CHAPTER 2

LITERATURE SURVEY

2.1 Composites

A composite is a material that consists of two or more distinct constituent materials that are bound together on a macroscopic scale to form an integral unit that has properties not attainable by the individual components by themselves [2]. The constituent materials which are significantly different in physical and chemical properties remain separate and distinct at the macroscopic and microscopic level within the composite. The primary phase that is continuous is the matrix and it holds the dispersed phase while sharing the applied load with it. The second phase embedded in the matrix in a discontinuous form is called dispersed phase. This phase is generally stronger than the matrix and hence is sometimes called the reinforcing phase. The reinforcements impart their special mechanical and physical properties to enhance the matrix properties. Properties like strength, stiffness, corrosion and wear resistance, fatigue life, temperature dependent behaviour and acoustical insulation can be improved by forming a composite material [18]. Composite materials can be tailored for various properties by appropriately choosing their components, proportions distributions, morphologies, degrees of crystallinity, crystallographic textures and the structure and composition of the interface between components [18]. The main advantages of the composite materials are low weight, corrosion resistance, high fatigue strength and faster assembly. Hence composites materials can be designed to suit a host of applications in automobile, aerospace, construction, electronics, energy and biomedical fields [18].

Classification of composites

Based on the matrix material the composite materials can be classified as metal matrix composites, ceramic matrix composites or polymer matrix composites. Metal matrix composites (MMCs) consist of metallic matrix like aluminium, iron, copper etc. and dispersed phase made up of ceramic or metal [6]. Ceramic matrix composites (CMCs) have ceramic matrix and embedded fibres of other ceramic material in the dispersed phase [6, 18]. Polymer matrix composites (PMCs) have thermoplastic, thermoset or elastomeric matrix with fibres of glass, steel or aramid dispersed in it [19].
Another classification of composites is based on the structure of the dispersed phase as particulate composites, fibrous composites or laminate composites. Particulate composites consist of dispersed phase made up of particles either randomly oriented or oriented parallel to each other. They are mainly used to improve properties or lower the cost of isotropic materials. The length to diameter ratio is in the order of unity. The shape of the reinforcing particles can be spherical, elliptical, cubic, platelet or any irregular or regular geometry [19]. Fibrous composites have fibres in the dispersed phase. Based on the length of the fibre, they are classified as short-fibre (discontinuous) reinforced composites and long-fibre (continuous) reinforced composites [1, 19]. Short-fibre reinforced composites consist of a matrix reinforced by a dispersed phase in the form of discontinuous fibres (length < 100 x diameter) which are either randomly dispersed or oriented. In long-fibre reinforced composites, the fibres are continuous and their orientation is either unidirectional or bidirectional. The fibres can be synthetic like glass, boron, Kevlar and carbon fibres or natural fibres like jute, sisal, hemp, bamboo fibres. Laminate composites consist of at least two different sheets or panels of materials bonded together. They generally have a preferred high strength direction [19]. A schematic representation of different types of composites based on the structure of the dispersed phase is depicted in Figure 2.1.

![Figure 2.1](image)

Figure 2.1 Classification of composites based on the structure of dispersed phase (a) particulate composite (b) laminate composites (c1) long fibre composite (c2) aligned short fibre composite and (c3) random short fibre composite

Yet another classification is based on the dimensions of the reinforcement species. In this classification, composites are divided as macro, micro and nanocomposites.
Polymer composites

Polymers are the most widely used matrix material for fibre composites and are used in almost 90% of the composite products. Polymer composites are prepared by dispersing inorganic materials in polymer matrix. The inorganic materials can be particulate solids like carbon black, calcium carbonate, talc or mica or reinforcing fibres like glass, carbon or aramid. Polymer composites exhibit physical properties synergistically derived from both the organic and inorganic components. Their physical properties like mechanical properties and heat deflection temperature are superior to pristine polymers [1, 19]. Polymer composites offer several advantages like excellent low temperature processability, lower cost, lower specific gravity, good strength to weight ratio and excellent formability. However their stiffness and strength are lower than metal and ceramic composites. The property improvements in polymer composites are the result of complex interplay between the properties of the polymer matrix, the filler and the interfacial region. The morphology of the filler, the size, structure and the aspect ratio influence the properties of polymer composites. Generally, conventional reinforcing agents and fillers are added at higher contents (typically > 10%) to achieve significant improvements in properties. Often, addition of these fillers imparts certain drawbacks like increase in weight, brittleness and loss of transparency [3, 4].

In most conventional polymer composites, the dispersed phase is in the macro or micrometer length scale. The last two decades saw the emergence of a new class of materials called polymer nanocomposites (PNCs). They have reinforcing phases that have dimensions in nanometre scale. The interest in polymer nanocomposites started when Toyota used Nylon-6 – nanoclay composites in their automobiles in 1990s [9]. The nylon nanocomposites developed by them exhibited superior mechanical properties, higher heat distortion temperature and enhanced barrier properties than neat nylon. Since then, there has been growing interest, in both academics and industry, to develop polymer nanocomposites with different matrices and different types of nanofiller. A detailed discussion on polymer nanocomposites is given in the following sections.

2.2 Polymer nanocomposites

Nanoparticles have much larger surface area than micro particles, enabling them to have far better interaction with the polymer matrix [7, 20, 21]. As a consequence,
incorporation of suitable nanofiller into a polymer matrix significantly enhances the mechanical, thermal, barrier, optical and electrical properties [3, 10, 14, 15, 22 – 27]. Significantly, the enhancement in properties is obtained at very low nanofiller content, typically ≤ 5 % by weight [15, 22]. The enhancement in properties can be attributed to the following [4, 28, 29]:

(i) large number density of particles per particle volume \( (10^6 – 10^8 \text{ particles/μm}^3) \)

(ii) extensive interfacial area per volume of particles \( (10^3 – 10^4 \text{ m}^2/\text{mL}) \)

(iii) short distances between particles \( (10–50\text{nm at ~ 1 – 8 vol. %}) \) and

(iv) low percolation threshold \( (~0.1–2 \text{ vol. %}) \)

The structural arrangements on the molecular scale and the efficient transfer of stress across the composite components depend on the interfacial region and hence maximizing the interfacial area maximizes the potential of defining new material properties [30]. The degree of enhancement of a particular property also depends on the filler/matrix material system used, the filler/matrix interfacial bonding and the state of dispersion of the filler throughout the matrix [3, 5, 7, 14, 20 – 23, 31 – 33].

2.2.1 Types of nanofillers

Based on geometry, i.e. how many dimensions are in the nanometre range, nanofillers are classified into one dimensional, two dimensional or three dimensional. In one dimensional fillers, nanoparticles are in the form of sheets of one to a few nanometres thick to hundreds to thousands of nanometres long and wide [7]. An example is nanoclay, also known as layered silicates. Two dimensional nanoparticles are elongated and have two dimensions in the nanometre range. They can be fibres, nanotubes or whiskers [6]. When all the three dimensions are in the nanometre size, it is a three dimensional nanofiller. Commonly used examples are nanosilica, nanocalcium carbonate and polyhedral oligomeric silsesquioxanes (POSS). Various classifications of nanofillers are shown in Figure 2.2. For particles and fibres, the surface area per unit volume is inversely proportional to the diameter of the particle [10]. Common particle geometries and their respective surface area-to-volume ratios are tabulated in Table 2.1.
Figure 2.2 Various types of nanofillers [29]

### Table 2.1 Common particle geometries and their surface area-to-volume ratios

<table>
<thead>
<tr>
<th>Type of nanofiller</th>
<th>Geometry of structural unit</th>
<th>Surface area to volume ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layered materials (1D)</td>
<td><img src="image" alt="Layered material diagram" /></td>
<td>$\frac{2}{l} + \frac{4}{t}$</td>
</tr>
<tr>
<td>Fibrous Materials (2D)</td>
<td><img src="image" alt="Fibrous material diagram" /></td>
<td>$\frac{2}{r} + \frac{2}{l}$</td>
</tr>
<tr>
<td>Particulate Materials (3D)</td>
<td><img src="image" alt="Particulate material diagram" /></td>
<td>$\frac{3}{r}$</td>
</tr>
</tbody>
</table>
2.2.2.1 Layered silicates

Layered silicate or nanoclay, belonging to phyllosilicate family, is the most widely used nanomaterial for preparing nanocomposites due to its easy availability, unique layered structure and lower cost compared to other nanomaterials [3]. They are aluminosilicates having structural framework consisting of octahedral layers of alumina and tetrahedral layers of silica joined together in varying proportions and stacked on top of each other [3, 7]. Based on the relative ratio of alumina and silica crystal sheets, there are three types of layered silicates. 1:1 type has one silica tetrahedron coupled with one alumina octahedron in unit lamellar crystal. Examples are kaolinite \((\text{Al}_2\text{Si}_2\text{F}_5\text{(OH)}_4)\) and halloysite \((\text{Al}_2\text{Si}_2\text{F}_5\text{(OH)}_4\cdot n\text{H}_2\text{O})\). In 2:1 type, a unit is formed by sandwiching one alumina octahedron in between two silica tetrahedrons. Sapiolite nanoclay belong to 2:2 type which consists of a unit formed with four crystal sheets in which silica tetrahedron and alumina or magnesium octahedron are alternately arranged [6]. Layered silicates are characterized by a surface charge called cation exchange capacity (CEC) expressed as mequiv/100 g [15]. Montmorillonite, hectorite and saponite are the most commonly used layered silicates of 2:1 phyllosilicate family. Their chemical structures and properties are given in Table 2.2.

Table 2.2 Properties of commonly used 2:1 phyllosilicates [3, 15, 31]

<table>
<thead>
<tr>
<th>2:1 phyllosilicates</th>
<th>Chemical formula</th>
<th>CEC (mequiv/100 g)</th>
<th>Particle length (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Montmorillonite</td>
<td>(\text{M}<em>x(\text{Al}</em>{4-x}\text{Mg}_x)\text{Si}<em>8\text{O}</em>{20}(\text{OH})_4)</td>
<td>110</td>
<td>100–150</td>
</tr>
<tr>
<td>Hectorite</td>
<td>(\text{M}<em>x(\text{Mg}</em>{6-x}\text{Li}_x)\text{Si}<em>8\text{O}</em>{20}(\text{OH})_4)</td>
<td>120</td>
<td>200–300</td>
</tr>
<tr>
<td>Saponite</td>
<td>(\text{M}_x\text{Mg}<em>6(\text{Si}</em>{8-x}\text{Al}<em>x)\text{O}</em>{20}(\text{OH})_4)</td>
<td>86.6</td>
<td>50–60</td>
</tr>
</tbody>
</table>

where \(\text{M} = \) monovalent cation, \(x = \) degree of isomorphous substitution (between 0.5 and 1.30) and CEC = cation exchange capacity.

Montmorillonite (MMT), a naturally occurring clay belonging to the 2:1 phyllosilicates family, has attracted much attention as nanofiller. MMT crystal lattice consists of 2 D layers with a central octahedral sheet of alumina or magnesia fused to two external silica tetrahedrons by the tip, so that the oxygen ions of the octahedral sheet also belong to the tetrahedral sheets. In many cases the \(\text{Al}^{3+}\) or \(\text{Si}^{4+}\) ions are isomorphically substituted by lower valancy ions like \(\text{Mg}^{2+}\) and \(\text{Fe}^{2+}\). The layer thickness is around 1 nm and the lateral
dimensions vary from 300Å to several microns. The stacking of layers gives rise to van der Waals gap between the layers. This gap is called interlayer or gallery. Negative charges that are generated due to isomorphic substitution within the layers are counterbalanced by alkali (e.g. Na\(^+\)) or alkaline earth (e.g. Ca\(^{2+}\)) cations inside the gallery. The structure of montmorillonite is shown in Figure 2.3.

