SUMMARY OF THE THESIS

Introduction

Effect of fillers on the composite properties mainly depends on their concentration, particle size and shape of the fillers and their interaction with the matrix as well as compatibility. Montmorillonite (MMT) is nanofiller of choice for polymer nanocomposites and it is an expandable dioctahedral smectite belonging to the family of 2:1 phyllosilicates. Its particles consist of stacks of 1 nm thick aluminosilicate layers (or platelets) with a regular interlayer gap. It has a large surface area of 750 m$^2$/g and high aspect ratio. It has a low surface charge density of 0.25-0.5 equiv. mol$^{-1}$, due to which the interparticle force of attraction that aids in either intercalation/exfoliation within the polymer system have been successfully used to improve mechanical, thermal, barrier and fire retardation properties at very low loadings of < 5 wt% of nanofillers. Thus, MMT based polymer nanocomposites are considered for applications in a wide variety of areas, such as aerospace, marine, electronics and automotive industries.

Polymer nanocomposites do not always offer improved material properties over the conventional composites. In fact, poorly dispersed nanocomposites may have degraded mechanical properties. Depending on the mixing technique used conventional nanoclay dispersed composites can take the form of phase-separated microcomposite, intercalated or exfoliated nanocomposites.

Phase-separated microcomposites offer a little improvement in material properties while exfoliated ones show greatest interfacial interaction and phase homogeneity. It also brings difficulties in dispersing the nanoparticles due to their strong interactions among themselves. Because of these internanoparticle interactions, it is extremely difficult to disperse nanoparticles uniformly, especially at higher particle loadings.

Among the available techniques, twin-screw extrusion may provide some advantages over others due to its effective dispersion performances. Some of the
factors such as properties of the polymer matrix and the type and concentration of the filler which influence the state of dispersion in twin screw extrusion have been reported. The ability of the clays to exfoliate or intercalate depends not only on the clay–polymer interaction, but also on the interactions between the polymers. The thermal properties are even more complicated since the properties of the composite can change continuously as the composite is heated to high temperatures and phase separation accelerates.

Traditionally, the incorporation of halogen-based compounds comprised an economical route for enhancing the flame retardancy of polymers without relinquishing product quality. However, regulatory concerns of human and environmental contamination caused by the toxic dioxins and furans which are evolved during the combustion of halogens have pushed the market trend to halogen-free flame retardants. While being non-toxic and environmentally sound, halogen-free compounds, especially inorganic substances, require high levels of loading, leading to additional costs, processing difficulties and deterioration of mechanical properties.

The largest groups of mineral fire retardants are metal hydroxides in that ATH and MH are the most widely used. Metal hydroxides act as fire retardants by releasing water vapor through endothermic decomposition leaving a thermally stable inorganic residue. When used as filler in polymer composites they dilute the combustible polymer decomposition products with water, cooling the condensed phase through the endothermic dehydration.

Vinylester resins are preferred in marine applications due to their lower moisture absorption and mechanical property degradations than other resins such as epoxy, polyester and iso-polyester which are traditionally used for marine vehicles. The dispersion of Nanoclay in vinylester further improves the barrier properties of vinylester. The scientific community has been attempting to tailor the structure and composition of materials at the nanometer scale. The effect of fillers on the composite properties depends on their concentration, particle size and shape of the fillers and their interaction with the matrix as well as compatibility.
Vinylester has the combination of superior mechanical properties of epoxy resin and the ease of processing of polyester resin. Vinylester/nanoclay has high potential for marine structural applications because of the inherent advantages of both the constituents. Vinylester has superior barrier properties and nanoclay dispersion in vinylester further improves the diffusion properties as well as fire retardation behavior.

Objectives of the Thesis

The main objectives of this thesis is to study the effect of nanoclay on the mechanical, thermal, barrier and fire retardation properties of vinylester nanocomposites and the effect of long chain alkyl ammonium cation modification of Na-MMT on the d-spacing, particle size and thermal stability. The main aspect of the research was the adoption of ultrasonication and twin screw extrusion for dispersing nanoclay in vinylester. The main objectives are

- Dispersion of nanoclay in vinylester using Ultrasonication and Twin Screw Extrusion for preparing nanoclay/vinylester gelcoat and its characterization.

- Fabrication of nanoclay/vinylester/glass and nanoclay/vinylester/carbon specimens using hand layup technique and characterization for mechanical properties such as microhardness, UTS, FS, ILSS, Impact energy and Fatigue.

