



## Investigation of water absorption characteristics of nano-gelcoat for marine application



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### ABSTRACT

This paper presents moisture diffusion behaviour of nano-gelcoat based on vinyl ester and Isophthalic polyester. Hydrolysis and influence of nanoclay on moisture diffusion of nano-gelcoats were studied using FTIR and gravimetric analysis. The gravimetric data, infrared spectroscopy and glass transition temperature indicated that addition of 1 wt.% nanoclay improved the moisture barrier, chemical retention and thermal properties of polymers. XRD confirmed dispersion of nanoclay in gelcoats. Hygrothermic behaviour of nano-gelcoat was studied at 30 °C and 50 °C in artificial seawater.

### 1. Introduction

Polymer Matrix Composites (PMCs) based on epoxy, vinyl ester and unsaturated polyester are widely used as coatings for boat hulls, cockpit soles, patrol boats, mine sweepers and submarine domes. These applications demand structural stability and performance of the composites in seawater [1]. Vinyl ester is superior to Isophthalic polyester in seawater medium due to the steric hindrance and faster curing of vinyl ester. Isophthalic polyester is superior to Orthophthalic polyester and also it bonds well with glass fibres [2]. Composites based on these polymers are widely used for marine infrastructure because of the cost effectiveness in fabrication, installation and repair [3].

PMCs degrade when exposed to moisture and alkali due to the etching and leaching actions. Rate of degradation of PMCs exposed to fluid environment is related to the rate of sorption of the fluid. Hydrothermal ageing of PMCs lead to both reversible and irreversible changes resulting in permanent degradation of mechanical properties. Degradation and durability of PMCs in seawater medium is widely reported [4–8]. As the salinity of seawater increases and temperature decreases, degradation due to water absorption decreases [9]. Water sorption leads to matrix plasticization [10], decrease in modulus and glass transition temperature [11], chain scission and hydrolysis [12] and weakening of fibre/matrix interphase [13].

Open literature suggests that nanoclay dispersed in PMCs can improve their moisture barrier properties by decreasing the diffusivity and lowering the rate of hydrolysis of the polymer. Clay platelets create a long tortuous path that slows the progress of penetrant molecules through the matrix resin. Polymer nanocomposites (PNCs) with small

amounts ( $\leq 5$  wt.%) of nanosized filler particles, which, if properly dispersed, have been found to cause significant reductions in both gas and moisture permeability. The degree of improvement in barrier properties of PNCs is directly related to degree of delamination of silicate layers in the polymer matrix. Addition of 5 wt.% organomodified Indian Bentonite to vinyl ester decreased its diffusivity and permeability in artificial seawater medium by 53.74% and 20% respectively [14]. Seawater absorption of vinyl ester based nanocomposites prepared using Cloisite-15A and Cloisite-Na indicated that organomodification and higher basal spacing of nanoclay improved their moisture barrier property and reduced hydrothermal degradation [15]. Vinyl ester based nanocomposites prepared using organomodified Montmorillonite (OMMT) and untreated nanoclay (UN) indicated that the specimens with 5 wt.% OMMT showed better resistance against both water diffusion and surface hydrolysis (immersed in NaOH solution) at 50 °C making them ideal choice for durability application [16].

Additionally, nanoclay increases the polymer stiffness, reduces compression index and plasticity index [17]. However, such improvements can be achieved only when nanoclay is well dispersed or exfoliated in the polymer. The exfoliated or intercalated structure is the most preferred morphology as it can provide excellent thermal, mechanical and barrier properties at lower clay loading. Shear mixing coupled with sonication has become the preferred technique for the preparation of PNCs among several other methods [18]. Nanoclay with its high specific surface area (750 m<sup>2</sup>/g) and aspect ratio (300–1000 Å) acts as nucleating agent leading to increase in the degree of crystallinity. Hence, nanoclay/polymer nanocomposites are less susceptible to hydrolysis with decrease in the rate of moisture diffusion [19,20].

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Marine structures are exposed to seawater for long durations. Extent of moisture absorption depends on the chemical composition, morphology and degree of curing of the composites. Raman spectroscopy is a means of examining chemical changes in the materials. It provides a straightforward means of non-destructively acquiring chemical data in a wide range of specimens. But, Fourier Transform Infrared (FTIR) Spectroscopy is more quantitative than Raman Spectroscopy [21]. FTIR provides a spectrum of characteristic bandwidths which helps to identify the chemical species and bond types present in the material. It offers potential to differentiate the rate of isothermal reactions dependent on the spectral changes of different functional groups [22,23].

While polyester based nano-coatings for marine applications [24–28] is widely reported, such studies on vinylester based nano-gelcoats are scarce. Though gravimetric data is widely used to study the effect of nanoclay on moisture diffusion behaviour of PNCs, such studies based on FTIR are scarce. Preparation of PNCs is usually carried out either by sonication, magnetic or mechanical stirring. But, a combination of sonication and twin screw extrusion process for preparing PNCs with Cloisite-15A is uncommon. Hence, the main objective of this research is to prepare PNCs with Cloisite-15A and study moisture diffusion behaviour (both Fickian and Langmuir) of vinylester and Isophthalic polyester and their nano-gelcoats. The study involves seawater exposure based on gravimetric data and FTIR spectroscopy. Hydrolysis reaction and the influence of nanoclay on the moisture absorption behaviour of polymer coatings is studied using FTIR spectroscopy. Specimens with (0, 1 and 2) wt.% Cloisite-15A were immersed in artificial seawater for a maximum duration of 1400 h at 30 °C and 50 °C. The specimens were characterized using Differential Scanning Calorimetry, XRD and viscosity measurements.

