Chapter I

Introduction
1.1 COMPOSITE MATERIALS

The first man made composite based upon polymer appeared in about 5000 B.C. in the Middle East where pitch was used as a binder for reeds in boat-building. (1,2,5)

The three key steps leading to modern composites were,

1. The commercial availability of fiberglass filaments in 1935
2. The development of strong aramid, glass and carbon fibers in the late 1960’s and early 1970’s which are parallel to the development of resins dating back to 1968 (phenolics) and 1937 (epoxies).
3. The promulgation of analytical methods for structures made from those fibers.

A composite material is a combined material created from at least two or more components, selected filler or reinforcing agent and a compatible matrix, binder (i.e. resin) in order to obtain specific characteristics or properties that were not there before. The matrix is the continuous phase, and the reinforcement constitutes the dispersed phase, combined primarily to increase the strength and stiffness of the matrix. It is the behavior and properties of the interface that generally control the properties of the composite. (2,5,6)

1.1.1 Types of composites

The most common man made composites can be divided into three main groups. (5)

- **Polymer matrix composites**: These materials use polymer based resin as the matrix and variety of fibers such as aramid, glass, carbon fibers etc. and particles such as calcium carbonate, talc, clay, aluminium trihydroxide, magnesium hydroxide, alumina, wood flour etc. as the reinforcement.

- **Metal matrix composites**: These materials use metal such as aluminium as the matrix and reinforce it with fiber such as silicon carbide. These types of materials are widely used in automotive industries.
• **Ceramic matrix composites:** These materials use ceramic as the matrix and reinforce it with short fibers or whiskers such as silicon carbide and boron nitride.

The major classes of structural composites exist today are being defined by the types of their matrices namely polymer, metal and ceramic as described above. Polymer matrixes composites are the most developed class of composite materials fabricated into large complex shapes and have been accepted in variety of commercial applications and hence research in the polymer based composites were boost drastically. (1)

1.1.2 **Advantages of composites in high performance applications**

Composites have lot of advantages in manufacturing products of high performance properties. These properties can be tailor made and find applications in different areas such as nonconductive electrical components, noncorroding and noncorrosive storage containers, transfer lines, aerospace, sporting goods and many more. (1, 2, 4-6)

The advantages include,

- Weight reduction (high strength or stiffness-to-weight ratio)
- Tailorable properties (strength or stiffness can be tailored to be in the load direction)
- Redundant load paths (fiber to fiber)
- Longer life (no corrosion)
- Lower manufacturing costs because of lower part count
- Inherent damping
- Increased (or decreased) thermal or electric conductivity
- The ease of formability.

Designers of structures have been quick to capitalize on the high strength-to-weight or modulus-to-weight ratios of composites. Composites provide the designer, fabricator, equipment manufacturer and consumer with sufficient flexibility to meet
the demands presented by different environments (e.g. heat or high humidity) as well as any other special requirements. (1, 2, 4-6)

1.1.3 Basic concepts of polymer composites

The combination of dissimilar materials can have unique properties. The desired key properties can be achieved by varying the different materials. These properties are obtained by reinforcing polymer matrix with filled materials such as fibers, fillers, modifiers and polymer additives. Usually, the reinforcements and the matrix are having different origins. The reinforcement may be in the form of organic, inorganic or metallic structures leading to enhancements in thermal, optical, mechanical and electrical properties of base resin matrix. (3, 4, 7, 8)

All polymers contain some form of additives ranging from small fractions of catalyst residue to large-scale incorporation of mineral fillers. The most important additives are those introduced for some specific purpose and would therefore include fillers, plasticizers, colorants, reinforcing fibers, blowing agents, stabilizers, flame retardants, processing aids etc. The strength-to-weight, modulus-to-weight and fatigue strength-to-weight ratios of these materials are superior to those of metallic materials because of low specific gravities. (1, 4, 6)

Heterogeneous nature of composite provides mechanisms for high-energy absorption on microscopic scale comparable to the yield process exhibiting gradual deterioration in properties, but they do not usually fail in catastrophic manner. (1, 2, 4, 6)

