Chapter 1

1.0 Introduction

The advances in synthesis techniques and the ability to characterize materials on nanoscale has led to a growing interest in nanocomposite materials. They exhibit improvements in material properties when compared to polymer matrix alone or to a conventional composite. These properties include high moduli, increased strength, barrier to moisture diffusion, increased thermal stability and decreased flammability [1-5].

According to a report by Bins and Associates, Sheboygan, U.S.A, a leading market-research firm, the usage of polymer clay nanocomposites in automotive applications is to be about 10,000 - 25,000 metric tonnes by 2015 in North America alone, with very high annual growth. By 2020, the market for nanocomposites could be in the order of millions of tonnes annually in North America alone and is valued at over US $4 billion [6].

1.1 Nanoclay composites

Nanocomposites are a new class of composites for which at least one dimension of the dispersed particles is in the nanometer range. Nanoparticles can be three-dimensional spherical and polyhedral (e.g., colloidal silica), two-dimensional nanofibres (e.g., nanotube, whisker) or one-dimensional disc-like nanoparticles (e.g., clay platelet) as shown in Figure 1.1 [7-9]. On the scale of the fibres, the nanofiller particles are still very small, for example, the thickness of an exfoliated silicate sheet is 10000 times smaller than the diameter of an average glass fibre as shown in Figure 1.2 [10]. The fibres are long, continuous and the particles fit between them without reducing the
fibre volume fraction. In these, three phase composites the objective is to use a high volume fraction of fibres as the main reinforcement and improve various properties.

![Common reinforcement geometries and their surface area/volume](image)

**Fig. 1.1** Common reinforcement geometries and their surface area/volume

![Nano-particle reinforcement of the matrix in a fibre composite](image)

**Fig. 1.2** Nano-particle reinforcement of the matrix in a fibre composite

Among all the potential nanocomposites, those based on clay and layered silicates have been most widely investigated. Nanoclay consists of two-dimensional nanometer thick platelets that are stacked up as layers about one nanometer apart. Ever since the development of nylon-6/clay nanocomposites by Toyota researchers, extensive
studies on clay/polymer nanocomposites have been investigated in order to obtain new organic nanocomposites with enhanced properties [11-14].

Polymer layered silicate nanocomposites, which is the subject of the present research, are prepared by incorporating finely dispersed layered silicate materials in a polymer matrix. The structural advantages of smectite clays such as, montmorillonite (Figure 1.3) and related layered silicates are the materials of choice for polymer nanocomposites for two principal reasons: (i) they exhibit a rich intercalation chemistry, which allows them to be chemically modified and made compatible with organic polymers and (ii) they occur freely in nature and can be obtained in pure form at low cost [15-17].

![Structure of Montmorillonite Clay](image)

**Fig 1.3** Structure of Montmorillonite Clay

Definite results are yet to be achieved, but trends indicate that when processed properly, small amounts (≤ 5 wt. %) of nanoclay can increase the modulus, strength, toughness, resistance to particle impact, gas impermeability, resistance to thermal degradation, flammability resistance, and dimensional stability of polymeric
materials. This is due to high aspect ratio (1:200) and high surface area (750-800 m²/g) of nanoclay with the resulting materials weighing lighter than the conventional composites. Among the different types of clays, montmorillonite (MMT) presents high swelling capacity as the gallery cations (Na⁺ and Ca²⁺) are small and easily hydrated, and hence MMT is the smectite clay with highest swelling capacity [18,19].

Nanoclay/polymer composites are classified as either intercalated, where the polymer matrix has migrated between the clay layers expanding the d-spacing or exfoliated where the clay layers are separated completely by the polymer matrix as depicted in Figure 1.4 [20]. The exfoliation or delamination configuration is of particular interest because it maximizes the polymer/clay interactions making the entire surface of layers available for the polymer. This should lead to significant changes in mechanical and physical properties [21-23]. However, due to the very large surface area of nanoclay and strong particle interactions are likely to result in cluster formation or agglomeration.

Fig.1.4 Schematic illustration of different types of polymer/nanoclay composites
It is not easy to achieve complete exfoliation of pristine nanoclay and indeed with a few exceptions, majority of the polymer nanocomposites reported in the literature are found to have intercalated or mixed intercalated-exfoliated nanolayers [24-26]. This is largely due to three reasons: (i) strong interactions of nanoclay among themselves resulting in stacks of agglomerated tactoids, (ii) silicate layers are highly anisotropic, with lateral dimensions ranging from 100 to 1000 nm, and even when separated by large distances (i.e. when exfoliated) cannot be placed completely random in the sea of polymer, and (iii) dispersion of the tactoids into discrete monolayers is hindered by the intrinsic incompatibility of hydrophilic layered silicates and hydrophobic polymers.

