymer with 13 volume % of nanosilica.

Masahiro Fujiwar et al (2004) developed nanocomposites materials of epoxy resin and silica by a simple procedure wherein diglycidylethers of bisphenol-A (DGEBA) as the pre-polymer of epoxy resin, tetraethoxysilane (TEOS) as silica source, and hexahydrophthalic anhydride (HHPA) were mixed together and heated at 170°C in a sealed autoclave. HHPA played two roles in this reaction system: one role is as a well-known curing reagent of epoxy resin; the other is as the condensation reagent of alkoxysilane, since transesterification promotes this reaction. These two reactions occurred simultaneously in homogeneous solution, and organic–inorganic composite materials were readily obtained. Field emission SEM/EDX images showed that silica particles of nano size (below 50 nm) were included in the epoxy resin matrix. Some of these epoxy resin/silica nanocomposites materials
displayed high thermal stability. When DGEBA bearing about three bisphenol-A units and five molar equivalents of TEOS were reacted, the obtained composite displayed no $T_g$ point below 300°C in the DSC thermogram. This high thermal stability is likely to be derived from the interaction of hydroxyl groups of DGEBA with silica.

Bandyopadhyay et al (2006) reports a comparative study on structure-property relationship of acrylic rubber (ACM)/silica, epoxidized natural rubber (ENR)/silica and poly (vinyl alcohol) (PVA)/silica hybrid nanocomposites prepared by sol-gel technique under different pH levels (pH = 1.0-13.0), probably for the first time. The initial concentration of tetraethoxysilane (TEOS) was kept at 45 weight% and tetrahydrofuran (THF) for ACM/ silica and ENR/silica while water for PVA/silica was taken as solvents. TEOS to water mole ratio was maintained at 1:2 for the rubber/silica systems to accomplish the sol-gel reaction. The structure of the resultant hybrid composites was determined by using electron microscopy, Fourier Transform infrared spectroscopy and solubility. Dynamic mechanical and mechanical properties were also investigated. The silica particles were found to exist as nanoparticles (average diameter <100 nm) at low pH (2.0) beyond which these aggregate, although the amount of silica generation was not strictly influenced by the various pH conditions in all the systems. These nanocomposites were optically clear and showed superior mechanical reinforcement over the micro-composites containing aggregated silica structures with lower optical clarity. The nanocomposites exhibited higher storage modulus both at the glassy and the rubbery regions as compared to those microcomposites. The loss tangent peak heights were also minimum and the $T_g$ shifted to higher temperature for those nanocomposites. The maximum improvement of mechanical properties was observed with the PVA/silica nanocomposites due to higher level of interaction between the hydroxyl groups of PVA and the silanol groups of the silica phase.
Wang et al (2006) discussed the effects of dimethyldiethoxysilane (DDS) addition on the sol–gel process of TEOS were investigated by varying the addition-time of DDS to acid-catalysed TEOS solutions in different water contents. At low water content, the solution is transparent until gelation takes place, while at a high water content; phase separation occurs and leads to hydrophobic particles which, according to scanning electron microscopy-energy dispersive X-ray analysis (SEM-EDX) and thermogravimetric analysis, show different morphology and thermal behaviour. The reaction between TEOS and DDS in different water contents and the structure of final polymers are discussed.

Matejka et al (1998) prepared the organic–inorganic hybrid through an epoxide–amine system and the silica formed by the sol–gel process from tetraethoxysilane (TEOS). Silica structure evolution is determined by catalytic conditions and the way of preparation: one- or two-stage process. The one-stage polymerization was base-catalyzed by an amine used as a cross-linker of the epoxide. The reaction results in formation of large overlapping polysiloxane clusters from the very beginning of the reaction. During polymerization more branched domains gradually appear within the structure. The two-stage procedure consisting in acid pre-hydrolysis of TEOS and basic catalysis in the second step leads to an acceleration of gelation. Primary particles are formed in the first step followed by aggregation into clusters in the second step. The inner structure of the clusters described by a fractal dimension does not change during the polymerization.

Johnsen et al (2007) reported the epoxy resin, cured with an anhydride, has been modified by the addition of silica nanoparticles. The particles were introduced via a sol–gel technique which gave a very well-dispersed phase of nanosilica particles which were about 20 nm in diameter.
Atomic force and electron microscopies showed that the nanoparticles were well-dispersed throughout the epoxy matrix. The glass transition temperature was unchanged by the addition of the nanoparticles, but both the modulus and toughness were increased.