Coefficients of thermal expansion (CTE) for many reinforced composites are much lower than that of metals exhibiting a better dimensional stability over a wide temperature range. (1, 2, 4, 6)

1.1.4 Resin systems used in composite:

The selections of polymer matrixes are very important in formulating the products of high performance properties. Any polymer system for use in a composite material will require the following properties, (5)
**Good mechanical properties:** The mechanical properties of resin used as matrix material in composites should give synergetic effect with the reinforcement material. Ideal resin system shows high ultimate strength, high stiffness, high strain to failure and does not suffer from brittle failure on combination with reinforcement. \(^{(4-6)}\)

**Good adhesive properties or wettability:** High adhesion between resin and reinforcement is necessary for any resin system. This will ensure that the loads are transferred efficiently and will prevent cracking or debonding when stressed. Wettability defines the extent to which a liquid will spread over a solid surface. Covering every bump and dip of the rough surface of the reinforcement and displacing with air carries out good wettability. \(^{(6,7)}\)

**Thermal properties:** The Glass transition temperature \((T_g)\), crystalline melting point \((T_m)\), heat distortion temperature \((HDT)\) and maximum use temperature for the polymer for continuous service define general thermal characteristics of a given polymer to be used. \(^{(4)}\)

**Good resistance to environmental degradation:** Solvent resistance, flame retardancy, moisture absorption capacity etc. are the main environmental considerations for the polymers to be used in composite manufacturing. Mostly related with their structures, the high performance thermoplastics have an excellent solvent resistance and highly aromatic polymers are inherently flame retardant because of their tendency to form char. \(^{(4,5)}\)

In general, polyester, vinyl ester, epoxy, phenolics, cyanate ester, silicones, polyurethanes, Bismaleimides etc. are widely used polymers in composite manufacturing. \(^{(5,6,7)}\)

**1.1.5 Reinforcement-matrix interface**

The load acting on the matrix has to be transferred to the reinforcement via the interface. Thus reinforcement must be strongly bonded to the matrix, if their high strength and stiffness are to be imparted to the composite. The fracture behavior is also dependent on the strength of the interface. A weak interface results in low
stiffness and strength, but high resistance to fracture, whereas a strong interface produces high stiffness and strength but often a low resistance to fracture i.e. brittle behavior. The exact role of interface may differ with the type of reinforcement. The interface can be viewed as a planar region of only a few atoms in thickness across in which there is a change in properties from those of the matrix to those of the reinforcement. Thus, the interface is usually a discontinuity in chemical nature, crystal and molecular structure, mechanical and other properties.\(^{(6,7)}\)

**Interfacial bonding**

Interfacial bonding is due to adhesion between the reinforcement and the matrix and mechanical keying. For adhesion to occur during the manufacture of a composite, the reinforcement and the matrix must be brought into intimate contact. Once the matrix has wet the reinforcement, therefore in intimate contact with it, bonding will occur. For a given system more than one bonding mechanism may be operative at the same time.

(i) **Mechanical bonding**

A mechanical interlocking or keying of two surfaces can lead to a reasonable bond. The rougher the interface, the greater the interlocking.\(^{(6,7)}\)

(ii) **Electrostatic bonding**

Bonding occurs between the matrix and reinforcement when one surface is positively charged and the other is negatively charged leading to electrostatic attraction between the components of the composite depending on the difference in charge on their surfaces. Electrostatic interactions are short range and are only effective over small distances.\(^{(6,7)}\)
(iii) Chemical bonding

Chemical bonding is the bonds formed between chemical groups on the reinforcement surface and the compatible groups in the matrix. Strength depends on the type of bond and the number of bonds. (6, 7)

(iv) Reaction or inter diffusion bonding

The atoms or molecules of two components of the composite may interdiffuse at the interface to give this type of bonding considered as due to the intertwining of molecules. The strength of this type of bonding depends on the distance over which the molecules have entwined, the extent of the entanglement of the molecules and the number of molecules per unit area of interface. (6, 7)