In pristine state, the phyllosilicates contain Na\(^+\) or Li\(^+\) or K\(^+\) ions that make them hydrophilic. To render the hydrophilic phyllosilicates more organophilic, the hydrated cations of the interlayer can be exchanged with cationic surfactants such as alkylammonium or alkylphosphonium (onium) \[4\]. The chain length of the organic modifier and the cation exchange capacity of the nanoclay define the equilibrium layer spacing in organoclays \[3\]. Several grades of organoclay with different types of chemical modifications are commercially available.

The modified clay (or organoclay) being organophilic, has lower surface energy than unmodified nanoclay, improved wetting with the polymer matrix and is more compatible with organic polymers. It also results in a larger interlayer spacing that facilitates intercalation of polymer chains into the gallery space \[3, 5, 23, 31, 32\]. In some cases, the organic modifier provides functional groups that can react with the polymer matrix or
improve the adhesion between the inorganic and the polymer matrix [35]. Depending on the functionality, packing density, and length of the organic modifiers, the organo-modified layered silicates (OMLSs, organosilicates or organoclays) may be engineered to optimize their compatibility with a given polymer [4].

Montmorillonite particles that are not separated are referred to as tactoids. The challenge in the preparation of nanoclay composites is to break down the tactoids to individual layers and disperse in them in the matrix [5]. There are three types of structures formed in polymer-clay nanocomposites as depicted in Figure 2.4.

![Figure 2.4 Schematic of different morphologies of nanoclay composites (a) phase separated microcomposite (b) intercalated nanocomposite and (c) exfoliated nanocomposite [14]](image)

When the polymer does not penetrate into the galleries of the nanoclay, the gallery distance of nanoclay is maintained in the nanocomposites and the nanoclay particles are agglomerated in the matrix, thus forming microcomposites as shown in Figure 2.4 (a). Intercalated structures are well ordered multilayer nanocomposites with alternating polymer/mineral layer structure having a repeat distance of a few nm. The polymer chains penetrate into the galleries and expand the silicate layers as shown in Figure 2.4 (b). The third structure is exfoliated nanocomposites (Figure 2.4 (c)) in which individual
delaminated mineral layers are randomly dispersed in the polymer matrix [14, 36, 37]. In reality, nanoclay composites exhibit a combination of these three ideal morphologies. A number of factors like interactions between the polymer and nanoclay, aspect ratio of the nanoclay, method of preparation of the composite and orientation of the nanoclay layers during processing influence the state of dispersion / morphology of nanoclay composites.

Another notable feature of polymer – nanoclay composites is that they have excellent barrier properties [39]. In polymer nanocomposite films, the sheet-like clay layers orient in parallel with the film surface creating a tortuous path for the diffusion of gas or solvent molecules through the polymer [40 – 42]. As a result, diffusing molecules have to take a long way around the impermeable clay layers in polymer nanocomposite than in pristine polymer matrix when they traverse an equivalent film thickness. It may be noted that the enhancement of barrier properties does not arise from the chemical interactions since it does not depend on the type of gas or liquid molecules [21]. A schematic representation of diffusion path through conventional composites and nanoclay composites is shown in Figure 2.5.

![Diagram](image)

Figure 2.5 Schematic of diffusion through (a) conventional composite (b) tortuous path in nanoclay composite [43, 44]

Polymer nanoclay composites also have the ability to form films with optical clarity. As the platelet thickness of nanoclay is less than the wavelength of visible light, they do not scatter light when the platelets are oriented normal to the direction of incident light [45].

### 2.2.2.2 Carbon nanotubes

Carbon nanotubes (CNTs) are needle-shaped tubular single crystals in which the walls of the tubes are hexagonal carbon often capped at each end. The properties of the CNTs depend on the atomic arrangement, chirality, dimensions (length and diameter) of the tube and overall morphology [46]. There are two types of CNTs: single wall carbon nanotubes
(SWCNTs) and multiwall carbon nanotubes (MWCNTs). Single wall CNT is a two dimensional graphene sheet containing a hexagonal array of carbon atoms rolled into a tube. The diameter of an SWCNT is approximately 1 nm and its aspect ratio can be 1000 or more. Multiwall CNTs contain multiple layers (2 to ≤ 30) of concentric graphene cylinders [6]. The specific surface area of CNTs is high, 100 – 200 m²/g. The earliest use of CNTs in polymer nanocomposites was for semi-conducting application [47]. The ends of the tube are capped by fullerene like structures. Depending on the twist along the length while graphene is rolled up the CNTs can have a variety of structures like armchair, zigzag or chiral as shown in Figure 2.6.

![Schematic models for single-wall carbon nanotubes](image)

Figure 2.6 Schematic models for single-wall carbon nanotubes (a) armchair (b) zigzag and (c) chiral [48]

Improvements in mechanical properties have been observed by adding a few weight percentages of CNTs [49]. To use CNTs as reinforcing fillers in polymer nanocomposites, it is first dispersed in a solvent or polymer fluid/melt by sonication or shear mixing followed by further processing. Though CNTs have excellent mechanical properties (SWNT has tensile modulus of 1 – 1.5 TPa and tensile strength of 11 to 63 GPa [6], the potential of polymer CNT composites has not been fully realized. The macroscopic properties of the composites are strongly influenced by the dispersion and alignment of the CNT in the matrix. The van der Waals forces in CNTs are strong and hence they have a strong tendency to agglomerate resulting in poor dispersion of CNTs in polymer matrix
Also, energy input to disperse the CNTs tends to break them into shorter segments decreasing their aspect ratio in the final composite while simultaneously increasing their dispersability [51]. To enable better dispersion of CNTs in the polymer, the nanotubes are chemically treated to give covalent and non-covalent attachments of functional groups to the nanotubes. Such CNTs are called functionalized CNTs [52]. Surface defects in the curved graphene planes of the nanofibres may have increased reactivity promoting the formation of the functionalities such as hydroxyl, carbonyl, and carboxyl groups. Nitric acid treatment has also been reported to successfully oxidize the surface of MWNTs. Functionalization of the CNT surface lead to increased dispersability of the CNTs in various organic solvents and polymers. It also increases the strength of the interface between the CNT and the polymer matrix. However, chemical functionalization may disrupt the bonding of the graphene sheet, and thereby reduce the mechanical properties of the functionalized CNT in the final composite [51].

2.2.2.3 Particulate nanofillers

Particulate nanofillers are those particles that are less than 100nm in diameter [5]. Various nanoparticles are used for preparing PNCs. They include metal (aluminium, nickel, gold, silver etc.), metal oxide (zinc oxide, titanium dioxide, calcium carbonate, alumina etc.), non-metal oxide (silicon dioxide) and others (silicon carbide, POSS) [5, 6, 53]. The selection of nanoparticles depends on the properties desired for the nanocomposites. For example, aluminium nanoparticles impart high conductivity, silicon carbide gives hardness, strength and corrosion resistance, nickel and iron nanoparticles impart magnetic properties, alumina improves dielectric properties and nanocalcium carbonate lowers the cost [5, 53].

Unlike layered silicates and fibrous nanofillers, particulate nanofillers have an aspect ratio of nearly 1. The mechanical properties of particulate–polymer composites depend strongly on the particle size, particle–matrix interface adhesion and particle loading. Stiffness can be improved by adding nanoparticulates since rigid inorganic particles generally have a much higher stiffness than polymer matrices [26].

Silica nanoparticles are used in both thermoplastics and elastomers [54 – 57]. Nanosilica has a three-dimensional network structure. Silanol and siloxane groups are created on the silica surface, leading to hydrophilic nature of the particles. Aggregates are formed when
the silanol groups on adjacent particles form hydrogen bonds [58]. Polymers reinforced with nanoscale silica particles possess higher rigidity and yield strength than those filled with microscale silica [26]. The dispersion of nanometer-sized particles in the polymer matrix has a significant impact on the properties of nanocomposites. A good dispersion may be achieved by surface chemical modification of the nanoparticles or physical methods such as a high-energy ball-milling process and ultrasonic treatment [58]. Use of coupling agents (e.g. silanes) that increase the particle–matrix adhesion and functionalization improve the performance of silica based nanocomposites [59]. Grafting of polymer chains to silica nanoparticles is also an effective method to increase the hydrophobicity of the particles and to bring about tunable interfacial interactions in nanocomposites [58]. Surface modification based on physical interaction is usually implemented by using of surfactants or macromolecules adsorbed onto the surface of silica particles [58].

Polyhedral oligomeric silsesquioxanes (POSS) are particulate nanofillers that have a supramolecular cage structure (Figure 2.7). The POSS molecule contains a basic polyhedral silicone-oxygen nanostructured skeleton or cage, with a precisely defined Si-Si diameter of 0.53 nm. The size of the cage varies from about 0.7 to 3 nm [60]. The basic molecular structure of a POSS molecule is shown in Figure 2.7. Most POSS compounds are crystalline, but changing the R-group may result in liquid crystal or liquid-like behaviour [6]. Organic/inorganic materials prepared using POSS have been found to offer attractive properties including increased thermal oxidation stability, high UV stability, chemical resistance, decreased flammability and enhanced mechanical properties [61]. Functionalization of POSS with hydrolysable functionality such as chloride, alkoxide, acrylates, silanes, silanols, olefins, epoxies, amines, esters, phenols, styrenics and thiols improves the interaction with the polymer matrix [62]. POSS based thermoplastic and thermoset nanocomposites are reported to have lower density, improved processability, reduced viscosity, extended useful temperature range, reduced flammability, increased mechanical properties and increased gas permeability compared to silica nanocomposites [63 – 66].
Nanocalcium carbonate (NCC) is a cost effective particulate nanofiller used extensively in polyolefins. They have size of 50-100 nanometres and specific surface area of 15-25 m$^2$/g. To improve dispersability, increase oxidation resistance and reduce wear on processing machinery, surface treated grades coated with lipophilic substances like stearic acid or calcium stearate are available [67]. The addition of NCC to composites improves the strength, modulus, and toughness significantly [68].

**2.2.2.4 Other nanofillers**

Natural flaked graphite is composed of layers of nanosheets in which the carbon atoms within each sheet are tightly held by covalent bonds while those in adjacent sheets are bound by weak van der Waals forces. As the interplanar forces are weak, it is possible to intercalate molecules into the interplanar spaces of graphite and increase the interplanar spacing [5]. The original graphite flakes with a thickness of 0.4–60 nm may expand up to 2–20,000 nm in length by rapid heating to high temperature [6]. In the exfoliated state, graphite nanosheets have high aspect ratio (200–1500), high modulus (1 TPa) and enormous interface surface area (2630 m$^2$/g) [5]. Another method used is to disperse graphite oxide in water followed by chemical reduction to give conductive graphene. Graphite has high stiffness, excellent thermal/electrical conductivity and lubricant properties, arising from its typical layered structure with anisotropy [13].