Macan et al (2004) investigated the cure kinetics of organic–inorganic hybrids based on epoxy resin was investigated, using differential scanning calorimetry (DSC). Thermoset hybrid materials were prepared from diglycidyl ether of bisphenol-A (DGEBA) as organic precursor, and 3-glycidyloxypropyltrimethoxysilane (GLYMO) as inorganic precursor. Precursors were polymerised simultaneously using poly (oxypropylene) diamine (Jeffamine D230) as a curing agent. Isothermal DSC characterisation of DGEBA/Jeffamine system and two hybrid DGEBA/GLYMO/Jeffamine systems, with DGEBA and GLYMO mixed in mass ratios of 2:1 and 1:1, respectively, was performed at different temperatures. Applicability of empirical models, commonly used to describe the curing kinetics of thermosets, to hybrid systems was investigated, and the resulting parameters were tested on dynamic DSC scans. Additionally, prepared materials were studied by FTIR and the extraction in tetrahydrofuran. The presence of inorganic phase was found to hinder complete cross-linking of organic phase and influence the kinetics of cure.

Hui et al (1989) investigated the kinetics of hydrolysis of TEOS and polycondensation of the hydrolysed products were studied by means of high resolution $^1$HNMR and gel permeation chromatography (GPC). It is found that: (1) the molecular weight distribution of polymer appears to be a bi-modal molecular weight distribution in the final stage of polycondensation when $H_2O$/TEOS; (2) polymerization reactions possess the characteristics of polycondensation; (3) the mechanism is similar to the polycondensation of silicic acid in weak-acid aqueous solution and (4) the increase of HCl
concentration retards the polycondensation. Rubio et al (1998) investigated hydrolysis and polymerisation of TEOS of non-catalyst system by FTIR and reported the time of complete hydrolysis of TEOS and the factor which governs the gelation time of sol.

Ming Qiu Zhang et al (2002) overcome the disadvantages generated by the loosened nanoparticle agglomerates dispersed in polymer composites; an irradiation grafting method was applied to modify nanosilica by covalently bonding polyacrylamide (PAAM) on to the particles. When the grafted nanosilica was added to epoxy, the curing kinetics of the matrix was accelerated. Moreover, the grafting PAAM can take part in the curing of epoxy so that chemical bonding was established between the nanometer fillers and the matrix. Sliding wear tests of the materials demonstrated that the frictional coefficient and the specific wear rate of nanosilica/epoxy composites are lower than those of the unfilled epoxy. Grafted nanosilica reinforced composites have the lowest frictional property and the highest wear resistance of the examined composites. Compared with the cases of micronized silica and untreated nanosilica, the employment of grafted nanosilica provided the composites with much higher tribological performance enhancement efficiency.

Ochi et al (2001) synthesised organic-inorganic hybrids containing 4 to 19.8 weight% of silica using diglycidyl ether of bisphenol-A (DGEBA) and a γ-glycidoxypropyltrimethoxysilane (GPTMS) or a tetramethylorthosilicate (TMOS) by sol-gel process. In the DGEBA/GPTMS hybrids, the storage modulus in the rubbery region increased and the peak area of the tan δ curves in the glass transition region decreased, respectively, with the hybridization of small amounts of silica. This may result from the suppression of the epoxy network moiety with the incorporation of the silica network. Observation using transmission electron microscopy (TEM) revealed that the silica
networks are uniformly dispersed in the hybrids. Furthermore, the hybrids with GPTMS show very high adhesion strength for the silicone rubber. Results from the X-ray microanalysis show that the silica networks are concentrated in the interfacial area of the adhesive joints with silicone rubber. In the swelling test of silicone rubber with the epoxy resin containing GPTMS, the degree of swelling increased with increasing GPTMS content. The high adhesion strength observed in the DGEBA/GPTMS hybrids was caused by the immersion of the adhesives into the surface layer of the silicone rubber substrate, which was attributed to the good affinity between GPTMS and the silicone rubber.