- Characterization of nanoclay/vinylester composites for fire retardation and studying the synergetic effect of fire retardants such as Aluminium trihydroxide (Al₂O₃) and Magnesium Hydroxide (Mg(OH)₂ on thermal and fire retardation behaviour of the nanocomposites

- Study of moisture diffusion behaviour of nanoclay/vinylester composites after alkaline solution ageing.

- Synthesizing long chained alkyl ammonium cationic surfactant modified Montmorillonite nanoclay (CTAB) and characterizing the organomodified nanoclay for particle size, layer d-spacing, functional group analysis and thermal stability using Zeta Particle Analyzer, XRD, FTIR and TGA.
Organization of the thesis

The work carried out on the above topic is described in seven chapters

Chapter-1

Introduction and Review on Polymer Nanocomposites

The first chapter carries the introduction, review of Montmorillonite and organomodified nanoclay as nanofillers in polymer nanocomposites, dispersion of nanoclay in polymers, influence of nanoclay addition to polymers on their mechanical, thermal, fire and moisture barrier properties, effect of fire retardants on the fire and thermal behaviour of nanoclay dispersed polymer composites and organomodification of nanoclay. The objectives adopted for the research are outlined. The literature gaps are discussed.

The main objective of the research is to study the exfoliation of nanoclay by adapting ultrasonication and screw extrusion their dispersion, study of the influence of nanoclay addition to vinylester on tensile, flexural, Inter laminar shear strength, Fatigue life, thermal, fire and moisture absorption behaviour of nanocomposites. Study of effect the effect of fire retardants and the modification of nanoclay on the basal spacing. The tests were performed as per American Standard for Testing Materials (ASTM).

Chapter-2

Experimental

This chapter describes the specification of the resins, nanoclays, fire retardants, modifiers and fibres. The specifications of the instruments used for dispersion of nanoclay in vinylester, procedure adopted for specimen preparation, ASTM standards for testing and characterization are discussed. Testing instruments such as XRD, TEM, SEM, AFM, DSC, TGA, LOI, Zeta Potential Analyzer, FTIR, Microhardness Tester, Universal Testing Machine (UTM), Fatigue Tester, Impact Tester are presented.
Chapter-3

Influence of MMT dispersion on Mechanical, Thermal and Fire Retardation Properties of Vinylester/Glass Composites

The influence of dispersing Montmorillonite (MMT) in 2 to 8 wt % in vinylester on the mechanical, thermal and fire retardation behavior of vinylester/glass composites. XRD and TEM results of MMT/vinylester showed exfoliation of MMT up to 4 wt % loading. Glass transition temperature (Tg) and microhardness of MMT/vinylester increased with increase in MMT loading.

Tensile strength, Interlaminar shear strength, Flexural strength, Impact strength and Fatigue life of vinylester/glass increased by the addition of 4 wt % MMT. TGA showed decrease in thermal degradation in 4 wt %/MMT/vinylester compared to 2wt%/MMT/vinylester. Horizontal and vertical burning rates of vinylester/glass decreased with the addition of MMT. LOI increased by 18 % and 25 % with the addition of 8 wt % MMT to vinylester and vinylester/glass respectively. SEM was used to study MMT, vinylester and glass fibre interfacial strengths and the fatigue damage mechanism.

Chapter-4

Effect of Twin Screw Extrusion on Mechanical, Thermal and Fire Retardation Behaviour of Nanoclay/Vinylester Reinforced with Glass/Carbon fibres

The dispersion of Montmorillonite nanoclay in vinylester using ultrasonication and co-rotating twin-screw extrusion for preparing nanoclay/vinylester gel coat. Two sets MMT/vinylester specimens, namely Type 1 and Type 2 were prepared for comparative studies. While Type 1 specimens were prepared using ultrasonication only Type 2 specimens were prepared using both ultrasonication and twin screw extrusion.
Dispersion of nanoclay in vinylester was studied using XRD and TEM. Type 2 specimens showed lower levels of nanoclay agglomeration and higher levels of exfoliation. DSC results showed that glass transition temperature in Type 2 specimens is better than that of Type 1 specimens. The TGA results showed that the residual weight in 4 wt % MMT/vinylester of Type 1 was 7.38 % and the corresponding value for Type 2 was 13.5 %, indicating lower thermal degradation in the latter.