1.2 NANOTECHNOLOGY

Nanotechnology is the understanding and control of matter at dimensions of roughly 1 to 100 nanometers, where unique phenomena enable novel applications. A nanometer is one-billionth of a meter; a sheet of paper is about 100,000 nanometers thick. Encompassing nanoscale science, engineering and technology, Nanotechnology involves imaging, measuring, modeling and manipulating matter at this length scale. At this level, the physical, chemical and biological properties of materials differ in fundamental and valuable ways from the properties of individual atoms and molecules or bulk matter. Nanotechnology Research & Development is directed towards understanding and creating improved materials, devices and systems that exploit these new properties. (9) It is multi-disciplinary and involves physicists, chemists and biologists in studying, researching and engineering ever smaller structures. Physics is different on the nanometer scale. Properties not seen on a macroscopic scale now become important, such as quantum mechanical and thermodynamic properties. Rather than working on bulk materials, one works on individual atoms and molecules. (9, 10)
1.3 NANOCOMPOSITE MATERIALS

From the viewpoint of today's industrial and economical activities, it can be easily assumed that the technology has opened window for us which determines the standards of our lives. These requirements result in continuous efforts for new, high performance besides low cost materials to meet increasing demands. Polymers are commonly mixed with a variety of both synthetic and natural compounds to improve their performance capabilities.\(^{(11,12)}\)

Nanocomposite materials are the composite materials in which one of the component possess nano scale dimension. Due to nano size, the volume to size ratio and surface area increases tremendously. High surface area leads to high interfacial area available for the interaction with other component of the composite. Only few weight percent nanosized component can interacts with the most of surface of other components of the composite. This increase in interfacial interactions increases the composite properties tremendously.

Polymer clay nanocomposites are new class of materials which consist of polymer matrices filled with low amount (<10%) of clay dispersed at nanoscale level. The essential raw material for nanoclay (nano-sized layered silicate) is montmorillonite, 2:1 layered smectite clay with platelet structure. This nanoclay technology provides high-surface area of clay (750-800 m\(^2\)/g) and high-aspect ratio (about 100 to 15000) in the composite.\(^{(11,13-15)}\)

In the case of the interaction between clay and macromolecule, the work by Bower, was the earliest one dates back to 1949.\(^{(16)}\) Polymer clay nanocomposite was first reported by Blumstein in the literature as early as in 1961, demonstrating the polymerization of vinyl monomers intercalated into montmorillonite clay.\(^{(17)}\) Two major findings have stimulated the revival of interest in these materials. First, the report from Toyota research group of Nylon 6/montmorillonite nanocomposite, for which very small amount of layered silicate loadings resulted in pronounced improvement of thermal and mechanical properties\(^{(18)}\) and second, the observation by Vaia et al that it is possible to melt mix polymers with layered silicates without use of organic solvents.\(^{(19)}\)
1.3.1 Development of interest in polymer clay nanocomposite technology

A number of factors are of interest in nanocomposite technology using clay minerals,

- Low loading levels
- Transparency
- Incorporation flexibility
- Safety
- Synergies with other additives
- Low cost

Nanocomposites typically contain 1-10 % loadings on weight basis, yet property improvements can equal and exceed traditional composites containing 20-35% mineral or glass. (8,11-15) Machine wear is reduced and processability is increased. (20-29)

Nanoclay particles have a dimension below the visible light wavelength.

- The particles are tough. They can withstand solvents, polymerization temperatures and compounding shear. They can be processed without concern about degradation
- Clays are generally innocuous materials and have been used safely in consumer products for decades
- A wealth of experience demonstrates that they act synergistically with other minerals.