Layered double hydroxides (LDHs), an unusual class of layered materials with positively charged layers and charge balancing anions located in the interlayer region, have received much attention in the past decades due to their vast applicability. They are represented by the general formula: $[\text{M}^\text{II}_{(1-x)}\text{M}^\text{III}_x(\text{OH})_2]A^{n^-} \cdot x\text{mH}_2\text{O}$, where $\text{M}^\text{II}$ includes: Mg$^{2+}$, Co$^{2+}$,
Cu\(^{2+}\), Ni\(^{2+}\), Zn\(^{2+}\) etc.; M\(^{\text{III}}\) may be Al\(^{3+}\), Cr\(^{3+}\), Ga\(^{3+}\), Fe\(^{3+}\); and A\(^{\text{n-}}\) might be any organic and/or inorganic anion [69]. The majority of important applications are based on their permanent anion-exchange and adsorption capacity, the mobility of interlayer anions and water molecules, their large surface areas, and the stability and homogeneity of the materials formed by their thermal decomposition. Because of their highly tuneable properties, LDHs are considered as a new emerging class of the most favourable layered crystals for preparing the multifunctional polymer/layered crystal nanocomposites [70]. Incorporation of LDH into polymer matrix has been shown to improve mechanical and thermal properties [71]. Other applications of LDH include antacids, flame retardants, PVC additives, drug delivery carriers and sensing devices [72].

A recent development is the use of biofillers in nanocomposites. Nanofibrils have been synthesized from naturally occurring plant fibers like bast, hemp and kraft by various chemical treatments [13]. Starch nanocrystals have been synthesized by Dufresne et al [73]. Other developments in bio-based nanofillers is cellulose nanofibril whiskers (with average diameter of 4–5 nm and the average length of 200–250 nm) [74] and cellulose nanopapers [75]. Acid treatment of cellulose nanofibres is found to improve the mechanical performance of nanocomposites.

### 2.2.2 Preparation methods

Polymer nanocomposites are prepared by the following methods: (i) in situ polymerization (ii) sol-gel process (iii) solution blending (iv) latex compounding and (v) melt mixing.

In in-situ polymerization method, the nanofiller is dispersed in the monomer and then polymerized (see Figure 2.8). The nanofillers are intercalated into the monomer using a suitable solvent before polymerization. This method has the advantage of producing nearly exfoliated nanocomposites. Nylon and polycaprolactone composites have been successfully produced by this method [9, 76]. The major disadvantage of this method is that separate production lines or major changes in the existing production facilities would be required for commercial production.
Sol–gel technology is a process in which the nanofiller is synthesised within the polymer matrix using an aqueous solution of the polymer and the building blocks for the nanofiller. A colloidal suspension (sol) is formed and gelated to form a network in a continuous phase. Nanometric dispersion of the inorganic phase is produced by the reaction of precursors that consist of a metal or metalloid compound with reactive ligands [6]. The polymer aids the nucleation and growth of the inorganic crystals and forms a network [4]. As the reaction conditions for the sol–gel process are relatively mild and well controlled, a wide range of compositions can be achieved for the nanocomposites [6]. The solvent is removed after the reaction before the dispersed phase has time to aggregate. This one step method has been successfully used for nanosilica based composites [77, 78]. However, it is not suitable for layered silicates for two reasons: (i) synthesis of most clay minerals generally requires higher temperatures which may decompose the polymer and (ii) tendency of the growing silicate layers to aggregate [4].

In solution blending method, polymer is dissolved in a suitable solvent along with the nanofiller [4, 15]. The nanofiller and the polymer can be mixed together after dissolution in solvent. After thorough mixing, the solvent is removed by vaporization or precipitation. In the case of layered silicates, the dispersion is easy because of the forces that hold the layers together are weak. In the case of rubber nanocomposites, the curatives may be added before removing the solvent or after complete or partial removal of the solvent. Vulcanization of the rubber compound is done after this step [14]. The effectiveness of this process depends on finding the best combination of polymer, nanofiller modifier and solvent. Industrial application of solution intercalation method is not feasible due to the environmental problems associated with large quantities of the
solvent and difficulties involved in dissolving polymer in the solvent that makes this option economically prohibitive [4, 15]. A schematic illustration of solution blending method for the preparation of polymer layered silicate (PLS) is depicted in Figure 2.9.

Figure 2.9 Schematic representation of PLS obtained by intercalation from solution [4]

Latex compounding is a promising route for preparing rubber nanocomposites. The nanofiller is mixed in the rubber latex and coagulated. This is effective in the case of layered silicates which can be easily dispersed in water. Further processing of coagulated rubber – nanofiller compound is similar to that of ordinary rubber compounds. A schematic illustration of the mixing and coagulation process is given in Figure 2.10.

Figure 2.10 Schematic illustration of the mixing and co-coagulating process [79]

Melt intercalation is the most direct, cost effective and environment friendly method for preparation of polymer nanocomposites from an industrial standpoint [14]. The polymer along with the nanofiller is heated above the softening point of the polymer. Due to the shearing in the mixing equipment, the nanofiller form smaller tactoids. In layered
silicates, the platelets are exfoliated by the combined action of shearing and diffusion of polymer chains into the stacks [80]. Surface modifications of the nanofillers improve the wettability of the polymer. Melt compounding of polymer nanocomposites can be done in polymer compounding equipment, including batch mixers and single- or twin-screw extruders [81].

The mechanism of exfoliation of layered silicate during melt mixing is illustrated in Figure 2.11.

Figure 2.11 Mechanism of organoclay dispersion during melt processing [80]

Majority of thermoplastics including nylons [82] and polyolefins [83-85] have been prepared by melt intercalation technique. Though rubber is not melted during processing, rubber nanocomposites have been successfully prepared by compounding in internal mixer.

2.2.3 Thermoplastic nanocomposites

As previously discussed, the first thermoplastic to be used for synthesis of nanocomposite was polyamide - 6. Since then thermoplastics like polypropylene, polyethylene, polyethylene terephthalate, polystyrene etc. have been used to prepare nanocomposites [4, 22]. The substantial increase in mechanical properties of polyamide nanocomposites was related to the constrained region around the clay nanoparticles along with the crystallinity of the nylon – 6 [9]. A critical parameter for the formation of intercalated and especially exfoliated hybrids is the presence of polar type interactions and hence intercalation into a polar matrix like nylon is favoured imparting significant enhancement in mechanical and
barrier properties [4]. Nylon clay nanocomposites have been commercialized in barrier films, packaging, molded parts and electrically conductive applications. Though in the initial years, nylon nanocomposites were prepared by in-situ polymerization [9], they were prepared by extrusion [86, 87] and injection molding [88] in later works. For most polyamides, when close to full exfoliation exist, conventional composite theories give reasonable fit for predicting increase in strength, modulus and heat deflection temperature (HDT), but inadequate for impact strength [86]. The effect of nanoclay on rheological properties of polyamides was studied by Incarnota et al [87]. Layered silicates have been found to decrease moisture absorption in polyamides [89]. Fracture toughness of nylon 6/organoclay nanocomposite was significantly improved by adding maleic anhydride grafted copolymer [90]. Silica nanoparticles have been used to produce functionally graded nylon nanocomposites [91].

Polyolefinic polymers, polyethylene (PE) and polypropylene (PP) have been widely used for preparing nanocomposites. Since they do not contain polar groups in their backbone, dispersion of layered silicate into their matrix is difficult [4]. Hence compatibilizers are used to facilitate the dispersion of layered silicate into polyolefin matrix [4, 92]. Incorporating nanoclay into PP matrix in the presence of maleic anhydride not only gives reinforcing effects but also increases the thermal oxidative volatilization temperature [83, 84, 93]. Gianelli postulated that unlike in nylon5s where delamination of nanoclay increased with molecular weight due to large shear forces contributed by large melt viscosity, in PP thermal diffusion control was the driving force for delamination [84]. On addition of nanoclay, there was increase in static and dynamic moduli and significant enhancement in gas barrier properties in low density polyethylene [85, 94]. High density polyethylene is effectively reinforced by nanoclay with improvement in elastic moduli while retaining impact strength and reducing gas and vapour permeation rate [95]. Nanocomposites with the compatibilizer exhibit improved thermal stability, better drawability and toughening as compared to neat polyethylene and nonexfoliated MMT composite [96]. Dong and Bhattacharyya investigated the effects of clay type, clay/compatibilizer content and matrix viscosity on the mechanical properties of polypropylene/organoclay nanocomposites [97]. Gas barrier property of PP and PP/ethylene propylene diene rubber (EPDM) was found to increase substantially when small percentage of nanoclay was added [98, 99].
Another class of nanofiller that has been extensively studied for polyolefins is nanocalcium carbonate (NCC). In PP, NCC acted as nucleating agent during crystallization and increased the crystallization rate [100]. In several studies it was found that the incorporation of nanosized CaCO$_3$ into PP increased the mechanical properties, toughness and thermal stability of the composites [101, 102]. Surface treatment of NCC with stearic acid or coupling agents promotes uniform dispersion of the nanoparticle by reducing the tendency to agglomerate and hence improves the mechanical properties [103]. NCC increased the apparent shear viscosity while reducing the extrudate swell by decreasing the molecular mobility of the matrix [103]. In both high and low density polyethylenes, addition of NCC has been shown to improve the impact strength without loss in yield strength [104, 105].

Low concentrations of nano-silica increased impact strength and tensile properties in PP [106]. Graphite nanoplatelets improved mechanical properties in polypropylene [107]. Functionalized CNTs impart improved modulus and tensile strength to PP [108]. Xu and Wang had reported that functionalized CNTs influence the kinetics of crystallization in PP [109].

In polyvinyl chloride (PVC), addition of nanoclay enhanced the mechanical properties, improved the processing and thermal stability while retaining optical clarity [110]. A masterbatch process combining intercalative polymerization and melt intercalation was developed which rendered significantly higher stiffness, mechanical and thermal properties compared to composites prepared by melt intercalation process [111]. Effect of nanocalcium carbonate on properties of PVC has been extensively studied. In PVC the presence of NCC particles improved impact energy and storage modulus [112]. In PVC / calcium carbonate (CaCO$_3$) nanocomposites synthesized by in situ polymerization, CaCO$_3$ nanoparticles stiffen and toughen PVC simultaneously and exhibited shear thinning behavior [113]. The dispersion of NCC in the matrix can be increased by modifying it with coupling agents [114].

Polystyrene (PS) – nanoclay composites are made by a variety of techniques like solution casting [115], melt intercalation [116] and in-situ polymerization [117]. Polystyrene – nanoclay composites exhibited improvement in thermal stability and water barrier properties compared to pristine polystyrene. In polystyrene, nanoclay enhanced the loss and storage modulus along with stress relaxation behavior [115] while melt elasticity and
extrudate swell were decreased [116]. Other nanofillers that have enhanced properties in polystyrene are nanocalcium phosphate [118] and nanoclacium carbonate [119]. Carbon nanotubes formed a conducting network and increased the electrical conductivity in PS [120].

Ethyl vinyl acetate copolymer (EVA) – organoclay composites have enhanced strength, toughness and thermal stability [121]. In EVA – nanoclay composites prepared by melt processing displayed incomplete exfoliation with small tactoids of clay but showed enhancement in shear viscosity, loss and storage moduli and shear thinning behavior compared to unfilled EVA [122].

The nanoclay reinforced polyurethane matrix and enhanced thermal and water resistance, while reducing the transparency [123]. In poly(dimethylsiloxane–urethane) (PDMS–PU) POSS nanocomposite membranes, the nature of POSS molecules and their compatibility with polymer matrix alters the permeation properties and the polar urethane linkages play a vital role in the gas pair selectivity of nanocomposite membranes [61]. CNTs have been used to produce PU nanocomposites with high electrical conductivity and enhanced the mechanical properties [124].