## 2. Experimental details

### 2.1. Materials and processes

The structure of Montmorillonite (MMT) nanoclay (Fig. 1) is a naturally occurring 2:1 phyllosilicate. The crystal lattice consists of

1 nm thin layers, with a central octahedral (O) sheet of alumina fused between two external silica tetrahedral (T) sheets (in such a way, that the oxygens from the octahedral sheet also belong to the silica tetrahedral). These layers organize themselves in a parallel fashion to form stacks with a regular van der Waals gap in between them, called interlayer or gallery. The  $\text{Na}^+$  or  $\text{K}^+$  ions residing in the interlayers can be replaced with organic cations such as alkyl ammonium ions or phosphonium ions by an ion-exchange reaction to render the hydrophilic layered silicate organophilic, so that polymer chains can be intercalated, thus causing the clay layer to be either swollen or exfoliated. This, results in the expansion of the clay galleries due to the larger molecules of polymer inserted between the layers. This reaction also changes the clay from hydrophilic to hydrophobic, making it more compatible with the organic matrix.

Specifications of materials used for specimen preparation are presented in Table 1. Nanoclay, C-15A (0, 1 and 2) wt.% was dispersed in two thermoset resins: vinylester (P222) and Isophthalic polyester (P444) using tip type ultrasonicator (Fig. 2, Vibronics Pvt. Ltd., Pune, India) of 37 kHz frequency for 20 min and further processed in co-rotating twin screw extruder (Steer Engineering Pvt. Ltd., Bangalore, India), shown in Fig. 3. Extrusion was carried out at 200 rpm screw speed and 5 °C. The extrudant C-15A/P222 and C-15A/P444 was mixed with curing additives 1.5 wt.% each of promoter, accelerator and catalyst at room temperature to activate the cross-linking process. C-15A/P222 and C-15A/P444 specimens cast molded to ( $100 \times 100 \times 1 \text{ mm}^3$ ) were cured at room temperature for 24 h followed by post curing at 90 °C for 3 h as per the resin manufacturers recommendation. The specimens (three of each type) were immersed in artificial seawater chamber (CM Environ Systems, Bangalore, India) for 60 days (1400 h) maintained at 30 °C and 50 °C for moisture diffusion studies. The hygrothermal effect on the physical, chemical and diffusion behaviour of the specimens was studied.

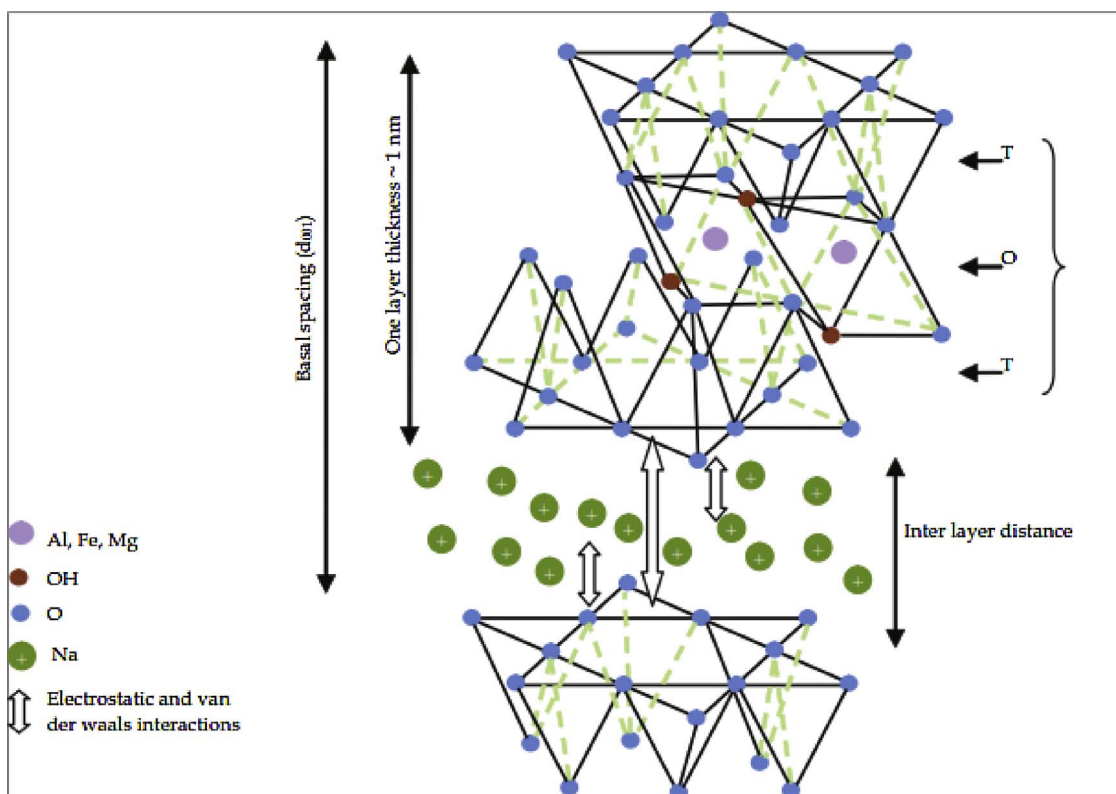


Fig. 1. Layered silicate (2:1) MMT clay structure [34].

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