1.4 CLAY MINERALS

Clay is natural earthy, fine-grained material comprised largely of group of crystalline minerals known as the clay minerals. Clay minerals were initially defined on the basis of their crystal size. Their very diverse physical and chemical properties are dependent largely on their structure and composition comprising of hydrous phyllosilicates. The phyllosilicates are generally platy in shape and differ from one
another with regard to the structural arrangement of the layers, water content and associated cations. Main clay groups are Kaolin, Bentonite, Saponite, Illites, Montmorillonite (MMT) and Hectorite etc. \(^8, 14, 20, 28\) Montmorillonite, Saponite and Hectorite are the most commonly used clay for the preparation of polymer clay nanocomposites. The ability of the clay particles to disperse into individual layers and the ability to fine tune the surface chemistry through ion exchange reactions with organic and inorganic cations are the two major characteristics of the clay which are considered for the preparation of polymer clay nanocomposite.

1.4.1 Physical properties of clay

The properties of clays are indeed dominated by their large surface area compared to the volume of the particles. The minerals have the particularity of being sheet shaped. This means that they have even more surface area than other minerals of the same grain size tending to be cubes or spheres in their fine-grained size. \(^27\) The uses and properties of clay minerals are dependent on the clay compositions, presence of organic materials, type and amount of exchangeable ions, soluble salts and texture. \(^8, 14, 30, 31\)

1.4.2 Exchange of Ionic Species (CEC)

A very important property of clay surfaces is their chemical activity and their interaction with ions in aqueous solution including dissolved species (charged ions or molecular species adsorbed onto surface). The adsorbed ions are normally accompanied by water molecules expanding the clay galleries. Figure 1.1 shows schematically the states of adsorbed and absorbed ions. The property of adsorbing and absorbing ionic species in solution is called cation exchange capacity (CEC) measured by the number of moles of ionic charge fixed on 100g of dry clay. The values are expressed in milli-equivalents of charges (moles)/100g. \(^32, 33\) The selection between different species present in aqueous solution depends upon the species of clay and its chemical constitution, affinity of ions to remain in free hydrated state and the concentration of ions in solution.
When an ion held on, it is displaced with another due to change in its aqueous concentration, it is desorbed. If this ion is replaced by another ionic species introduced into the media, it is exchanged and this process is known as an ion exchange. The normal laws of mass action are active in the exchange process.\textsuperscript{29,34}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{clay_particle.png}
\caption{Absorbed and adsorbed ions on clay particles}
\end{figure}

1.4.3 Structures and properties of clay

The major silicate groups of phyllosilicates are mica, talc, montmorillonite, vermiculite, hectorite, saponite etc. The layered silicates or clay commonly used in nanocomposites belong to the structural family known as the 2:1 phyllosilicates. Their crystal lattice consists of two-dimensional layers where a central octahedral sheet of alumina or magnesia is fused to two external silica tetrahedron by the tip so that the oxygen ions of the octahedral sheet do also belong to the tetrahedral sheets. The layer thickness is around 1 nm and the lateral dimensions of these layers may vary from 300 A to several microns and even larger depending on the particular silicate.\textsuperscript{8,14,22}

The structure of the clay can be seen in \textbf{figure 1.2}.\textsuperscript{35} These layers organize themselves to form stacks with a regular gap in between them called the interlayer or the gallery. Isomorphous substitution within the layers (for example, Al\textsuperscript{3+} replaced by Mg\textsuperscript{2+} or by Fe\textsuperscript{2+}, or Mg\textsuperscript{2+} replaced by Li\textsuperscript{+}) generates negative charges that are counterbalanced by alkali or alkaline earth cations situated in the interlayer. As the forces that hold the stacks together are relatively weak, the intercalation of small molecules between the layers is easy.\textsuperscript{36-42} The partial positive charge thus formed for each cation within the gallery makes it highly hygrophilous. Montmorillonite neutralizes these partial charges by ion-dipole interactions with holding water.
In order to render these hydrophilic phyllosilicates more organophilic, the hydrated cations of the interlayer can be exchanged with cationic surfactants such as alkylammonium or alkylphosphonium (onium). The modified clay (or organoclay) being organophilic, its surface energy is lowered and is more compatible with organic polymers.