2.2.4 Thermoset nanocomposites

Thermoset resins of epoxy and polyester type have been used to prepare nanocomposites. Nanoclay has been found to facilitate the curing reaction in epoxy nanocomposites [125]. The exfoliation mechanism and thermal–mechanical properties of surface-initiated epoxy nanocomposites were studied by Chen et al [20]. Dramatic enhancements in stiffness and thermal properties were achieved in epoxy nanocomposites with small amounts of particle that were partly exfoliated into single nanolayers randomly distributed in the matrix and partly intercalated in the form of randomly dispersed clusters of nanolayers [10]. In a comparison between the effects of modified and unmodified nanoclay on the properties of epoxy – clay nanocomposites, it was found that bending, impact and barrier properties were better with organoclay [126]. Effect of coupling agents on morphology and properties were studied by Mascia et al [127]. In cyanate esters, a good increase in modulus was obtained without sacrificing the impact strength by addition of very small quantity of nanoclay [128]. In unsaturated polyester resins, nanoclay gave increase in tensile and dynamic storage moduli at low loadings [129]. The organic modifications of
the pristine clay improved the thermal and mechanical properties of the polyester-acrylate/clay nanocomposite films considerably [130]. Polyester–polyurethane nanocomposites based on unmodified and modified montmorillonite exhibits excellent improvement in tensile strength, thermal stability, storage modulus and adhesive properties over the pristine polyurethane [131]. In polyurethanes, nanoclay decreased gas permeability by tortuous pathways for the permeant molecule [132].

In epoxy – NCC composites prepared by in-situ polymerization, glass transition temperature, tensile strain, impact strength, modulus and flame retardance properties increased compared to pure and micro-CaCO$_3$ filled epoxy [133]. The mechanical interfacial properties, together with impact strength and flexural strength were improved on addition of NCC into epoxy resin [134]. NCC also improves dynamic mechanical properties, dimensional stability and maximum use temperature in epoxy resins [135].

Amine functionalized CNTs have been shown to accelerate curing reaction and enhance mechanical properties of epoxy systems [136]. They also improve the impact resistance and fracture toughness [137]. Epoxy composite showed higher electrical conductivities and mechanical properties such as the Young’s modulus and tensile strength along the stretched direction than perpendicular to it, and the electrical property of composite rise with the increase of SWNT concentration [138]. Chen et al demonstrated that CNT functionalization can be used to introduce either a stiff or a flexible interphase in thermoset nanocomposites, depending on the nature of surface grafts and their interaction with the matrix system [139]. The mechanical properties of phenolic matrix were reinforced by multi-walled carbon nanotubes and carbon fibers [140].

2.2.5 Elastomer nanocomposites

Elastomers are a very important class of materials that are used in varied applications in the fields of automobile, aerospace, biomedical, construction etc. To attain good mechanical properties, elastomers are reinforced with 20 – 40 % by weight of fillers like carbon black and silica. Though they impart reinforcement, the conventional fillers have certain drawbacks at high filler contents like reduced processability and increase in weight of the product [13]. Incorporation of nanofillers at low weight percentage have significantly enhanced the mechanical, anti-ageing and gas barrier properties of elastomer nanocomposites and also expanded their application potential. Though several nanofillers
like layered silicates (LS), carbon nanotubes (CNT), nanosilica, nanobiofillers, talc and nanometric calcium carbonate have been used in elastomers, the bulk of literature relates to nanoclay and CNT nanocomposites. The major challenge in rubber nanocomposites is uniform dispersion and complete exfoliation of nanofillers in the rubber matrix because unlike thermoplastics, rubber matrix is not melted during processing. Attempts have been made to model properties of rubber nanocomposites using composite theories [141]. The major studies done in this field are based on natural rubber, styrene butadiene rubber, chloroprene rubber, nitrile rubber, EPDM, butyl rubber, elastomeric polyurethane etc. and are reviewed below.

2.2.5.1 Natural rubber nanocomposites
The first attempt to prepare rubber nanocomposite was the work by Okada et al who prepared natural rubber (NR) – layered silicate composites and found improvements in mechanical properties [142, 143]. Natural rubber (NR) - nanoclay composites prepared by both melt compounding and latex blending exhibited improved mechanical properties and thermal stability [144 – 148]. NR nanoclay composites prepared by compounding in two-roll mill also had improved mechanical and thermal properties [149, 150]. In all the above cases the nanoclay was mostly intercalated with some exfoliation. Organo-modified clay has been found to accelerate the cure reaction in rubber vulcanizates [144, 151, 152]. Aliphatic modifiers in nanoclay gave higher degree of intercalation and faster cure kinetics than aromatic modifier [153]. Nanoclay reinforced natural rubber had lower diffusion coefficients for solvents and excellent gas barrier properties [143, 151, 154, 155]. Epoxidized natural rubber (ENR) has been found to be an effective compatibilizer for NR – nanoclay composites that improve the exfoliation of nanoclay platelets [156].

Another type of nanofiller used in natural rubber make high performance composites is nano-silica. Sol-gel process was used to generate in situ silica and the reinforcement effect of the in situ silica for NR vulcanizates increased with increasing in situ silica content [157]. Peng et al combined self-assembly and latex-compounding techniques to produce composites with SiO$_2$ nanoparticles homogenously distributed throughout NR matrix as nano-clusters and having enhanced thermal resistance and mechanical properties [158].

NR – CNT nanocomposites have attracted much attention in recent years. Several studies have shown that mechanical reinforcement and increase in electrical conductivity can be
achieved by adding relatively smaller amounts of CNT into the NR matrix [159, 160]. Though earlier works involved fabrication of CNT based nanocomposites by solution method to ensure proper dispersion of CNT in the rubber, recently melt compounded CNT – NR composites have also shown improved properties [161]. Functionalization of CNT and use of coupling agent have shown to improve the filler – matrix interaction and consequently improve mechanical, thermal and electrical properties [162].

2.2.5.2 Acrylonitrile butadiene rubber (NBR) nanocomposites

Acrylonitrile-butadiene copolymer (NBR) is a special purpose elastomer that is used in applications which require oil resistance. The amount of acrylonitrile content determines the oil resistance of the rubber [163, 164]. NBR – nanoclay composites were prepared by methods like melt mixing [165, 166], latex compounding [79, 167 – 170] and solution casting techniques [171 – 174]. While cure time and scorch time of the NBR – nanoclay composites were decreased, they had improved mechanical properties and thermal stability compared to unfilled NBR [79, 166 – 174]. Kim et al investigated the effect of chain length of the organo-modifier and found that as the chain length of the modifier increased, organo-MMT was distributed more uniformly during the formation of the nanocomposites [166, 167]. The NBR – nanoclay composites showed higher hysteresis and tension set than carbon black and silica filled NBR which was attributed to greater chain slipping on the surfaces and interfaces of intercalated organoclays and reduced recovery during cyclic deformation, respectively. At low nanoclay contents, exfoliated structures were obtained whereas at higher amounts of nanoclay intercalated structures were formed [175]. Polarity of the intercalant showed considerable effect on the properties of NBR - layered silicate composites. The most polar intercalant gave the best dispersion and better mechanical properties in NBR [176, 177]. Polarity imparted higher elasticity to the composites when subjected to dynamic load [178] and caused significant reduction in creep compliance values [177]. Wu et al investigated the applicability of composite theories to predict the Young’s modulus of NBR – nanocomposites and modified the equations with a modulus reduction factor for better fit of experimental data with theoretical predictions [141]. Sadhu et al studied the effect of acrylonitrile content on properties of NBR nanocomposites and found that the extent of intercalation for high acrylonitrile content NBR was lower than that for low acrylonitrile content NBR [172].
The nanocomposites showed shear thinning behavior with shear viscosity and the die swell decreased with addition of modified nanoclay [175].

A comparative study of the effect of particle geometry on the mechanical properties of nitrile rubber nanocomposites showed remarkable changes due to the differences in particle geometry and the chemical nature of the fillers. The filler geometry had significant effect on the mechanical properties of the composites owing to the availability of interfacial area per unit volume. The layered silicate showed maximum enhancement in mechanical properties because of the very high surface area to volume ratio in comparison with calcium phosphate and titanium dioxide fillers [179]. A study on the effect of curing systems on the orientation and the dispersion of the layered silicates in acrylonitrile butadiene rubber nanocomposite revealed that in peroxide cured vulcanizates the silicate layers are orientated in a preferred direction compared to sulphur cured vulcanize. It was also found that use of excess stearic acid induced better exfoliation in the latter case [180]. Silane coupling agent was found to be effective in enhancing the dispersion of clay and that clay and silane contents were the dominating factors in determining the thermal properties and water-vapour permeability of the nanocomposites [42, 181]. To improve exfoliation of nanoclay in NBR matrix, epoxidized natural rubber (ENR) was used as compatibilizer. The resulting nanocomposites showed greater exfoliation of nanoclay, thereby increasing the overall static and dynamic mechanical properties, swelling resistance in oil and solvent and decrease in compression set due to higher reinforcing efficiency of nanoclay in the NBR matrix [182].

The gas permeability of NBR – organoclay composites was found to decrease considerably with increase in nanoclay content [41, 42, 79, 169, 171]. Modified montmorillonite reduced the flammability of cross-linked nitrile rubber and considerably limited its fire hazard [183]. Elastomeric superhydrophobic, self cleaning nanostructured NBR based composite coatings scalable to large areas were prepared by spray casting particle-polymer dispersions consisting of nanostructured carbon black particles and submicrometre-sized poly (tetrafluoroethylene) [184].

Though majority of literature reported deals with nanoclay based NBR nanocomposites, there are a few studies on other nanofillers. Verge et al prepared NBR – CNT nanocomposites by a two-step process by first melt blending in a Brabender internal mixer followed by sulfur curing. It was shown that during the blending process, the
polymer chains were grafted onto the CNT surface via a free-radical mechanism. The CNT bundles were more intensively disrupted and the individualized nanotubes more finely dispersed in NBR at higher acrylonitrile (ACN) content [185]. High-performance rubber nanocomposites that combined improved mechanical and tribological properties were obtained by finely dispersing multi-walled carbon nanotubes to in NBR matrix by melt compounding, which resulted in a large extent of exfoliation and intercalation of nanotubes in (H)NBR matrix, followed by cross-linking [186]. Nanocomposites of nitrile rubber (NBR) and cellulose II (Cel II) were prepared by co-coagulation of nitrile rubber latex and cellulose xanthate mixtures. Addition of Cell II to NBR led to a gradual change in the stress at break, and the samples with 20 phr of Cel II showed the highest resistance [187].

There are studies on hydrogenated NBR (HNBR) and carboxylated NBR (XNBR). Highly reinforced HNBR nanocomposites with good tensile and tear resistant properties have been prepared using very low fraction of organophilic layered silicates [16]. Incorporation of organo– clay filler resulted in significant improvement of degradation profile of the HNBR nanocomposite at elevated temperatures and hence gave tremendous improvement in the useful service of the composite [188]. Gatos and Karger-Kocsis studied the effect of aspect ratio of silicate platelets on the mechanical and barrier properties of HNBR nanocomposites [189]. In a comparative study of the ablative properties of hydrogenated nitrile butadiene rubber (HNBR) composites filled with fumed silica, organically modified montmorillonite (OMMT), or expanded graphite (EG), it was found that HNBR/OMMT composite had the best ablation resistance followed by HNBR/silica composite, while thermal stability was independent of the type of nanofiller [190].