By using the MMT/vinylester gel coat so prepared by the two different routes, MMT/vinylester/glass and MMT/vinylester/carbon specimens were fabricated and tested for mechanical and fire retardation behaviour. Type 2 based nanocomposite laminates showed greater values of ultimate tensile strength, flexural strength, interlaminar shear strength, impact strength, Horizontal burning rate, and Vertical burning rate than that of Type 1 based laminates. SEM of tensile fractured Type 2 based laminates showed no or less agglomeration of nanoclay than that of Type 1 based laminates.

Chapter-5

Combined Effect of Nanoclay and Fire Retardants on the Thermal Stability and Flammability of Vinylester based Nanocomposites

The effect of organomodified nanoclay and fire retardants on the thermal decomposition, glass transition temperature and fire retardation behaviour of nanoclay/vinylester composites was investigated. Two nanoclays Cloisite-Na and Cloisite-15A and two fire retardants Aluminium Tri Hydroxide (ATH) and Magnesium Hydroxide (MH) were selected for the research. The nanoclay/vinylester gel coat specimens were developed by ultrasonication followed by twin screw extrusion. XRD, TEM and AFM of nanoclay/vinylester specimens revealed that 4 wt % Cloisite-15A/vinylester exhibited exfoliation and distribution of nanoclay superior to that of Cloisite-Na/vinylester.
The synergistic effect of Cloisite-15A and 30 % ATH increased glass transition temperature by 18 % and reduced thermal degradation by 47 %, Vertical Burning Rate by 51 %, Horizontal Burning Rate by 68 %, and Limiting Oxygen Index by 52 % when compared with that of vinylester. Also, the corresponding increase in micro hardness was 85 % in the Cloisite-15A/vinylester specimens.

Chapter-6

The Effect of Nanoclay on the Moisture Absorption Behaviour of Vinylester Composites

The moisture diffusion behaviour of nanoclay/vinylester nanocomposites in alkaline solution aging was studied. Cloisite-Na with lower d-spacing and Cloisite-15A with higher d-spacing were selected for the research. Alkaline solution of 13.5 pH at room temperature and 50° C was selected the medium. The duration of exposure was 100 days. Diffusion parameters such as Diffusivity, solubility and permeability of the nanocomposite specimens were studied. C-15A/vinylester specimens showed superior resistance to moisture ingress due to superior exfoliation. Diffusivity and permeability reduced by 80 % and 45 % respectively by the addition of 5 wt % Cloisite-15 in vinylester composites.

Moisture diffusion behaviour of the nanocomposites was studied using Fick’s Law of Diffusion and Langmuir model. Fick’s Law was found to be inadequate in the non-linear regions of moisture uptake, in all the cases. However, Langmuir model showed deviation from the experimental data only in case of moisture uptake in alkaline solution at 50° C in the specimens with 4 wt % nanoclay loading. The percentage drops in microhardness of the specimens due to moisture absorption was studied. C-15 A / vinylester showed lower levels of microhardness drops than that of C-Na / vinylester. Increase in temperature of the medium resulted in greater moisture ingress and greater levels of microhardness degradation.
Chapter-7

Synthesis and Characterization of Organomodified Na-MMT Using Cation and Anion Surfactants

The improvement of Na-MMT platelets separation by organically modifying it with a cation and anion exchanges using Cetyl trimethyl ammonium bromide (CTAB) and Sodium dodecyl sulfate (SDS) respectively. Basal spacing, presence of functional groups, Zeta-potential with particle size analysis and thermal stability of the Organomodified Na-MMT (OMMT) were characterized using XRD, FTIR, Zeta-potential analyzer and TGA respectively.

The basal spacing of CTAB modified OMMT increased to 19.5 Å from 11.0 Å which corresponds to the basal spacing of Na-MMT. The SDS modified OMMT did not show any increase in the basal spacing. FTIR spectra of CTAB modified Na-MMT illustrated attachment of CTAB functional groups to Na-MMT, while the same was absent in case of SDS modified Na-MMT. Zeta-potential of Na-MMT shifted from -24.88 mV to 15.66 mV in case of CTAB modified Na-MMT and 12.49 mV for SDS modified Na-MMT, indicating greater surface potential of the modified nanoclay. The TGA showed greater weight loss for CTAB modified Na-MMT than that for Na-MMT indicating effective Na⁺ ion exchange with alkyl amines.