Figure 1.2: Structure of 2:1 layered silicate (clay)

1.5 COMPATIBILIZING AGENTS

1.5.1 Quaternary Ammonium/Phosphonium Compounds

The use of silicates as such, however, greatly limits the use area of the intercalate polymers because of their hydrophilic structure. This limitation is overcome by their alternation to form organically modified layered silicates.

Figure 1.3: Schematic representation of cation-exchange reaction between silicate and alkylammonium salt
These are produced by replacing the cations originally present in the galleries with organic cations. Alkylammonium ions are mostly used, showed in figure 1.3 compound. The other ‘onium’ salts can be used, such as sulfonium and phosphonium. The cationic head of the alkylammonium salt preferentially resides towards the walls of the gallery via columbic interaction and its aliphatic tail radiates away from the wall making normally hydrophilic surface hydrophobic. Water swelling of the silicate is needed to obtain the exchange process of onium ions with cations in the galleries. Two or higher valent cations prevent water swelling, thus, the hydrate formation of monovalent intergallery cations is the driving force for water swelling.

1.5.2 Surface Modifiers

(a) Silane surface modifier

Silane modifiers are silicon-based chemicals that contain two types of reactivity, inorganic and organic, in the same molecule. A typical general structure is \((\text{RO})_3 -\text{Si}-\text{CH}_2\text{CH}_2\text{CH}_2-\text{X}\), where \(\text{RO}\) is a hydrolyzable group, such as methoxy, ethoxy or acetoxy and \(\text{X}\) is an organofunctional group, such as amino, methacryloxy, epoxy etc. A silane act at interface between inorganic substrate (such as glass, metal or mineral) and organic material (such as organic polymer, coating or adhesive) to bond, or couple, the two dissimilar materials. A simplified picture of the coupling mechanism is shown in figure 1.4. A simplified picture of the coupling mechanism is shown in figure 1.4.

![Figure 1.4: Coupling mechanism of silane modifiers.](image)

When organic polymers are reinforced with glass fibers or minerals, the interface between the polymer and the inorganic substrate is involved in a complex interplay of physical and chemical factors. These factors are related to adhesion, physical strength, coefficient of expansion, concentration gradients and retention of
product properties. A very destructive force affecting adhesion is migration of water to the hydrophilic surface of the inorganic reinforcement. Water attacks the interface, destroying the bond between the polymer and reinforcement, but a “true” surface modifier creates a water-resistant bond at the interface between the inorganic and organic materials. Silanes have the unique chemical and physical properties not only to enhance bond strength but also, more importantly, to prevent de-bonding at the interface during composite aging and use. The surface modifier provides stable bond between two otherwise poorly bonding surfaces.\(^{(49,50)}\)

In composites, a substantial increase in flexural strength is possible through the use of the right silane compound. Silanes also increase the bond strength of coatings and adhesives as well as their resistance to humidity and other adverse environmental conditions.

Other benefits, silane modifiers can provide include:

- Better wetting of inorganic substrates
- Lower viscosities during compounding
- Smoother surfaces of composites
- Less catalyst inhibition of thermoset composites
- Clearer reinforced plastics

**Silane bond formation on inorganic substrate**

Silane modifiers that contain three inorganic reactive groups on silicon (usually methoxy, ethoxy or acetoxy) will bond well to the metal hydroxyl groups on most inorganic substrates, especially if the substrate contains silicon, aluminum or a heavy metal in its structure. The alkoxy groups on silicon hydrolyze to silanols, either through the addition of water or from residual water on the inorganic surface. Then the silanols coordinate with metal hydroxyl groups on the inorganic surface to form bond by eliminate water. \textit{Figure 1.5} shows the mechanism of the silane bond formation on inorganic substrate.\(^{(49)}\)
Chapter 1

Silane molecules also react with each other to give a multimolecular structure of bound silane on the surface. More than one layer, or monolayer equivalents, of silane is usually applied to the surface. This results in a tight siloxane network close to the inorganic surface that becomes more diffuse away from the surface. \(^{(49, 51, 52)}\)

Silane bond on the clay surface is schematically represented in *figure 1.5*. \(^{(49)}\)