In order to increase the compatibility of nanoclay with polymers, naturally occurring nanoclay is organically modified by an ion exchange of cations in the cavities or galleries of silicate structures by alkylammonium surfactants to make them hydrophobic [27, 28]. The intercalation of organic cations makes it hydrophobic and organophillic increasing the miscibility within the polymer matrix. The use of clay or organically modified clay as precursors for preparation of nanocomposites has been studied into various types of polymer systems including polyamide-6 [29], epoxy [30], polyimide [31], polyester [32], polypropylene [33], polystyrene [34], polyethylene oxide [35] polycaprolactone [36] and polymethyl methacrylate [37]. Figure 1.5 shows commercially available nanoclays with varied d-spacing values.

**Cloisite Na+** is a natural montmorillonite, a well known additive used to improve various plastic physical properties, such as reinforcement, heat deflection temperature (HDT) and Coefficient of Linear Thermal Expansion (CLTE). Cloisite additives have been used in injection-molded parts, films, bottles, trays, blister packs, and wire and cable coatings.
**Fig. 1.5** Organomodified clays with d-spacing values

**Cloisite-15A** is an organo-modified natural montmorillonite with quaternary ammonium salt containing organic modifier, dimethyl dehydrogenated tallow [2M2HT], where HT is hydrogenated tallow with approximate composition of 65% C-18, 30% C-16, 5% C-14. Specific gravity of Cloisite-15A is 1.66 and bulk density is 172.84 kg/m³. Particle size distribution is such that 90% are less than 13 microns and 50% are less than 6 microns and 10% less than 2 microns. Average particle diameter as determined by X-Ray Diffraction is 31.5 Å.

### 1.2 Vinylester resin

Generally, polymer based materials are not water soluble but they are capable of absorbing various amounts of water, depending on their chemical nature and formulation as well the environment to which they are exposed [38]. The gain of water content enhances the probability of material degradation which generally follows three main mechanisms: (i) direct diffusion of water molecules through the matrix and, in some cases, through the fibres, (ii) capillary flow of water molecules along the fibre/ matrix interface followed by (iii) diffusion from the interface into the
bulk resin. This is a consequence of debonding mechanisms between fibres and matrix caused by water attack at the interface and diffusion through micro-cracks, pores, defects in the material.

Many polymer systems such as epoxy, vinylester, polyurethanes, polyamides and polyesters have been used with nanoclay to reduce the moisture permeability. Vinylester are preferred in marine and civil applications due to their lower moisture absorption and mechanical property degradations to other resins such as epoxy, polyester, iso-polyester, etc. Vinylester consists of the chemical backbone of an epoxy resin with the curing mechanism of polyester. Vinylester resins possess improved chemical resistance and are easily processable. Vinylester resin is an addition product of various epoxy resins and ethylenically unsaturated mono-carboxylic acids as shown in Figure 1.6 [39]. It contains two aromatic rings chemically bonded along the main linear polymeric chain in the two para positions as shown in Figure 1.7. The more compact vinyl network avoids fluid gains in marine environment and the ester groups are less subjected to hydrolytic reactions [40, 41]. This explains higher chemical resistance of the ester groups in the vinylester resin.

Visco et al. conducted comparative studies of seawater absorption of thermoset based composites and reported that vinylester resin based composites had lower water diffusion co-efficient along with higher chemical stability, stiffness and strength during its immersion in seawater [42]. Ray et al. conducted experiments to determine the effect of organoclay by dispersing 1-10 wt % of Cloisite-30B in vinylester and reported an increase in flexural modulus by 13 % for 5 wt % clay loading [43]. Shahryar et al. observed improvement in mechanical and thermal behavior by dispersing OMMT in vinylester by in-situ polymerization technique [44].
Characteristic features of vinylester resin

- Very high chemical/environmental resistance
- Higher mechanical properties than epoxies
- Post cure generally required for high properties
- Higher cost than epoxies

![Chemistry of vinylester resin](image1)

**Fig. 1.6** Chemistry of vinylester resin

![Schematic structure of DERAKNE (DOW chemicals) vinylester resins](image2)

**Fig. 1.7** Schematic structure of DERAKNE (DOW chemicals) vinylester resins
1.3 Dispersion of Nanoclay

Several mixing techniques such as ultrasonication, ball mills, shear forces, in-situ polymerization and many others have been reported to disperse nanofillers in thermoset polymers [45]. Figure 1.8 represents different mixing techniques for the dispersion of nanoclay. In-situ polymerization is one of the conventional approaches in the preparation of nylon-MMT nanocomposites [9]. Organically modified silicate is swollen in a monomer and the polymerization reaction takes place in the mixture. The growing polymer chains can push the layers apart leading to an exfoliated structure. The silicate is swollen in one of the reactants, or in the mixture, and the reaction takes place to form a crosslinked network depending on the glass transition temperature of the network [46, 47]. One of the methods later used to prepare epoxy/nanoclay composites was the exfoliation-adsorption technique, where the nanofiller is exfoliated in a solvent such as acetone, toluene, etc. in which the polymer is soluble. The polymer is adsorbed between the layered stacks and evaporation or precipitation of the solvent results in exfoliated nanocomposite [48].