Ying-Ling et al (2003) studied the effect of silicon source on the mechanism and efficiency of silicon–phosphorus synergism of flame retardation. The studied systems composed of a phosphorus-containing epoxy resin and various types of silicon additives including nanoscale colloidal silica (CS), TEOS, and diglycidylether terminated polydimethylsiloxane (PDMS-DG). Thermal stability and degradation kinetics of cured epoxy resins, elemental analysis of degraded residues, and evolved gases analysis of degradation reactions were conducted with a thermogravimetric analyser, energy-dispersive X-ray spectrometry, and gas chromatography–mass spectrometry, respectively. Addition of silicon compounds showed significant effect on enhancing the thermal stability and char yields of the cured epoxy resins. During thermal degradation, TEOS and PDMS-DG exhibited silicon migration to sample surface and CS did not. Self-degradation of PDMS-DG resulted in a silicon loss for PDMS-DG-containing epoxy resin. From the results it was concluded that using TEOS as an additive for epoxy resins and formation of epoxy-silica hybrid structure through sol–gel reactions was a good approach for achieving phosphorus–silicon synergism in flame retardation.
Jian et al (2008) synthesized silica hollow spheres from nano- to micro size level by adjusting the hydrolysis and condensation kinetics of silane precursors in a mild buffer solution (NaH$_2$PO$_4$-Na$_2$HPO$_4$, pH \(\approx 7.0\)) in the presence of surfactant. Characterization using transmission electron microscopy, field-emission scanning electron microscopy, and nitrogen sorption techniques reveals that the silica hollow nanospheres with outer diameter of about 12 nm can be obtained with tetramethoxysilane as silane precursor. Silica hollow nanospheres (\(\sim 20\) nm) can also be prepared using tetraethoxysilane (TEOS) as silane precursor with the addition of hydrolysis and condensation catalyst NH$_4$F. Using TEOS as the silane precursor without F-, the formation of silica hollow microspheres (0.5\(\sim\)8 \(\mu\)m) was observed. Time-resolved insitu UV-Raman results show that TEOS does not hydrolyse at room temperature, and the hydrolysis of TEOS occurs immediately at room temperature when NH$_4$F was added to the buffer solution. The fast hydrolysis and condensation rates of silane precursor favour the formation of hollow nanospheres through the condensation of silicate around a single micelle of in buffer solution. The construction of hollow microspheres is attributed to the formation of O/W emulsion by the hydrophobic TEOS with the aid of surfactant due to the existence of unhydrolyzed TEOS at room temperature under current synthetic conditions.

Zhihai Cao et al (2012) prepared silica capsules with submicrometer sizes with hydrolysis and condensation of TEOS in pH controlled hydrophilic droplets. The pH-controlled hydrophilic droplets used by them were poly (ethylene-co-butylene)-b-poly (ethylene oxide) (P (E/B)-PEO) or SPAN 80 as surfactant. The silica shell was formed by the deposition of silica on the surface of droplets. The formation of capsule morphology was confirmed by transmission electron microscopy (TEM) and field emission scanning electron microscopy (FESEM).
Roger Richer & Louis Mercier (2001) prepared a wide range of organically functionalized wormhole-motif and hexagonal mesoporous MSU-X silicas by a one-step synthesis process involving the simultaneous addition of tetraethoxysilane (TEOS) and 3-mercaptopropyltrimethoxysilane (MPTMS) to solutions of structure-directing non-ionic surfactant micelles, followed by fluoride-mediated hydrolysis/cross-linking and surfactant extraction. The effect of various synthesis parameters, including relative reagent concentration (MPTMS/TEOS ratio), temperature, and surfactant type, on the structure and composition of the mesostructures was investigated. Generally, higher MPTMS/TEOS ratios resulted in materials with higher functional group loadings, while increasing temperature also produced more highly functionalized materials. Although increasing synthesis temperature produced materials with greater pore diameters and lattice spacing’s, increased organosilane content in the mesostructures produced materials with diminished pore diameters and lattice spacings. Thus, MSU-X materials with fine-tuned composition and pore dimensions were produced by systematically varying these synthesis parameters. It was found that the amphiphilic character of the non-ionic surfactants is affected both by temperature and by the addition of the comparatively hydrophobic organosilane constituent in the micelle, thus forming mesostructures with corresponding compositional and structural features.

Matejka et al (2000) also compared the nanocomposite formation of epoxy-silica system (epoxy in this case was cured with a rubbery hardener leading to rubbery network) under two conditions-i) generation of epoxy network and nano phase i.e. silica formation concurrently and ii) formation of nanophase in the pre cured epoxy network by swelling the sheet/film in the silica precursor. They concluded that the latter approach led to a nanocomposite with finer nanophase formation but with inhomogeneous silica distribution. The surfaces of the films were seen to
be richer in silica compared with the interior of the films. This was attributed to anisotropic swelling of the epoxy network in TEOS.