A functional composite with unique photoluminescence property, excellent mechanical property and fine thermal stabilities was prepared through reactive blending of the hydrogenated carboxylated nitrile rubber (HXNBR) and modified zinc carbonate basic [191]. Le et al found that in XHNBR – nanoclay composites, the time-independent reinforcement component decreased with clay dispersion degree as the spatial effect of clay platelet hindered the cross-linking of the rubber matrix [192].
2.2.5.2 Nanocomposites based on other elastomers

Styrene butadiene rubber (SBR) is an elastomer with good abrasion resistance that has several applications like manufacture of tyre. One of the earliest works on SBR nanocomposites was to improve the mechanical and processing properties of SBR – nanoclay composites prepared by latex blending [193]. Sadhu and Bhowmick studied the influence of styrene content and processing parameters on structure property relationship in SBR – nanoclay composites prepared by solution method and concluded that the higher the styrene content the larger the extent of increase in properties [37, 172, 173]. Zhang et al synthesized SBR – nanoclay composites by in situ living anionic polymerization that possessed higher glass-transition temperature, thermal stability, tensile strength and elongation at break than SBR [194]. A two stage compounding step involving a rubber – clay masterbatch to replace carbon black was developed by Chakraborty et al [195]. Jia et al and Bhattacharya et al have found that silane coupling agents were effective in SBR – nanoclay composites to aid dispersion and improve strength [196, 197]. In SBR – nanoclay composites prepared from latex by Ping et al, gas permeability of 20 phr nanoclay filled SBR was found to be 50% lesser than gum vulcanizates [79]. Praveen et al studied the synergistic effect between the fillers that resulted in remarkable improvement in strength properties in SBR – nanoclay hybrid nanocomposites containing dual structure based on carbon black and silica [198]. A comparative study of the effect of various nanofillers by Bhowmick et al revealed that while nanoclay brought about increment in tensile properties, tear strength was improved on using carbon nanofibre [197].

Use of NCC produced remarkable improvement in mechanical properties, swelling index, thermal stability, flame retardancy and abrasion resistance in SBR [199, 200]. Styrene butadiene rubber (SBR) matrices filled with functionalized multi-wall carbon nanotubes prepared by solution process gave significant improvement in the mechanical as well as thermal properties of the nanocomposites [201]. A novel technology to prepare styrene-butadiene rubber (SBR)/carbon nanotubes composites with enhanced reinforcement effects was developed by combining a spray drying method and a subsequent mechanical mixing process [202]. Other nanofillers like fibrillar silicate and nano-BaSO$_4$ have been used recently [203, 204].

EPDM rubber (ethylene propylene diene monomer rubber) is another rubber that has exhibited excellent enhancement in performance on incorporation of nanofillers. It has
been found that addition of organo-modified nanoclay imparted improvement in tensile, dynamic mechanical, thermal and gas barrier properties while lowering tan δ and glass transition temperature [206 – 208]. The dispersion and mechanical properties were influenced by processing conditions (mixing temperature and rotor speed) and nanocomposites prepared in internal mixer gave better mechanical properties than those prepared on a two roll mill [17, 209]. Increasing the polarity of the rubber by adding compatibilizer or grafting enhanced the nanoclay – rubber interaction and improved the mechanical performance [17, 209 – 212]. Longer chains in the modifier which are less reactive facilitated the exfoliation of clay platelets [209, 210]. Recently high performance EPDM composites have been developed with nanofillers like fibrillar silicate (FS) nanofibres [213], halloysite nanotubes [214] and NCC [215].

Polychloroprene rubber nanocomposites prepared from organically modified montmorillonite clays exhibited better static and dynamic mechanical characteristics, good compression set and stress relaxation properties while accelerating thermal degradation in the initial stage [216, 217]. Organoclay has been proved to be an effective reinforcement for polyurethanes to impart better mechanical properties, thermal and water resistance [123]. Another class of rubbers that have produced appreciable enhancement in properties by incorporation of nanoclay is fluoroelastomers [218]. In silicone rubbers, nanoclay imparted tear resistance, improvement in compression set and reduction in vapour permeability [219, 220].

2.2.6 Applications of elastomer nanocomposites

From the above discussions, it is evident that polymer nanocomposite materials exhibit properties superior to conventional composites, such as strength, stiffness, thermal and oxidative stability, barrier properties and flame retardancy. Often, these enhancements in properties are achieved at very low filler content. A major advantage of polymer nanocomposites is that they can be designed without compromising performance, mechanical properties, cost and processability as required in conventional blends and composites [4, 25]. Also, advancement in technology has made processing of nanocomposites commercially more viable. These characteristics make polymer nanocomposites amenable to a variety of applications like automotive, packaging, aerospace, construction, textiles etc. [221]. The first commercial polymer nanocomposite was a timing-belt cover made from nylon – 6 / nanoclay composite manufactured by
Toyota. The timing-belt cover exhibited good rigidity, excellent thermal stability, no wrap and also saved weight by up to 25% [21]. Since then a number of plastics have been commercially used in automotive and other applications mentioned earlier.

Rubber nanocomposites are used in commercial applications to achieve efficient reinforcement, lower density, good balance of stiffness with toughness and tear resistance, dimensional stability, permeation and absorption resistance, flame retardancy, chemical resistance and good appearance [13]. Rubber nanocomposites are used in tyre, membranes, coatings, aerospace applications and medicine.

In tyres, rubber nanocomposites are used to enhance the overall performance including reduced heat build-up (rolling resistance), improved traction, flex fatigue properties, excellent gas barrier properties for air retention, reduced heat build-up and recyclability [13, 222]. In tread compound, fumed nanosilica imparted greater reinforcement, improved tear strength, abrasion and ageing resistance and adhesion properties compared to carbon black [223]. Silicon carbide nanoparticles can be used to improve the skid resistance and reduce abrasion [224].

Inner liners in tyre are made from rubbers and they are periodically refilled with air. As nanoclay decrease gas permeation flux by creating a tortuous path, nanoclay was incorporated into rubber to improve the air retention capacity of liner [225]. Another approach is to remove the inner liner to reduce weight and thereby decrease fuel consumption. This can be achieved by a protective layer of elastomer nanocomposite coating [222].

In the nanorub project initiated by RAPRA, rubber materials or components that could be advantageously replaced by nanorubber composites were identified. The products were based on natural rubber, styrene-butadiene rubber (SBR), SBR/nitrile-butadiene (NBR) blends, NBR and chloroprene (CR)/polybutadiene (BR) blends. The nanoclay-rubber composite materials had at least three times higher abrasion resistance, 50% improved stiffness, 30% improved strength and 20% delayed ignition with respect to the equivalent reference non-nanoclay reinforced product. The nanorubber materials were used in the production of prototypes of improved moulded parts, rubber bearings, rubber cords and conveyor belts [223].
Rubber nanocomposites are used in membranes for their excellent barrier properties. Nanoclays have been used in different rubber matrices to obtain lower permeability [39]. A team of researchers from Massachusetts Institute of Technology has developed thermoplastic polyurethane elastomer (TPU) in which the harder glassy areas are reinforced by nanoclay particles, imitating the crystallites in the natural materials like spider silk. It has potential application in lightweight membranes and gas barriers used in fuel cells [228]. NBR/graphite nanocomposites possess significantly improved wear resistance and gas barrier properties, and superior electrical/thermal conductivity [229].

The reinforcing effect of NCC in different compounds – NR and NR/NBR blends was used in sports goods such as laminated sheet for inflated balls and NR based cycle tubes with improved barrier properties and air retention [13]. Thermoplastic elastomer polyurethanes (TPU) based nanocomposites are used in shoe soles to reduce wear and to improve the dry sliding behavior [230].

InMat LLC developed aqueous nanocomposite elastomeric coatings used in butyl rubber gloves to improve flame and petroleum oil resistance [222]. These coatings can also be used in sports balls, tyres, hoses, gaskets and bladders. The elastomeric coatings are compatible with standard processing conditions and can be applied using spray or dip coatings. Adhesion and toughness are improved during vulcanization. They maintain the barrier properties without brittle fracture at large strains [222].

Elastomer nanocomposites have several applications in aerospace industry. Hydrogenated nitrile rubber (HNBR) – nanoclay composite has high thermal stability, high operating temperature and resistance to air, water and oil [231] and hence can be used in applications like gasket, seal and bladders exposed to high temperature and severe environment. Rubber nano-sized metal composites are used in sensors to detect fatigue, impact and large strain for aerospace applications [232]. In recent years, elastomer nanocomposites have found application in biomaterials. Webb et al developed biodegradable elastomeric nanocomposite materials consisting of nanofibrous poly(L-lactic acid) (PLLA) nanophase and an elastomeric poly(diol citrate) macrophase for soft tissue engineering applications. The tensile mechanical properties of these materials were comparable to human cartilage, ligament, and blood vessel and the compressive modulus was very similar to those of human and bovine articular cartilage [233]. Silicone nanocomposites with gold nanoparticles have potential application in artificial muscles.
Other commercially available elastomer nanocomposite for medical application include Elastoguard, a pro-active antimicrobial HNBR or EPDM rubber containing silver nanoparticles and InMat’s elastomer nanocomposite used as coating for medical packaging [235].

### 2.3 Modelling approaches for polymer nanocomposites

In the previous sections it was seen that improvement in mechanical properties of nanocomposites arose from the low-percolation threshold, large number density of particles and surface area (interfacial area) per particle volume and short distances between particles of nanostructured materials [29]. To develop and optimize the use of nanostructured materials, it is essential to measure and model the properties, either by applying existing models or developing new models. The various modelling methods and the broad classes of modelling tools are represented in Figure 2.12.

![Figure 2.12 Classification of material modelling techniques](image)

This section reviews the different modelling approaches to predict the mechanical properties of polymer nanocomposites.
2.3.1 Analytical models

Conventionally mechanics-based models have been widely used for predicting mechanical properties of micro and macro composites with reliable accuracy [26, 237, 238]. Micromechanics theories predict the effective properties of composite materials as functions of properties of constituents, volume fraction of components, shape and arrangement of inclusions and matrix-inclusion interfaces [221]. The applicability of the micro-mechanics based models for nanostructured materials and nanocomposites have been explored in recent years [26, 141, 239 – 241]. In micromechanical models, the elastic modulus of the composite is generally determined by the elastic properties of its components (filler and matrix), particle loading and aspect ratio. They are either empirical or semi-empirical equations. These models consider filler particles as fibres, platelets (either disk type or ribbon type) or particulates which are aligned or randomly oriented in the matrix. A schematic representation of filler type and orientation is shown in Figure 2.13.

Figure 2.13 Schematic representations of filler type and orientation in nanocomposites [242]

Recent research work on applicability of these models to nanocomposites provided in some cases [10, 86] but did not address many of the issues like partial exfoliation and increased interaction at the nanofiller-matrix interface [240]. There are several
modifications suggested to composite theories to adequately describe the experimental data obtained for mechanical properties of polymer nanocomposites [141, 241]. Some of the micromechanical models used to predict the mechanical properties of composites are discussed below.

One of the earliest models developed to predict mechanical properties of composites is the Einstein’s model [26]

\[
\frac{E_c}{E_m} = 1 + 2.5\varphi_f
\]  

(2.1)

where \(E_c\) and \(E_m\) are the moduli of the composite and matrix respectively. \(\varphi_f\) is the volume fraction of the filler in the matrix. This equation implies that the composite modulus is independent of particle size and predicts a linear relationship between \(E_c\) and \(\varphi_f\). It also assumes perfect adhesion between filler and matrix, and perfect dispersion of individual filler particles. But this model is valid only at low concentrations of filler and is not suitable for large loadings due to the interaction of the strain fields around the particles.