Giannelis et al. [15] revealed that intercalation of polymer chains into the galleries of an organoclay can occur spontaneously on heating a mixture of polymer and silicate clay powder above the polymer glass transition or melt temperature [9]. Once sufficient polymer mobility is achieved, chains diffuse into the host silicate clay galleries, thereby producing an expanded polymer–silicate structure [49]. Ultrasonication for dispersion of nanofillers in polymeric resins is widely reported. High shear forces during the dispersion exfoliate the nanoclay by breaking the agglomerates. Extruders and three-roll mill or ball mill are designed to achieve exfoliation of nanoclay through high shear forces by controlling speed and temperature [50-52].
Fig. 1.8 Processing techniques for clay based polymer nanocomposites: a) In-situ polymerization b) Solution exfoliation and c) Melt intercalation

Extruders and three-roll mill or ball mill are designed to achieve exfoliation of nanoclay through high shear forces by controlling speed and temperature [53, 54]. Among the available techniques, twin-screw extrusion provides some advantages over others due to its effective dispersion performances. In twin-screw extrusion, several factors such as the properties of the polymer matrix, type and amount of filler that determine the state of dispersion have been reported [55–57]. Ray et al. [43] conducted experiments to determine the effect of organoclay by dispersing 1–10
wt. % of Cloisite-30B in vinylester at room temperature with the help of mechanical
stirrer at 4000 rpm and reported an increase in Flexural Modulus by 13 % for 5 wt.%
clay loading. Gefu and Guoqiang [58] studied six different combinations of
sequencing and duration of three mixing techniques such as manual stirring,
ultrasonication and three roll shear mixing to disperse 1 wt. % MMT in vinylester and
arrived at the best combination to achieve maximum gain in mechanical, thermal and
fire retardant properties of vinylester based nanocomposites. The authors studied five
mixing combinations for dispersion of nanoclay in vinylester resin and reported an
increase of 29 % in Flexural Modulus for 1 wt. % MMT.

Regardless of the mixing technique used, complete exfoliation, a state in which all
layers are separated from all tactoids of clay is very difficult to achieve. Despite
recent progress in polymer nanocomposite technology, there are many fundamental
questions which are not yet answered. For example, how to disperse nanoclay in
polymer structure to homogenize overall composite properties? How does one tailor
organoclay chemistry to achieve high degrees of exfoliation reproducibility for a
given polymer system? How do process parameters and fabrication affect composite
properties? Further research is needed to address these issues [53]. So far, twin screw
extrusion for dispersion of nanoclay in thermoset polymeric resins has not been
reported.

1.4 Diffusion studies
Organically modified layered silicate composites show barrier properties,
flammability resistance, and thermal stability superior to that of unmodified nanoclay
dispersed polymer composites. Incorporation of nanoclay increases the barrier
properties by creating additional ‘tortuous path’ that impedes the diffusion of gas or
solvent molecules while passing through the matrix resin as shown in Figure 1.9
[54]. The intercalation of organic cations (Figure 1.10), such as alkylammonium ions in the galleries of MMT, gives it hydrophobic behavior and renders it organophillic for compatibility with the polymer matrix [55]. The cationic exchange of the nanoclay is dependent on the polymer system.

It is common in open literature to find the diffusion reports on treated nanoclay. Shah et al. performed diffusion studies by dispersing Cloisite-10A which is organomodified clay, in epoxy and vinylester resins in distilled water medium [56]. The authors observed 50 % decrease in diffusivity with 1 wt. % addition of nanoclay. S.C. See et al. conducted moisture absorption studies in boiling water and reported reduction in diffusivity by 9.74 % and 11.63 % for 0.5 wt. % and 1.0 wt. % addition of organomodified nanoclay respectively. The authors reported that the treated nanoclay formed an organic layer which provided a covalent bonding between the clay and the polymer layer, due to which the clay behaved as part of the polymer resulting in better miscibility with the polymer system [57]. Manfredi et al. performed water diffusion studies by adding Cloisite-10A up to 5 wt% to glass/epoxy and reported greater water absorption with increased clay content. The improvement was accounted for the diminution in the cross linking density of the polymer matrix [58]. Organomodified nanoclay (4 wt %) dispersed in the polymer increased its Young’s modulus and flexural modulus [59]. Review of literature on moisture diffusion through polymer nanocomposites indicated that such studies are mainly focused on Fick’s Law of Diffusion and the application of the Langmuir Model for their diffusion behaviour is scarce. The influence of basal spacing of the nanoclay on the diffusion behaviour of nanocomposites is also not reported.
1.5 Erosion behaviour of nanocomposites