Epoxy films (based on UV cured cycloaliphatic epoxy and also epoxy modified by epoxy terminated poly dimethyl siloxane i.e. silicone) were swollen in tetra methoxy silane (TMOS) at higher temperature, followed by exposure to humidity (Kothandaraman et al 2012). The studies showed submicron level silica concentrated more on the surface of the films and also in the silicone phase.

1.9 NEED FOR THE PRESENT STUDY

Many parameters determine the sol-gel process like temperature, catalyst and [water]:[TEOS] ratio. Brinker and Scherer (1990) emphasised the importance of R value ($H_2O$/TEOS) in sol-gel process. The purpose of this study is to clarify the relationship between R value, amount of silica precipitated, morphology, mechanical properties and thermal stability of the composites. The pH of the sol-gel process too plays a role-acidic pH leads to more open structures which lead to lower particle sizes of the nanofiller while base catalyst lead to larger particles. Acid hydrolysis speeds up the precipitation of the nanofiller. Literature studies on the sol-gel process, without a base or acid catalyst, are very few. We have attempted sol-gel process on epoxies, without a basic or acid catalyst with the expectation that they may lead to smaller particles of the nanofiller. Since the hydrolysis and condensation are slow in neutral medium, particle growth too may be expected to be slow and hence, the expectation of smaller particles in the epoxy matrix (Matejka et al 2000).

In this present work, sol-gel process is used for insitu generation of silica in epoxy matrix, through varying R value ($H_2O$ / TEOS), under neutral conditions. In acidic condition, hydrolysis reaction is faster than condensation
and leads to formation of dense micro porous networks with pore size less than 2 nm. Whereas in alkaline conditions, condensations reaction is faster than hydrolysis and leads to formation of mesoporous networks with pore size ranging from 2 nm to 50 nm, which may also lead to aggregate formation (Steven et al 2003). The effect of pH change is a good tool to design pore network for specific applications. This work focus on insitu generation of nano silica in epoxy matrix by sol-gel process using neutral condition, where hydrolysis and condensation reactions can be optimised to get a good dispersion and distribution of silica particle network which will enhances the mechanical and thermal properties of the composites.

The thesis also covers some work done on swelling an epoxy sheet/film (DGEBA type) and a modified DGEBA (by amine containing silicone-coded AN102 by the supplier) in TEOS at high temperature followed by hydrolysis by exposure to humidity at high temperature and studying its effect on a few mechanical properties and also the morphology of the resulting composites. Sol-gel process on a cured epoxy film can help in getting finer morphology of the dispersed phase-this will avoid interference of the curing of epoxy by the sol-gel process.

1.10 OBJECTIVES OF THE RESEARCH

The present research work, studies on insitu generation of nanosilica network in polymer matrix by sol-gel process has the following objectives:

i) To prepare epoxy-silica composites by sol-gel reaction using simultaneous and sequential process by varying R value under neutral condition.

ii) To prepare modified epoxy using amine containing liquid silicone rubber (ACS).
iii) To prepare modified epoxy-silica composites by sol-gel process.

iv) To study the kinetics of sol-gel reaction of epoxy-silica composites and hydrolysis of TEOS using FTIR.

v) To evaluate the mechanical and morphological properties of epoxy-silica composites and modified epoxy-silica composites.

vi) To evaluate the thermal behaviour of epoxy-silica composites and modified epoxy-silica composites.

vii) To evaluate the mechanical and scratch resistance properties of plain and modified, cured, epoxy sheets/films soaked in TEOS and hydrolysed followed by condensation.

1.11 ORGANISATION OF THE THESIS

The chapters in the thesis are organised as given below.

Chapter 1 deals with introduction of polymers, polymer nanocomposites, sol-gel process, material selection and literature review in the area of organic-inorganic hybrid composites.

Chapter 2 describes the various materials and experimental methods for in situ generation of nano silica-epoxy composites by sol-gel process, optimization of R values, kinetics, characterization and testing of the composites.

Chapter 3 deals with the results from the experimental work and discussions and the inference of the outcome of the work.

Chapter 4 summarises the conclusions drawn based on the investigations carried out and the scope for the future work.