![Hydrolysis and Condensation of Alkoxy Silane](image)

**Figure 1.5:** Hydrolysis of alkoxy silane and bonding to inorganic surface

**Silane bond to the Polymer**

The bond to the organic polymer is complex. The reactivity of a thermoset polymer should be matched to the reactivity of the silane. With thermoplastic polymers, bonding through a silane can be explained by inter-diffusion and inter-penetrating network (IPN) formation in the interphase region. *Figure 1.6* shows the IPN network formation by silane. \(^{(49)}\)

To optimize IPN formation, it is important that the silane and the resin be compatible. One method is to match the chemical characteristics of the two materials. This will help to improve the chances of forming a good composite with optimum properties. Even with thermoset polymers, where reactivity plays an important role, chemical structure matching will enhance the physical properties of the composite. \(^{(49)}\)
Organotitanates are very interesting class of surface modifier. They can all be regarded as derivatives of ortho-titanic acid, Ti (OH)₄, and hence are commonly known as organo-titanates rather than by their systematic names.

Conceptually, the organo-titanates are similar to silanes. Thus, they are designed to have groups that readily hydrolyze to titanium hydroxy groups which can condense with surface hydroxyls and to also carry other organic groups, which are more hydrolytically stable, and may also provide some reactive functionality. Depending on their chemical nature, organo-titanates can be pre-coated from organic or aqueous solution, dry blended or used in situ.

The most important factor is that, unlike the silicon to carbon bond, the titanium to carbon bond is very unstable and cannot be used to permanently attach organic groups for surface treatment applications. The organo-titanates are thus generally based on tetra-substituted titanium, where all the substituents are linked by titanium – oxygen – carbon bonds, and their chemistry is dominated by the hydrolytic sensitivity of these. Alkoxy radicals are rapidly hydrolysed, with the rate in water decreasing as the chain length increases, due to reduced solubility. Acyloxy derivatives are also fairly readily hydrolysed, again with a chain length effect. They are generally thought to be somewhat more stable than the alkoxides. Fairly good
hydrolysis resistance can be obtained with chelate groups attached to titanium, particularly where a five or six membered ring is formed.

Alkanolamines, diketones, keto esters, hydroxy acids and certain glycols are useful chelating agents. In some instances inorganic acids such as phosphates are used to attach organic groups to titanium, the titanium-oxygen-phosphorus bond being fairly hydrolytically stable.

Crosslinking occurs through alcoholysis reactions with polymers containing active hydrogen atoms. A wide variety of catalytic effects are also observed. The most important ones are esterification, trans-esterification, polyamide formation and olefin polymerization. (53)

**Organo-Titanate used for surface modification**

The alkoxy group is used as the hydrolysable group on the titanium and acid groups (carboxylate, phosphate, sulfonate) to give stable attachment of other organic groups. Initially single isopropoxy group was used as the hydrolysable group and these products are described as monoalkoxytitanates. More recently neopentyly (diallyl) oxy groups have also been used. These are claimed to have better thermal stability and be more suited to ‘in situ’ use in thermoplastics compounding. Derivatives of this type are known as neoalkoxytitanates. Chelate, co-ordinate and quaternary types based on pyrophosphates are also available.

While no comprehensive study has been made, it is generally claimed that organo-titanates are effective on a wide variety of particulate mineral surfaces, including calcium carbonates and carbon black. This claim is however often based on dispersant action in simple tests, where adsorption rather than strong surface bonding is often sufficient to produce an effect. Based on the proposed mode of action, one would expect best performance on heavily hydroxylated surfaces such as silica, silicates and hydroxides.

The simplest organo-titanates in general use as filler modifiers are nominally triacyloxy isopropoxy derivatives. (54, 55) Where these acyloxy groups are long chain
fatty acids, then simple hydrophobing and dispersion effects should be observed. If however they contain some reactive functionality, then chemical coupling to the matrix polymer is theoretically possible. Typical compounds of these types are shown as below.