Solid particle erosion refers to gradual loss of surface material due to mechanical interaction of erodent particles; it results in surface roughening, surface degradation and reduced life span of components [60]. FRP are often used in many structural applications where erosion occurs [61]. While studying the erosive wear behavior of thermoset glass reinforced composites eroded by 300 μm size iron spheres, Dhar et al.
[62] and Gomes et al. [63] postulated that there was a threshold value of velocity below which deformation was elastic and hence no damage occurred. Tilly et al. [64] observed that the threshold velocity depended on the particle size of the erodent and obtained a value of 2.7 m/s for 225 μm quartz against 11 % chromium steel.

In depth research has been carried out on erosion behavior of FRP whereas very limited reports are available on nanoparticulate dispersed FRP. The incorporation of hard particles in polymer system provides improved wear resistance [65]. Patnaik et al. [66] conducted erosion experiments using air jet erosion test rig and Orthogonal Array Technique on polyester/glass and reported that erodent size, fibre loading, impingement angle and impact velocity were the significant factors in their declining sequence affecting the wear rate. Ismail et al. [67] reported superior erosive performance of carbon/epoxy filled with fly ash censospehre (CSP). Yilmaz et al. [68] reported improved erosive wear performance of polyester/glass/CaCO₃ when compared with polyester/glass/Al₂O₃ due to higher hardness of CaCO₃ than that of Al₂O₃. But, the volume fraction of the material removed was greater at higher filler percentages of CaCO₃. Patnaik et al. [69] conducted experimental studies using three different particulate fillers using SiC, Al₂O₃ and flyash with glass/polyester. The authors concluded that the erosion was minimum in case of hardest particulate dispersed in the composites. However, particle impact erosion of nanofiller dispersed FRP is not adequately investigated so far. Mechanical characterization reports suggest that dispersion of nanoclay in FRP improves their hardness and hence is expected to improve their erosion behavior.

To summarize the following are the benefits of layered silicate nanocomposites:

- Increased modulus at very low filler concentration: 5 % nanoclay can typically improve the tensile modulus by more than 40 % [70].
- Lower density, because the layered silicate filler is used in much smaller quantities [71].

- Increased barrier properties against fluid transport through the nanocomposite. The high aspect ratio of the impermeable silicate layers increases the path length for diffusion of molecules [72-74].

- Reduced flammability; the barrier function of the silicate layers reduces the transport of oxygen and waste-gasses and a silicate-platelet char layer forms that blocks the burning polymer from the atmosphere [75-78].

- Better surface and optical properties; due to the small particle size the surface of a nanocomposite is very smooth, and nanocomposites can be transparent because the particle size is below the wavelength of visible light [79].

Based on the review of literature [1-79], the research was aimed at dispersing nanoclay in vinylester by adopting combination of ultrasonication and co-rotating twin screw extrusion which is a novel technique. Taguchi’s Orthogonal Array technique was used to optimize the parameters of co-rotating twin screw extruder for dispersing nanoclay in vinylester. Nanoclay/vinylester composites were characterized for mechanical properties such as Ultimate Tensile Strength (UTS), Interlaminar Shear Strength (ILSS), Flexural Strength (FS), Vicker’s hardness and moisture diffusion in artificial sea water medium. Parametric study of erosion behaviour of nanoclay/vinylester/glass was undertaken using Design of Experiments. The dispersion and morphology of the nanocomposites were studied using Scanning Electron Microscopy (SEM), X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM).
1.6 Materials, Processing and Testing

1.6.1 Materials

The raw materials used in this study, specifications and suppliers are shown in Table 1.1.