Voigt upper bound and Reuss lower bound models are three parameter models that consider simple arrangement of fibres in a matrix, assuming iso-stress and iso-strain criteria. Voigt model considers fibre and matrix to be in parallel combination while Reuss model considers them to be in series combination. For composites subjected to the same uniform strain in the direction of filler alignment, the modulus is given by Voigt upper bound rule (Rule of mixtures) [26, 29]

\[
E_L = \varphi_f E_f + (1- \varphi_f) E_m
\]  

(2.2)

where \(E_L\), \(E_m\) and \(E_f\) are moduli of the composite in longitudinal direction, matrix and filler, respectively. \(\varphi_f\) is the volume fraction of the filler in the matrix.

In the Reuss model (Inverse rule of mixtures), the stress is applied in the transverse direction of the fibre. The modulus in the transverse direction is given by [26, 29]

\[
\frac{1}{E_T} = \left( \frac{\varphi_f}{E_f} \right) + \left( \frac{1-\varphi_f}{E_m} \right)
\]  

(2.3)
These models can be used irrespective of the filler shape and contain only three parameters – filler volume fraction and moduli of the filler and the matrix. Both these models provide very poor estimates of the elastic parameters of nanoclay-reinforced polymers since the interfacial characteristics and morphology of the nanoparticles are not taken into account. The modulus of real composites lies between these two bounds [26].

The reinforcing effect of spherical colloidal fillers on elastomers was studied by Guth and Gold and the modulus is given by equation [26]

$$E_c = E_m [1 + 2.5 \varphi_f + 14.1 \varphi_f^2]$$

(2.4)

The modified Guth and Gold equation has a shape factor ($\alpha = \text{length} / \text{breadth}$) to account for the accelerated stiffening at higher loadings and particles that are non-spherical, rod like particles [141] and is given by

$$E_c = E_m [1 + 0.67 \alpha \varphi_f + 1.62 (\alpha \varphi_f)^2]$$

(2.5)

where $\alpha = \text{length} / \text{breadth}$ of the filler.

Halpin-Tsai model is a semi empirical model that gives both longitudinal and transverse moduli. This model has the advantage that filler geometry is accounted for by the 5 independent parameters and hence gives better prediction of the properties for a variety of reinforcement geometries [93]. The assumptions used in Halpin-Tsai model are (i) the filler and matrix are linearly elastic, isotropic, and firmly bonded (ii) the filler is perfectly aligned, asymmetric, and uniform in shape and size (iii) particle–particle interactions are not explicitly considered and (iv) the properties of the matrix and filler are considered to be identical to those of the pure components. The elastic modulus of unidirectional composites reinforced by discontinuous cylindrical fibres or lamellar particles as a function of aspect ratio is given by equation (2.6) [93].

$$E_c = E_m \left(1 + \frac{\xi \eta \varphi_f}{1 - \eta \varphi_f}\right)$$

(2.6)

$$\eta = \left(\frac{E_f}{E_m}\right)^{-1} - 1$$

(2.7)
where $\xi$ is a shape parameter dependent on the geometry of the filler and the loading direction. For disk-like platelets, $\xi = 2(l/t)$, where $l$ is the length and $t$ the thickness of the dispersed filler. It may be noted that as $\xi \to 0$, the Halpin–Tsai theory converges to lower bound rule.

For rubber–nanoclay composites, since $E_f \gg\gg E_m$, $[(E_f/E_m) - 1] \approx [(E_f/E_m) + \xi]$ and the Halpin–Tsai equation reduces to

$$E_c = E_m \left[1 + 2 \frac{\left(\frac{1}{t}\right) \phi_f}{1 - \phi_f} \right]$$

(2.8)

Several researchers have reported that there is good agreement between Halpin-Tsai model and experimental data at lower nanofiller content, deviations occur at higher values. The main reason is that due to aggregation and change of the platelet morphology during processing the effective aspect ratio is at least an order of magnitude smaller than the theoretical aspect ratio [240]. Apart from this, assumptions like firm bonding between filler and matrix, uniform size, shape and alignment of filler in the matrix and varying tactoid thickness in the matrix due to incomplete exfoliation makes it difficult to accurately predict the properties of nanocomposites [93]. In the recent past several modifications to Halpin-Tsai model to account for incomplete exfoliation, non-uniform orientation and imperfect surface adhesion of filler have been suggested [241].

Hui-Shia developed the equation for overall modulus of composites applicable to aligned fibre-like and flake-like reinforcements. In this case also it is assumed that the fillers are aligned uniformly in the matrix. Like the Halpin-Tsai model, the geometry of the filler is accounted for by the model parameters [29]. The Hui-Shia equation is given by [243]

$$E_c = \frac{E_m}{\left[1 - \frac{\phi_f}{4} \left(1 + \frac{3}{\zeta + \lambda}\right)\right]}$$

(2.9)

where $\zeta = \phi_f + \frac{E_m}{E_f - E_m} + 3(1 - \phi_f) \left[\frac{(1 - g)\alpha_i^2 - \frac{g}{2}}{\alpha_i^2 - 1}\right]$.

(2.10)
\[ g = (\pi / 2) \alpha_i \]

\[ \Lambda = (1 - \varphi_i) \left[ \frac{3(\alpha_i^2 + 0.25)g - 2\alpha_i^2}{\alpha_i^2 - 1} \right] \]

\( \alpha_i \) is the inverse aspect ratio of the filler. \( \alpha_i = t/l \) for disk-like platelets.

The Cox model, also called the shear lag model, is used for predicting the moduli of fibre–filled composites. This model incorporates an efficiency factor that is dependent on length and a packing factor for fibre arrangement for different fibre shapes [29].

\[ E_L = \eta_l \varphi_if + (1 - \varphi_i)E_m \]  

(2.11)

where \( E_L \) is the longitudinal modulus and \( \eta_l \) is the length dependent efficiency factor that is dependent on the fibre packing arrangements.

Mori Tanaka model relates the stiffness tensor of the composite to that of the matrix phase and the filler. It is valid for composites with moderate volume fractions of inclusions (25% - 30%). This model includes a concentration tensor \( A^{(dil)} \) (calculated from volume tensors of the matrix and filler) and the fourth order Eshelby’s tensor (S) which relates average inclusion strain to average matrix strain, and approximately accounts for fibre interaction effects [10].

\[ A^{(dil)} = \left[ I + SC_1^{-1} (C_2 - C_1) \right]^{-1} \]  

(2.12)

where \( C_1 \) is the matrix phase stiffness tensor, \( C_2 \) the inclusion stiffness tensor and I is the fourth order unit tensor. S is the factor that accounts for fibre interaction effects fibre interaction effects.

Mori – Tanaka model assumes complete exfoliation of the clay layers, full dispersion and uniform orientation and also takes into account the interaction between inclusions. This model is based on Eshelby’s elasticity solution for inhomogeneity in infinite medium. Fourth-order tensor relates average inclusion strain to average matrix strain and approximately accounts for fibre interaction effects. The Mori–Tanaka theory predicts fibre reinforcement to have a stronger dependence on aspect ratio at a given filler modulus than does the Halpin–Tsai; this theory predicts lower reinforcement at low
aspect ratios from disks than does the Halpin–Tsai equation [86]. To account for partial exfoliation and intercalation, Luo et al modified the Mori-Tanaka model by including a parameter called exfoliation ratio obtained from TEM micrographs and obtained a very reasonable agreement between experimental results and predictions [10]. Another model based on Mori–Tanaka approach is the Wang and Pyrz model that deals with the composite materials reinforced with randomly oriented and transversely isotropic spheroids [29]. By varying the aspect ratio, the oblate spheroids can be approximated to platelets, and the prolate spheroids can be approximated to fibres. Chen et al evaluated the relationships between the interfacial adhesion strength and the work of adhesion of the components, the shape and size of the particle, and the mechanical properties of both constituents based on Eshelby’s equivalent inclusion method [244].

Models based on mean field theory assume that the nanoparticles (of uniform size) concentration in the matrix is low and they form parallel arrays (preferential exfoliation) included in a homogenous and isotropic elastic media. The theory assumes the existence of a volume element statistically representative of the overall composite material. At high concentrations, the interaction between the inclusions becomes an influencing factor and the analytical derivations of such interaction effect become quite complicated [245].

The various theories considered are based on several assumptions like uniformity in size, shape and alignment of fillers. They also assume that the filler and matrix are linearly elastic, isotropic, and firmly bonded. These, along the existence of an interphase with properties different from those of the matrix and filler, which was not considered in the theoretical models, may be the reason for large deviation in the predicted value. Brune et al showed that incomplete exfoliation and deviation of the platelet orientation from perfect biaxial in-plane have significant detrimental effect on the reinforcement efficiency. Their model considered the angle between the applied normal stress and symmetry axis of the nanofiller platelets for predicting modulus [246]. Thus it may be concluded that the choice of composite theory determines how well the predicted and experimental data agree.

2.3.2 Molecular modelling

Molecular modelling enables visualisation of three dimensional characteristics of molecules participating in reactions. The computer images are interactive allowing us to
rotate, scale and change the type of model viewed and can rapidly calculate many properties of molecules in view; the combination of visualisation and calculation is called molecular modelling. In molecular modelling, composition of the material is assumed to be non-continuous. The method is based on studies of atomic interactions at the nanometre length scale. They are discrete in nature and therefore are often limited by the length and time scales that can be achieved in the simulations, while being computationally exhaustive. The three approaches to molecular modelling are Molecular Dynamics (MD), Monte Carlo (MC) and Ab initio simulation [29].

Molecular dynamics simulation determines the physical properties of materials in nanoscale by finding the configuration of atoms (position, velocity and forces) in a molecule. This is done by solving equations of motion with atoms interacting through assumed interaction potentials and periodic boundary conditions. Molecular dynamics simulation usually consists of three constituents: (1) a set of initial conditions (e.g., initial positions and velocities of all particles in the system) (2) the interaction potentials to represent the forces among all the particles (3) the evolution of the system in time by numerically solving a set of classical Newtonian equations of motion for all particles in the system [29]. The force field may be obtained by quantum method, empirical method or quantum-empirical method. The force field is selected based on accuracy, transferability and computational speed. Molecular dynamic simulations have been widely used for predicting properties of nanocomposites based on nanoclay [247, 248], CNT [249, 250] and particular fillers [251, 252].

Monte Carlo (MC) is a class of probabilistic mathematical models for the prediction of the behaviour of a system. The MC predictions are statistical in nature and subject to laws of probability. In most cases it involves a multidimensional integration over the sample space [236]. MC approach can be used to predict modulus and study deformation in polymeric materials. Ab initio methods are based on the principles of density functional theory and involve solution of Schrödinger’s equation for each electron together while considering the potential created by other electrons and nuclei. Though these methods can be applied to a wide range of systems, they are computationally exhaustive and are used on a limited basis for the prediction of mechanical properties of polymer nanocomposites.
2.3.3 Computational continuum modelling

Finite element method (FEM) and boundary element method (BEM) are the two popular continuum-based computational modelling techniques. They do not always supply exact solutions but they can provide very accurate estimates for a wide range of assumptions [29, 236].

There are several approaches to finite element modelling like multiscale representative volume element (RVE) modelling, unit cell modelling and object-oriented modelling [29]. In RVE and unit cell modelling, two assumptions are made (i) nanofillers can be idealized to simple geometries such as spheres, ellipsoids, cylinders, or cubes and (ii) nanocomposites can be reproduced by assembling a large number of such RVEs (or unit cells). These assumptions limit the applicability of these techniques in complex and highly heterogeneous nanocomposites. In object oriented modelling, both matrices and organoclay particles are assumed to behave as linear elastic materials with perfect interfacial bonding between two constituents. The scanning electron microscopy (SEM) or transmission electron microscopy (TEM) micrographs with details with micro/nano-structure details are used for image segmentation to finite element grids. The tensile moduli are predicted by calculating the resulting stresses obtained from sums of the boundary forces acting on the boundary subjected known strains and appropriate constraints. Dong et al predicted tensile moduli of PP-nanoclay composites using object-oriented finite element analysis (OOF) code and established good agreement with the experimental data and theoretical models [253]. There are several publications on use of FEM methods to model mechanical properties of nanoclay and CNT based nanocomposites [254, 255].