Non-reactive:

$$[\text{CH}_3(\text{CH}_2)_{16}\text{COO}]_3 - \text{Ti} - \text{OR}$$

Reactive:

$$\text{CH}_3(\text{CH}_2)_{16}\text{COO} \quad \text{Ti}\text{OR}$$

$$[\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}]_2$$

The sort of structure claimed to be formed on filler surfaces is shown in *figures 1.7 and 1.8.*

Figure 1.7: Structures proposed for the reaction of organotitanates with filler surfaces (a) Monofunctional reaction (b) bifunctional reaction (c) complex
1.6 NANOCOMPOSITE PREPARATION AND STRUCTURE

1.6.1 Structure of nanocomposites

Nanocomposites are hybrid between matrix and nano sized reinforcement. They can be classified depending on the shape of the nanofiller. Nanoparticles are characterized as three dimensional nanosized materials. Nanotube’s or whisker’s nanosize is limited to two-dimensions in space and phyllosilicates (e.g. clay) single silicate layers are characterized as one-dimensional nanosized materials.\(^{(43)}\)

Materials at interfaces can constitute separate phase, including interfacial interactions, contributing to materials’ properties increase. Because of the similarity between length scales of nanocomposite materials, it is possible to make materials completely interphase rather than the bulk form.\(^{(50,56)}\)

Mainly due to their very high interfacial area, and very short distance between reinforcing particles’ surface, nanocomposite materials show specific features. For polymer based nanocomposites, the percolation of reinforcing particles depending on their shape factor plays an important role in determining the final type of the network, either stiffer or softer.\(^{(57,58)}\)
1.6.2 Types of polymer clay nanocomposites

In the preparation of polymer clay nanocomposites, interplay of entropic and enthalpic factors in the reaction media determines the structure of outcome by affecting the dispersion characteristics of organically modified montmorillonite (ommt) in polymer. (41, 59, 60)

Dispersion of montmorillonite clay in polymer requires sufficiently favorable enthalpic contributions to overcome entropic penalties. (41) Confinement of the polymer inside the interlayers results in decrease in conformational entropy of the polymer chains. However, this penalty can be compensated in part by the increased conformational freedom of the tethered surfactant chains locating in less confined environment as the layers separate. Favorable enthalpy of mixing for the polymer-o-mmt is achieved when the polymer/mmt interactions are more favorable compared to the surfactant/mmt interactions. (61)

For most polar polymers, an alkyl-ammonium surfactant is adequate to offer sufficient excess enthalpy and promote nanocomposite formation. The structure of these nanocomposites does not change markedly with processing. If the dispersion of organically modified montmorillonite is not thermodynamically favored, the layers will be in low d-spacing parallel stacks during the high temperature processing, forming conventionally-filled composite. (62)

Polymer/clay composites are divided into three general types, namely conventional, intercalated and delaminated or exfoliated. Illustrated structures are shown in figure 1.9. (63)
Conventional (micro composite)

This structure occurs when the miscibility between the polymer matrix and the filler does not support favorable interactions to overcome the thermodynamic considerations leading the silicate layers to collapse. In these structures, system is totally immiscible.

Intercalated

The single polymer chains are intercalated between unaltered silicate layers with their regular alternation of galleries. The space occupied by the polymer is typically in the order of few nanometers. These systems display limited miscibility.
Delaminated (or Exfoliated)

The silicate layers are totally delaminated and dispersed in the polymer matrix. Its ordered structure is lost and the distance between the layers is in the order of the radius of gyration of the polymer. System is totally miscible.\(^{(43, 64-67)}\)

1.6.3 Methods for preparation of nanocomposites

Polymer layered silicate nanocomposites are prepared in four ways.\(^{(43)}\)

In Situ Polymerization

First, all monomers and filler are mixed and swollen. A molecule (the monomer) is absorbed into host compound containing interplanar spaces (channels or cavities) and then polymerized. The polymer thus obtained is called ‘intercalated’ if confined between layers, or ‘flocculated’ if confined between cavities.\(^{(68-70)}\) The process is illustrated schematically in figure 1.10.\(^{(71)}\)