**Table 1.1 Materials and Chemicals used for the specimen preparation**

<table>
<thead>
<tr>
<th>Materials</th>
<th>Specifications</th>
<th>Suppliers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Montmorillonite</td>
<td>Density: 0.7-1.1 g/cc</td>
<td>Southern Clay Products, USA</td>
</tr>
<tr>
<td></td>
<td>Composition: Alumino Magnesium Silicates.</td>
<td></td>
</tr>
<tr>
<td>Cloisite-Na</td>
<td>Density: 0.7-1.1 g/cc</td>
<td>Nanocor corporation, USA</td>
</tr>
<tr>
<td></td>
<td>Composition: Alumino Magnesium Silicates.</td>
<td></td>
</tr>
<tr>
<td>Cloisite-15A</td>
<td>Density 172.84 kg/m³</td>
<td>Nanocor corporation, USA</td>
</tr>
<tr>
<td></td>
<td>Composition: Dimethyl Quaternary Ammonium</td>
<td></td>
</tr>
<tr>
<td>Polyflex GR 200-65 superior vinylester resin</td>
<td>Density: 1.05 g/cc, Tensile strength: 60Mpa Flexural</td>
<td>Naptha Resins &amp; Chemicals (p), Bangalore, India</td>
</tr>
<tr>
<td></td>
<td>Strength: 130Mpa Heat distortion temperature: 125°C</td>
<td></td>
</tr>
<tr>
<td>Di-Methyl acetamide as promoter.</td>
<td>Density: 0.94 g/cm³</td>
<td>Suntech Fibres &amp; Polymer, Bangalore, India.</td>
</tr>
<tr>
<td>Cobalt napthalate as accelerator</td>
<td>Density: 0.98 g/cm³</td>
<td></td>
</tr>
<tr>
<td>Methyl Ethyl Ketone peroxide (MEKP) as catalyst.</td>
<td>Density: 1.17 g/cm³</td>
<td></td>
</tr>
</tbody>
</table>
1.6.2 Nanoclay

Two types of nanoclay were selected: Cloisite-Na, a naturally occurring clay and Cloisite-15A, an organomodified clay. Cloisite-15A is selected since it has highest basal spacing and highest surface hydrophobicity when compared to other modified nanoclay as shown in Figure 1.5. Table 1.2 represents the chemical modifier and its structure.

<table>
<thead>
<tr>
<th>Organic modifier</th>
<th>Chemical structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>CH₃</td>
</tr>
<tr>
<td>(1) 2M2HT: dimethyl, dehydrogenated tallow, quaternary ammonium</td>
<td>CH₃—N⁺—HT</td>
</tr>
<tr>
<td></td>
<td>HT</td>
</tr>
</tbody>
</table>

Where HT is Hydrogenated Tallow (~65% C18; ~30% C16; ~5% C14), Anion: Chloride

1.6.3.1 Ultrasonicator

Ultrasonicator is a device used at the first stage for the dispersion of nanoclay in polymer. It has been used as a means to separate nanoclay particles into its constituent layers in a polymer. This technique is based on imparting high-energy vibrations in a localized region causing separation of nanoclay platelets. Ultrasonic frequency, power, and mixing time are the variables in this process. Figure 1.11 and Table 1.3 shows the ultrasonicator and its specifications used for the studies.
1.6.3.2 Screw Extruder

An extruder is a vessel for continuous processing of polymer and other additives where mixing of the ingredients occur, that may be accompanied by a chemical reaction. The various ingredients in the material are forced to interact physically by passing through a series of constricted passages between a barrel and a screw thereby creating a shearing action generally termed as ‘KNEADING’ to create homogeneous mass.

In a co-rotating twin screw extruder that is setup to deliver the nanoclay/polymer composite (as a result of application of the shear forces) at kneading region (in the various extruder processing zone) for the required amount of time (narrow residence time distribution considering all molecules in a give volume), the progress of material through the extruder is highly controlled and such a system can be used for effective dispersion of nanoparticles in a polymer system.

Separation of bundles, reduction of size of agglomeration particles, uniform distribution, wetting or impregnation constituents in the matrix are the most common

**Table 1.3 Specification of Ultrasonicator**

<table>
<thead>
<tr>
<th>Model VPL-P2 of and dia. 1 inch</th>
<th>Supplier</th>
<th>Vibronics Pvt. Ltd., Pune</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequency</td>
<td></td>
<td>37 kHz</td>
</tr>
<tr>
<td>Voltage</td>
<td></td>
<td>220V</td>
</tr>
<tr>
<td>Capacity</td>
<td></td>
<td>500ml</td>
</tr>
<tr>
<td>Power</td>
<td></td>
<td>250 watts</td>
</tr>
</tbody>
</table>
terms used in describing mixing requirements. The two aspects namely, establishing homogeneity and wetting are normally referred to as kneading. The essential aspect of kneading is to completely surround every individual immiscible particulate matter with the wetting medium in a manner that ensures homogeneous composition of the polymer material. Figure 1.12 shows a longitudinal cross section of a typical screw extruder [80]. The various nomenclatures of a screw element and the screw elements are shown Figure 1.13a and 1.13b respectively [81, 82]. The co-rotating twin screw extruder used for the dispersion of nanoclay in vinylester for the present study and its specifications are shown in Figure 1.14 and Table 1.4 respectively.