Boundary element method involves solving boundary integral equations for the evaluation of stress and strain fields. This method uses elements only along the boundary, unlike FEM, which involves elements throughout the volume. Hence the computational resources required in BEM are considerably less than FEM. In BEM, it is assumed that a material continuum exists, and therefore, the details of molecular structure and atomic interactions are ignored. Liu et al showed that BEM can be very useful for first-order approximation of mechanical properties in large-scale modelling of CNT composites [236].
However, these methods are still in their infancy and there are discrepancies between experimental and predicted values [198]. Though many models that account for the shape, aspect ratio and alignment of the nanofiller have been proposed to model nanocomposite properties, they do not give accurate predictions over a range of nanofiller contents, as the aggregation of the particles observed at higher contents of nanoclay and interfacial interactions between the filler and polymer matrix are not taken into account in these theoretical models [27, 141, 240, 241]. Also, the success of these approaches often depends on the accurate determination of aspect ratio for the nanocomposite for which a thorough analysis of TEM photomicrographs at different magnifications is required [10].

Figure 2.14 Illustration of complications in the determination of the aspect ratio of layered silicate fillers within polymer nanocomposites [4]

Figure 2.14 depicts various complications of calculating an aspect ratio from TEM micrographs that arise from variations in both length/diameter and thickness. The recovery, refinement, chemical treatment, and post-treatment of these clays may contribute to the variation in filler geometry. Also, melt processing steps will amplify the range of particle shapes and sizes, particularly when the layered silicate is not completely exfoliated. Another complication is that microtoming nanocomposite samples into thin sections results in apparent distribution of observed particle sizes even if all particles have uniform size [4].
2.3.4 Composite theories for permeation

The diffusion process through nanocomposites is a complex process. The particles act as barriers for the diffusion of penetrant which must follow elongated or tortuous path for diffusion. The tortuosity depends on the concentration, shape, location and orientation of particles in the matrix [256]. There are several theories that predict the permeability coefficient of composites, some of which are discussed here.

A simple relation between the permeability coefficient of the composite \( (P_c) \) with that of unfilled polymer matrix \( (P_m) \) is given by

\[
P_c = P_m (1 - \varphi_f) f
\]  

(2.13)

where ‘\( f \)’ is the tortuosity factor found by solution to Fick’s law.

Neilson model for calculating permeability coefficient assumes that the filler as rectangular platelets with finite width (ribbon) arranged in regular array in the matrix. The Neilson model is given by equation (2.14) [41, 256].

\[
\frac{P_c}{P_m} = \frac{1 - \varphi_f}{1 + (\alpha \varphi_f/2)}
\]  

(2.14)

where \( \varphi_f \) is the volume fraction of the filler in the matrix and \( \alpha \) is the aspect ratio of the filler. Nah et al applied Neilson model to elastomer – nanoclay systems and found reasonable agreement between experimental and theoretically predictions [41].

Another equation suggested by Cussler for regular array of ribbon like fillers is given by [256, 257]

\[
\frac{P_c}{P_m} = \frac{1 - \varphi_f}{1 + (\alpha \varphi_f)^2/4}
\]  

(2.15)

Some of the theories for predicting permeability coefficients were developed for randomly oriented disk like particles used as fillers. Gusev and Lusti developed an exponential model using finite element analysis. Equation (2.16) represents this model [256, 258].

\[
\frac{P_c}{P_m} = \exp\left(\alpha \varphi_f / 3.47\right)^{0.71}
\]  

(2.16)
2.4 Design of experiments

As discussed in the previous section, for nanocomposites, there exist significant discrepancies between experimental values and those predicted by theoretical models. The reason is that these models are based on several assumptions such as uniform size, shape, alignment, uniform exfoliated distribution of nanoparticles and excellent bonding between the nanoparticles. Also, as the size of the filler decreases, the interface between the filler and the matrix increases greatly and the effect of low adhesion and imperfect contact at the interface plays a significant role in deciding the properties of the nanocomposite. For polymer nanocomposites, in addition to the aspect ratio and filler-polymer interface, several factors like orientation, dispersion and processing method significantly influence their properties. This is especially true in the case of elastomer based nanocomposites in which the presence of other ingredients like cross-linking agents, accelerators, activators and other particulate fillers etc. determine the properties of the elastomer composites. Another important factor that influences the properties of elastomer vulcanization is the type of cross-linking agent and the type of vulcanisation system (determined by the ratio of sulphur to accelerator) used for curing the rubber compound. Vulcanisation of elastomers, especially of diene rubbers like NBR, can be carried out using peroxide type of cross linking agent [163, 164]. In these types of polymer systems, where the assumptions used in conventional models rarely hold good and where a number of parameters influence polymer properties, Design of Experiments (DoE) can be effectively used for modelling, analysis and optimizing properties.

Design of Experiments (DoE) is a structured statistical technique to investigate a system or a process. It allows simultaneous evaluation of a number of factors influencing the properties, eliminating the need for large number of independent runs that is required in a conventional step by step approach, especially in cases involving multiple parameters and multiple properties to be studied. DoE is a multipurpose tool that can be useful in choosing between alternatives, selecting the key factors affecting a response, reduce variability, maximize or minimize a response, make a process robust and to generate regression models between the properties and various parameters considered [259 – 264].

In the conventional one variable at a time [OVAT] approach, all but one variable is held constant while methodically changing one at a time. This method carries the risk that while one input variable may be found to have a significant effect on the response
(output), the effect of changing another variable on the former may not be evident. Therefore, the conventional experimentation procedure is a failure when there is the influence of combined factor effects on the response.

If there are three factors $X_1$, $X_2$, $X_3$ that have been identified as influencing the outcome of the experiment, then in an OVAT in the first step $X_1$, $X_2$ are held constant and the experiment is carried out by changing $X_3$. From the experimental data obtained, the best of $X_3$ is found ($X_{3b}$). In the second step, experimental procedure is carried out by changing $X_2$, by keeping $X_1$ constant at best $X_{3b}$. This gives the best value of $X_2$ ($X_{2b}$). Then in the final step the value of $X_1$ is optimized by keeping $X_{2b}$ and $X_{3b}$ constant. Thus the best value of $X_1$ ($X_{1b}$) is obtained. The major fallout of this method is that the best value of these variables is not the best of all i.e. the value of $X_1$ is best only at the fixed values of $X_{2b}$ and $X_{3b}$. The interaction effect of two or more factors can be explained in the Fig 2.15.

![Figure 2.15 Levels of interaction between variables X1 and X2](image)

Figure 2.15 Levels of interaction between variables X1 and X2

In the DoE approach, a series of structured tests are designed in which planned changes are made to the input variables of a process or system and the effects of these changes on a pre-defined output are assessed. All possible dependencies are planned in the first place, and the data needed to assess them are laid out. In terms of resource the exact length and size of the experiment are set by the design (i.e. before testing begins). The main advantages of statistical design are:

- It generates relatively accurate data with minimum number of experiments thereby saving valuable materials and time.
• Ability to evaluate factor effects mathematically.

• It covers a large experimental region with minimum number of experiments.

In many types of experimentation, it is often required to characterize the relationship between a property (response) and a set of variables (such as composition and nature of ingredients, process conditions). The different stages include selection of design, conduct of experiments, regression analysis and generation of contour diagrams, response surfaces and factor plots.

The first step in DoE is to identify the input variables and the response (output) that is to be measured. For each input variable, a number of levels are defined that represent the range for which the effect of that variable is desired to be known. This approach requires coding of levels for predictor variables. Coding of levels for the independent variables is achieved by the identification of maximum (+1) and minimum (-1) levels which lead to a significant change in the property being measured and determination of midrange of the factor levels. The experimental plan determines where to set each test parameter for each run of the test. The response is then measured for each run. The method of analysis is to look for differences between response (output) readings for different groups of the input changes. These differences are then attributed to the input variables acting alone (called a single effect) or in combination with another input variable (called an interaction) [259 – 267].

In order to draw the maximum amount of information a full matrix is needed which contains all possible combinations of factors and levels. If this requires too many experimental runs to be practical, fractions of the matrix can be taken dependent on which effects are of particular interest. The fewer the runs in the experiment the less information is available.

2.4.1 Choice of experimental design

The choice of an experimental design depends on the objectives of the experiment and the number of factors to be investigated. Types of designs are listed here according to the experimental objective they meet [259 – 264].

50
• Comparative objective: If there are one or several factors under investigation, but the primary goal of the experiment is to make a conclusion about one important factor, (in the presence of, and/or in spite of the existence of the other factors), and the question of interest is whether or not that factor is "significant", (i.e., whether or not there is a significant change in the response for different levels of that factor), then it is a comparative problem and the solution needed is a comparative design solution.

• Screening objective: The primary purpose of the experiment is to select or screen out the few important main effects from the many less important ones. These screening designs are also termed main effects designs.

• Response surface method (RSM) objective: The experiment is designed to allow us to estimate interaction and even quadratic effects, and therefore give us an idea of the (local) shape of the response surface we are investigating. For this reason, they are termed response surface method designs.

• Optimal fitting of a regression model objective: If we want to model a response as a mathematical function (either known or empirical) of a few continuous factors and we desire "good" model parameter estimates (i.e., unbiased and minimum variance), then a regression design is needed.

Choice of a design from within these various types depends on the amount of resources available and the degree of control over making wrong decisions that the experimenter desires.

2.4.2 Response surface designs

Response surface method (RSM) allows simultaneous evaluation of a number of factors and eliminates the need for a large number of independent runs (experiments) that are otherwise required in a conventional one – factor – at – a – time or trial – and – error approach. It is a statistically sound technique which increases the productivity of the experiments by minimizing the number of experiments involving multiple parameters. Use of RSM allows generation of an adequately fitting second order polynomial equation that contains the significant factors affecting the responses as well as the interactions between the parameters. The steps in this method involve identifying the objective functions, selecting the influencing factors and determining the main and interaction
effects of the factors on the responses [259 – 264]. Response surface models may involve just main effects and interactions or they may also have quadratic and possibly cubic terms to account for curvature. Under some circumstances, a model involving only main effects and interactions may be appropriate to describe a response surface when

1. Analysis of the results revealed no evidence of "pure quadratic" curvature in the response of interest (i.e., the response at the centre approximately equals the average of the responses at the factorial runs).

2. The design matrix originally used included the limits of the factor settings available to run the process.

In other circumstances, a complete description of the process behaviour might require a quadratic or cubic model. These are the full models, with all possible terms; rarely would all of the terms be needed in an application.

2.4.2.1 Factorial design

When the investigator selects two levels for each of a number of variables (k factors) and runs the experiments with all possible combinations, it is referred to as a $2^k$ factorial design [259, 260, 268]. The number of runs required by a full $2^k$ factorial design increase geometrically as k is increased. The design table for three factor factorial design is given in Table 2.3.