![Figure 1.10: Schematic representation of nanocomposite obtained by in situ polymerization](image)

Solution Process

Intercalation of polymer from solution is two-stage process in which polymer is exchanged with appropriate solvent. Solution intercalation has similar limits on the polymer-clay-solvent combinations that can be employed due to preferential absorption of the solvent instead of the polymer inside the galleries.\(^{(72)}\) Typically, solvent and clay are mixed and sonicated to disperse and distribute the platelets.
Polymer solution is then added to the clay solution and mixed. Spontaneous exchange requires negative variation in the Gibbs free energy. The diminished entropy due to confinement of the polymer is compensated by increase due to desorption of intercalated solvent molecules. Solvent is then removed from the polymer/clay solution. The process is shown in figure 1.11. (43)

Figure 1.11: Schematic representation of nanocomposite obtained by intercalation from solution

Melt Compounding

A polymer and clay mixture is annealed above the Tg (glass transition temperature) or Tm (melting temperature) of the polymer in either static or flow conditions. The polymer chains spread from the molten mass into the silicate galleries to form hybrids according to the degree of penetration. The decreased entropy in this case is compensated due to the greater conformational energy of the aliphatic chains of the alkylammonium cations due to the increase in the size of the galleries caused by insertion of the polymer. Semi-quantitative calculations show that this gain is enough to offset the loss of entropy and make the process isoentropic. Maintenance of spontaneity requires enthalpy as the driving force. (74, 75) The process is illustrated schematically in figure 1.12. (43)
Figure 1.12: Schematic representation of nanocomposite obtained by direct polymer melt compounding

**Sol-gel process**

It consists of direct crystallization of the silicate clays by hydrothermal treatment of a gel including polymer. Gels contain organics and organometallics, such as silica sol, magnesium hydroxide, lithium fluoride etc. It has the potential of promoting the high dispersion of the silicate layers in one-step process, without requiring an onium ion as a surfactant. \(^{(76, 77)}\)

**1.6.4 Importance of the melt compounding process**

Melt processing is environmentally sound since no solvents are required, making the production of industrially significant polymeric nanocomposites practicable. It shifts the nanocomposite production downstream by giving end-use manufacturers many degrees of freedom with regard to final product specifications (e.g. selection of polymer grade, choice of organoclay, level of reinforcement etc.).
Chapter 1

Application of this process also minimizes capital costs due to its compatibility with existing processes. (62, 73, 76-80)

1.7 AIM AND OBJECTIVE OF THE THESIS

At present, most of solid insulation systems used in electrical industries are composites filled with fillers like clay, mica, talc, calcium carbonate, alumina etc. The fillers used are of micron size. Almost more than 40 % loading of the filler is required to get the desired properties of the composite materials.

Nanoparticles like organoclay, nano calcium carbonate, nano aluminium trihydroxide (ATH) etc. possess very high surface area compare to their micron size. Only few weight % nano filler particles offer more surface area to polymer in composite for interaction than micron sized filler filled almost more than 40 weight %. (44, 80-86) A few weight % nano filler particles increase the performance properties of the composite drastically. In recent years, significant improvement in mechanical and thermal properties has been observed by the researchers by using nanofillers in composite. (44, 80) In this thesis attempts have been made to synthesis nanoparticles like organoclay, nano calcium carbonate, nano aluminium trihydroxide by chemical and physical methods. Surface modification of organoclay has been carried out by silane and titanate surface modifiers in different concentration. Nanocomposites of Highdensity Polyethylene (HDPE), Polypropylene (PP) and Epoxy with organoclay have been prepared and their electrical, mechanical, thermal, rheological morphological properties etc. have been studied. Some thermal tests like glow wire and ball pressure were carried out, according to their respective standards, on thermoplastic nanocomposites keeping in view to use these materials for wiring accessories in power industries.

The main objective of this thesis is to prepare nano particles of clay, calcium carbonate, aluminium trihydroxide and surface modifier to improve the performance properties of nano filler filled composites with thermosetting and thermoplastic polymers.