Fig. 1.12 Longitudinal cross section of a typical extruder
Fig. 1.13 a) Screw nomenclature b) Twin screw elements

Fig.1.14 Alpha-18 Co-rotating Twin Screw Extruder
Table 1.4 Twin screw extruder specifications

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barrel diameter</td>
<td>18.8mm</td>
</tr>
<tr>
<td>Centre distance</td>
<td>16mm</td>
</tr>
<tr>
<td>Screw diameter</td>
<td>18.5mm</td>
</tr>
<tr>
<td>L/D Ratio</td>
<td>26</td>
</tr>
<tr>
<td>Do/Di Ratio</td>
<td>1.48</td>
</tr>
<tr>
<td>Screw speed</td>
<td>1200 rpm</td>
</tr>
<tr>
<td>Nominal torque per shift</td>
<td>30 Nm/shift</td>
</tr>
<tr>
<td>Specific torque</td>
<td>7.1 Nm/cm cube</td>
</tr>
<tr>
<td>Length of the barrel section</td>
<td>1200mm</td>
</tr>
<tr>
<td>Number of zones</td>
<td>6</td>
</tr>
<tr>
<td>1D Adaptor</td>
<td>Nil</td>
</tr>
<tr>
<td>Barrel cooling medium</td>
<td>Water</td>
</tr>
</tbody>
</table>

1.6.4 Nanocomposite preparation

1.6.4.1 Nanoclay/vinylester/glass specimens

The specimens were fabricated with woven mat 2-D glass fibres using wet hand lay-up process as shown in Figure 1.15. The number of fibre layers was derived based on the resin: fibre proportion 35: 65 wt % in all the cases. The specimens were cured at room temperature for 24 hours in a hydraulic press as most of the materials for marine applications are naturally cured, before exposing to experimental conditions. The edges of the panels were sealed using the matrix resin before exposing to the experimental medium. This was to prevent the moisture permeation through the sides.
Steps for preparation of nanoclay/vinylester/glass laminates:

(i) Cutting the fibres as per the required dimensions (25 × 25 cm) (Figure 1.16)

(ii) Weighing the nanoclay dispersed vinylester and stirring it with curing agents in a container (Figure 1.17)

(iii) Applying the resin uniformly throughout the fibre plies and stacking them one after the other (wet hand lay-up) in the Teflon mould (Figure 1.18)

(iv) Pressing the mould in the hot press and curing at room temperature for 24 hours.

(v) Removing of the cured sample from the mould. (Figure 1.19)

(vi) Cutting of the cured specimens for tests as per ASTM standards. (Figure 1.20)

![Fig. 1.15 Schematic Diagram of a) hand lay-up process b) Orientation of fibre layers](image-url)
Fig. 1.16 Cutting of glass fibres

Fig. 1.17 Weighing calculated amount of resin

Fig. 1.18 Application of resin to glass fibres

Fig. 1.19 Cured sample of nanoclay/GFRP

Fig. 1.20 Cutting the laminates as per ASTM dimensions
1.6.4.2 Hydraulic press

Hydraulically operated hot press of 2 ton capacity, shown in Figure 1.21 was used for the final pressing of the laminate stacked in the mould to ensure the uniform distribution of the resin throughout the laminate. The pressing in the machine also improves the uniform wetting of the fibre used in the laminate. The uniform wetting and bonding of the nanoclay/vinylester and glass reinforcement helps to improve the interphase in the nanoclay composite. It also helps faster curing of the laminates. Pressing helps in minimizing the number of imperfections and voids of the laminates.

The thickness of the laminate can be governed through the pressing process. All the specimens were cured at room temperature as per the manufacturer’s recommendations for naval applications. Hence, only uniform pressure was applied on the laminates at room temperature using the press.

![Image of hydraulic hot press with nanoclay/vinylester/glass laminate](image)

**Fig. 1.21** Hydraulic hot press with nanoclay/vinylester/glass laminate

1.6.5 MMT/vinylester specimens

Nanoclay in 2 - 5 wt % were dispersed in vinylester by ultrasonication at 37 kHz for one hour using tip sonicator followed by co-rotating twin screw extruder at 5 °C, 10 passes and 100 rpm [83]. The screw extrudent was mixed with 2 wt % each of
di-methyl acetamide as promoter, cobalt naphthalate as accelerator and methyl ethyl ketone peroxide as catalyst at room temperature to initiate the cross-linking process. It is then poured into the moulds made of sun maker’s sheet as shown in Figure 1.22 to obtain samples of less than 1 mm thickness. The mould is placed on a teflon sheet to prevent any resin adhering to its bottom surface. The nanoclay/vinylester gelcoat is poured into the mould and left to curing for 24 hours. Once the specimens are cured they are taken out of mould and used for the diffusion studies.

**Fig. 1.22** Teflon mould

The same procedure is repeated to both Cloisite-Na and Cloisite-15A with the loading level between 2 to 5 wt %. Figure 1.23 shows the cured neat samples of Vinylester, Cloisite –Na/vinylester and Cloisite-15A/vinylester.