Table 2.3 Design table for three factor factorial design

<table>
<thead>
<tr>
<th>Trial no.</th>
<th>X1</th>
<th>X2</th>
<th>X3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>2.</td>
<td>+1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>3.</td>
<td>-1</td>
<td>+1</td>
<td>-1</td>
</tr>
<tr>
<td>4.</td>
<td>+1</td>
<td>+1</td>
<td>-1</td>
</tr>
<tr>
<td>5.</td>
<td>-1</td>
<td>-1</td>
<td>+1</td>
</tr>
<tr>
<td>6.</td>
<td>+1</td>
<td>-1</td>
<td>+1</td>
</tr>
<tr>
<td>7.</td>
<td>-1</td>
<td>+1</td>
<td>+1</td>
</tr>
<tr>
<td>8.</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
</tr>
</tbody>
</table>
2.4.2.2 Fractional factorial design

When \( k \) is not small the desired information can often be obtained by performing only a fraction of the full factorial design called as fractional factorial designs. If we were to test 4 factors at 2 levels there would be 16 possible combinations. The test matrix would include 15 columns for the following terms: A, B, C, D, AB, AC, AD, BC, BD, CD, ABC, ABD, ACD, BCD and ABCD (including the interactions). In most applications, interactions of more than two factors are seldom significant. By ‘aliasing’ D with ABC interactions, a half fraction of the full factorial can be built. The design table fractional factorial design for three factors is given in Table 2.4.

Table 2.4 Fractional factorial design for three factors

<table>
<thead>
<tr>
<th>Trial no.</th>
<th>A</th>
<th>B</th>
<th>AB</th>
<th>C</th>
<th>AC</th>
<th>BC</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>2.</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>+1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>3.</td>
<td>-1</td>
<td>+1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>4.</td>
<td>-1</td>
<td>+1</td>
<td>-1</td>
<td>+1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>5.</td>
<td>+1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>6.</td>
<td>+1</td>
<td>-1</td>
<td>-1</td>
<td>+1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>7.</td>
<td>+1</td>
<td>+1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>8.</td>
<td>+1</td>
<td>+1</td>
<td>1</td>
<td>+1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

2.4.2.3 Central composite design

The central composite design (CCD) is the most popular of the many classes of RSM designs as it is very efficient, providing much information on experiment variable effects and overall experimental error in a minimum number of required runs. CCDs are very flexible and availability of several varieties of CCDs enables their use under different experimental regions of interest and operability. CCD is a rotatable design that provides equal precision for fitted response at points (factor level combinations) that are equal distances from the centre of the factor space. The CCD is a rotatable design (Table 1.8) which would require 5 levels of each factor (-a, -1, 0, +1, +a). Three main varieties of CCD are available in most statistical software programs: Face-cantered, rotatable and inscribed. The right variety of CCD is chosen based on the region of interest and the region of operability [259 - 262, 264, 267]. Table 2.5 summarizes properties of the
classical quadratic designs. It also provides broad guidelines that one might use when attempting to choose from among available designs.

Table 2.5 Summary of properties of types of central composite design

<table>
<thead>
<tr>
<th>Central composite design type</th>
<th>Schematic diagram</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Circumscribed Central Composite (CCC)</td>
<td><img src="#" alt="Diagram" /></td>
<td>The original form of the central composite design. CCC designs provide high quality predictions over the entire design space, but require factor settings outside the range of the factors in the factorial part. The star points are at some distance $\alpha$ from the centre based on the properties desired for the design and the number of factors in the design. The star points establish new extremes for the low and high settings for all factors. These designs have circular, spherical, or hyper spherical symmetry. Requires 5 levels for each factor.</td>
</tr>
<tr>
<td>Inscribed Central Composite (CCI)</td>
<td><img src="#" alt="Diagram" /></td>
<td>For those situations in which the limits specified for factor settings are truly limits, CCI design uses the factor settings as the star points and creates a factorial or fractional factorial design within those limits but do not provide the same high quality prediction over the entire space compared to the CCC. Requires 5 levels of each factor.</td>
</tr>
<tr>
<td>Face Centred Central Composite (FCCD)</td>
<td><img src="#" alt="Diagram" /></td>
<td>Star points are at the centre of each face of the factorial space, so $\alpha = \pm 1$. FCCD designs provide relatively high quality predictions over the entire design space and do not require using points outside the original factor range. However, they give poor precision for estimating pure quadratic coefficients. Requires 3 levels of each factor.</td>
</tr>
</tbody>
</table>
2.4.2.4 Box-Behnken design

Unlike the CCD, which employs five levels of each factor, Box – Behnken designs enable use of minimum number of levels. This system uses a subset of points in the corresponding full three - level factorial. The Box-Behnken design is an independent quadratic design in that it does not contain an embedded factorial or fractional factorial design [259, 260, 269]. It is a rotatable design characterized by a set of points lying at the midpoint of each edge of a multidimensional cube and centre point replicates (see Figure 2.16). This design does not contain any points at the vertices. Hence it is very useful in situations where physical constraints in upper and lower limits of the variables make it impossible to test these points. Box-Behnken DoEs allow us to vary each design parameter at three levels, giving the ability to capture second-order behaviour. They do a reasonable job of covering the design space as points are on the edges of the hypercube. However, Box-Behnken DoEs should not be used in capturing the behaviour at the design parameter extremes (corner points). For three factors, the Box-Behnken design offers some advantage in requiring a fewer number of runs. For 4 or more factors, this advantage disappears.

Figure 2.16 Geometry of Box-Behnken design for three variables

Table 2.6 gives a comparison of the structures of four common quadratic designs discussed above when investigating three factors. As CCC (Central Composite Circumscribed) and CCI (Central Composite Inscribed) designs are structurally identical, they are combined in Table 2.6.
Table 2.6 Structural comparisons of CCC / CCI, FCCD and Box-Behnken designs for three factors

| Rep | X1  | X2  | X3  | Rep | X1  | X2  | X3  | Rep | X1  | X2  | X3  |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 1   | -1  | -1  | -1  | 1   | -1  | -1  | -1  | 1   | -1  | -1  | 0   |
| 1   | +1  | -1  | -1  | 1   | +1  | -1  | -1  | 1   | +1  | -1  | 0   |
| 1   | -1  | +1  | -1  | 1   | -1  | +1  | -1  | 1   | -1  | +1  | 0   |
| 1   | +1  | +1  | -1  | 1   | +1  | +1  | -1  | 1   | +1  | +1  | 0   |
| 1   | -1  | +1  | +1  | 1   | -1  | +1  | +1  | 1   | -1  | 0   | +1  |
| 1   | +1  | +1  | +1  | 1   | +1  | +1  | +1  | 1   | +1  | 0   | +1  |
| 1   | -1.682 | 0  | 0  | 1   | -1  | 0  | 0  | 1   | 0   | -1  | -1  |
| 1   | 1.682  | 0  | 0  | 1   | +1  | 0  | 0  | 1   | 0   | +1  | -1  |
| 1   | 0   | -1.682 | 0  | 1   | 0  | -1  | 0  | 1   | 0   | -1  | +1  |
| 1   | 0   | 1.682  | 0  | 1   | 0  | +1  | 0  | 1   | 0   | +1  | +1  |
| 1   | 0   | 0   | -1.682 | 1   | 0  | 0  | -1  | 3   | 0   | 0  | 0   |
| 1   | 0   | 0   | 1.682  | 1   | 0  | 0  | +1  |
| 6   | 0   | 0   | 0   | 6   | 0  | 0  | 0  |

Total Runs = 20  Total Runs = 20  Total Runs = 15

* Rep indicates the number of repetitions and X1, X2 and X3 are the factors considered

While choosing an appropriate response surface design, in addition to the number of experiments and other aspects discussed above, the extremes for the factors generated in the design should also be considered.

2.4.3 Interpretation of results

The interpretation consists of three parts described below

(i) Determining the set of factors that are statistically significant for each response measured in the experiment - A quantitative measure for reporting the result of a test of hypothesis is the $p$-value. The $p$-value is the probability of the test statistic being
at least as extreme as the one observed given that the null hypothesis is true. It quantifies how significant each term is in the polynomial model. A smaller number is better as a small p-value is an indication that the null hypothesis is false. Using the p-value, the factors which are required for plotting in the contour plots can be determined. Another parameter of interest when a response surface design is run is the $R^2$ value. When the objective of the experiment is to optimize, higher R-squared values are important, implying that the polynomial model is a very good predictor of the response. The higher the R-squared values, the better the polynomial is at either describing the system or making predictions about the system.

(ii) Quantifying the relationship between each measured response and the statistically significant factors (done using regression analysis). Regression analysis is a statistical procedure used to predict the value of an unknown variable (dependent variable) from the values of one or more known variables (independent variables). It also measures the relationship between each of the independent variables and the dependent variable. For appraisal purposes this means it can be used to estimate the contribution to property value of each of the property characteristics included in the regression equation. The regression analysis generates a response equation, which consists of the main, quadratic and the interaction terms. The general form of a regression equation for a response consisting of 2 variables is

$$\text{Property} = \beta_0 + \beta_1 x + \beta_2 y + \beta_{11} x^2 + \beta_{22} y^2 + \beta_{12} xy.$$  

where $\beta_0$, $\beta_1$, $\beta_2$, $\beta_{11}$, $\beta_{22}$, $\beta_{12}$ are the coefficients; $x$, $y$ are variables. The coefficient, $\beta_i$ indicates the change in the value of the response for a unit change in the value of $x$ when all the other variables are held constant. A positive sign in front of the coefficient indicates the increase in the response with the increase in the value of the corresponding variable.

(iii) Determining the ranges of the statistically significant factors (or “process windows” or “process set points”) that lead to certain optimal/desired ranges for the measured responses. For this purpose contour plots are useful. A contour plot is a graphical technique for representing a 3-dimensional surface by plotting constant $z$ slices, called contours, on a 2-dimensional format. That is, given a value for $z$, lines are drawn for connecting the $(x, y)$ coordinates where that $z$ value occurs. The contour plot is an alternative to a 3-D surface plot. The contour plot is formed by an
independent variable on vertical axis, the 2\textsuperscript{nd} independent variable on horizontal axis and iso-response values as lines. In DoE, contour plots show lines of equal responses, usually equally spaced in response values. They provide an easy way to determine a response value for a response surface. A contour plot shows the response surface for two factors with all of the other factors held constant at levels you specify. When the factors of interest are selected, one can zero in on an area of interest by limiting the range to be plotted. The factors of interest can be selected based on the values obtained from regression analysis.

The actual techniques for determining the correct iso-response values are rather complex and are almost always computer generated. Contour plots are available in most general purpose statistical software programs. They are also available in many general purpose graphics and mathematics programs. These programs vary widely in the capabilities for the contour plots they generate. The different types of contour plots are shown in Figure 2.17.

![Figure 2.17 Types of contour plots](image)

2.4.4 Multiple response optimization

The quality of a product is measured by many different quality characteristics. When there are multiple responses, each response is modelled with a different polynomial equation. Some models will be linear while others are quadratic. Accordingly, each will have different contour plots with differing “optimal” factor settings. Statistical software packages typically have a mathematical multiple response optimization routine where the polynomial models are optimized and a set of conditions that is a compromise to all the stated goals are determined. To get the optimal factor settings, the contour plots are overlaid within the applied constraints.
DoE has been successfully utilized to optimize the performance and model the properties of polymer nanocomposites [270, 271]. Dong et al used DoE to model effect of clay type, clay/compatibilizer content and matrix viscosity on the mechanical properties of PP nanoclay composites [88, 97]. DoE has been effectively used to optimize the process variables in nanocomposite preparation [272]. Thus DoE can be used as an effective tool to model and optimize the properties of polymer nanocomposites.