**Fig.1.23** Cured samples a) Neat vinylester b) Cloisite-Na/vinylester  c) Cloisite-15A/vinylester
1.6.6 Mechanical testing of nanoclay/vinylester/glass specimens

Mechanical properties such as Ultimate tensile strength (UTS), Flexural strength (FS) and Interlaminar shear strength (ILSS) of nanoclay/vinylester/glass composites are computed from the test conducted using universal testing machine (UTM) in accordance to ASTM standards. The 10 ton capacity computer-interfaced UTM machine supplied by M/S Kalpak instruments and controls, Pune, India is shown in Figure 1.24 and specifications are shown in Table 1.5.

![Universal Testing Machine](image)

**Fig 1.24** Universal Testing Machine
Table 1.5 Specifications of Universal Testing Machine

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity</td>
<td>10 tonnes</td>
</tr>
<tr>
<td>Load frame</td>
<td>Mild steel C channel with double ball screw mechanism pre-loaded ball screw with zero backlash covered with bellow</td>
</tr>
<tr>
<td>Mounting</td>
<td>Free standing</td>
</tr>
<tr>
<td>Load range</td>
<td>1 kg-1000 kg using 1 ton load cell</td>
</tr>
<tr>
<td></td>
<td>1 kg-10000 kg using 10 ton load cell</td>
</tr>
<tr>
<td>Length measurements</td>
<td>Rotary encoder mounted on to the screw rod</td>
</tr>
<tr>
<td>Length resolution</td>
<td>0.01 mm</td>
</tr>
<tr>
<td>Cross head speed</td>
<td>0.1 to 100 mm/min</td>
</tr>
<tr>
<td>Controls</td>
<td>Emergency off, up and down key</td>
</tr>
<tr>
<td>Input power</td>
<td>220V±10% VAC,50 HZ,1500 VA</td>
</tr>
<tr>
<td>Net weight</td>
<td>225 kg</td>
</tr>
<tr>
<td>Grippers</td>
<td>Tensile, Compression, Three point Bending</td>
</tr>
<tr>
<td>Length accuracy</td>
<td>±0.1 mm</td>
</tr>
</tbody>
</table>

1.6.6.1 Tensile strength of nanoclay/vinylester/glass composites

ASTM 3039: Standard test method for tensile properties of polymer composite materials. Test specimen geometry 216 mm x 19 mm x 3 mm as specified in the above standard for balanced symmetry is shown in Figure 1.25. The specimen is positioned vertically in the grips of the machine. The grips are tightened evenly and firmly to prevent any slippage. The cross head speed of 1 mm / min was employed. Distance between the two grippers was maintained at 90 mm. The ultimate load carrying capacity of the composite laminates is recorded.
Ultimate tensile strength (UTS)

The UTS ($\sigma$) and Young’s modulus are calculated using equations (1.1) and (1.2) respectively [80].

$$\sigma = \frac{P}{bd} \text{ N / mm}^2$$  \hspace{1cm} (1.1)

Where $P = \text{maximum load in Newton's}$

$b = \text{width in mm}$

$d = \text{thickness in mm}$

Strain ($\varepsilon$) = change in length / original length

Young’s modulus (E) = $\sigma / \varepsilon \text{ N / mm}^2$  \hspace{1cm} (1.2)
1.6.6.2 Flexural strength of nanoclay/vinylester/glass composites

ASTM D 790: Standard test method for flexural properties of polymer composites. The test specimen geometry as specified in the above standard for balanced symmetry is 80 mm x 8 mm x 3 mm was tested with a span length of 50 mm. The test is conducted at a strain rate of 0.5 mm / min. The Test Setup is shown in Figure 1.26. Flexural test is done using a three point bend setup. The ultimate load carrying capacity of the composite laminates is recorded. The flexural strengths of the composites were determined as in equation (1.13) [81]

\[
\sigma_f = \frac{3PL}{2bd^2}
\]

(1.3)

\( P = \) peak load in N,

\( b = \) width in mm,

\( L = \) span length

\( d = \) thickness of the specimen in mm

Fig 1.26 Fixtures for flexural strength and ILSS measurement
1.6.6.3 Interlaminar shear strength of nanoclay/vinylester/glass composites

ASTM D 2344: Standard Test Method for ILSS Properties of Polymer Matrix Composite Laminates. The testing was done on short beams of 24 mm x 6.35 mm x 3 mm at a crosshead speed of 0.5 mm / min as shown in Figure 1.26. ILSS is determined using the equation (1.4) [78]

\[
ILSS = \frac{0.75P}{bt}
\]  

(1.4)

Where,

ILSS = Interlaminar shear strength in MPa

P = peak load in N

b = width in mm

t = the thickness of the specimen in mm

1.7 Morphological characterization of nanoclay composites

XRD, TEM and SEM techniques were employed for the dispersion studies of nanoclay in vinylester.

1.7.1 X-ray diffraction (XRD)

XRD is one of the most useful methods to evaluate the d-spacing between the clay layers and hence is used to study the degree of dispersion of the nanoclay in the polymer matrix. This analytical tool probes the crystal lattice structure of the nanoclay composite. X-Rays are obtained by bombarding the target specimen with a beam of high-voltage electrons inside a vacuum tube. Choice of the specimen determines the applied voltage and the output wavelength. X-Rays of a given wavelength are diffracted only for certain orientations of the sample. If the structures are arranged in
an orderly array or lattice, the interference effects with structures are sharpened. The information obtained from scattering at wide angles describes the spatial arrangements of the atoms, while low angle X-Ray scattering is useful in detecting larger periodicities. X-Ray diffraction patterns of un-oriented nanoclay polymers are characterized by rings. As the nanoclay is oriented, these rings break into arcs, and this structure reaches the relatively sharp patterns at high degrees of orientation [78]. Due to its easiness and availability, this technique is commonly used to study nanocomposite structures. However, the XRD can only detect the periodically stacked montmorillonite layers where individual silicate layers are separated by 2-3 nm, indicating peaks in XRD while others remain silent [84].

XRD measurements can characterize these structures if diffraction peaks are observed in the low-angle region, indicating the d-spacing of ordered-intercalated or delaminated nanoclay composites. A schematic representation of the theory can be seen in Figure 1.27, where X-Ray beams of wavelength \( \lambda \), are incident on the planes of the layers at an angle \( \theta \). These rays are scattered by atoms while constructive interference of them occur at the same angle \( \theta \), to other planes. A whole number \( n \), of wavelengths are equal to the distance between SP+PT. Angles of SP and PT are also equal to the angle of diffraction. This method is characterized by Bragg’s Law given by equation (1.5)

\[
\begin{align*}
  n \lambda &= 2d \sin \theta
\end{align*}
\]

(1.5)

where \( d \) is the interplanar spacing of the crystal
1.7.2 Transmission Electron Microscopy (TEM)

This analytical tool is fashioned after a traditional light microscope. However, instead of transmitting light, it uses electron beams which can give a higher resolution picture due to the decrease in wavelength. An electron gun emits an electron beam which moves through a condenser aperture and then bombards the specimen. The beam that passes through the sample is then filtered and magnified. The electrons impact a phosphor screen which allows for the viewing of the image.

Conventional optical microscopes can investigate structure to the resolution of few micrometers. But much higher resolution is required to study the fine structural details of the polymer nanoclay composites. TEM is used to observe the fine scale structure [46]. TEM functions exactly as its optical counterpart except that it uses a focused beam of electrons instead of visible light to "image" the specimen and gain insight about the structure and composition.

The four basic operations involved are [85]: 1) stream of electrons is formed and accelerated towards the specimen using a positive electrical potential, 2) this stream is
confined and focused using a metal aperture and magnetic lenses into a thin, monochromatic beam, (magnetic lenses are circular electro-magnets capable of projecting a precise circular magnetic field in a specified region) 3) the focused beam is impinging on the sample by a magnetic lens, 4) the energetic electrons then interact with the irradiated sample. These interactions and effects are detected and transformed into an image. TEM work was done on relatively thin samples at the Department of Pathology, Rajiv Gandhi Center for Biotechnology (RGCB), Thiruvananthapuram, India employing a JEOL Transmission Electron Microscope with an accelerating voltage of 80 kV. Micrographs were taken on 100 nm thick microtomed sections, cut parallel to the face of the sample. A representative diagram of the sectioning is shown in Figure 1.28 [86].

Fig. 1.28  Schematic representation of sample microtoming for TEM analysis
1.7.3 Scanning Electron Microscopy (SEM)

The Scanning Electron Microscope enables morphological observation of microstructures. This analytical tool can be used to view samples in three dimensions. SEM differs from TEM by the fact that the beam is used to scan across the surface of the specimen. Secondary electrons are released from the specimen due to the increased energy and are then detected by a phosphor screen producing an image. Sputtering of a thin film of gold on the surface to be examined is essential for FRP’s as polymers are insulators of electricity. There are three reasons for this operation: (i) the surface of sample must be electro conductive to minimize charging from initial beam (ii) the surface of sample must be thermo conductive to minimize local heating (as a result of high density current on the area of focus) and (iii) the material of sample must have high atomic number to increase the coefficient of secondary electron emission.

The tungsten cathode is a source of electrons emission. The electron optical system consists of a three-stage magnetic lens and a double deflection scan system. The objective lens focuses the electron beam to a small area (size is about 5-9 nm) as shown in Figure 1.29 [87]. The electrons pass the distance between the electron gun and the specimen through the column and interact with sample substance. As a result, different types of radiations are generated resulting in images with different contrasts and thus enabling the morphological studies.
Fig. 1.29 Schematics of working principle of SEM