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Durability of GFRP nanocomposites subjected to hygrothermal ageing

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ABSTRACT

This paper presents long term durability prediction of 0–5 wt.% nanoclay/vinylester/glass fibre nanocomposites based on their tensile strength retention in accelerated hygrothermal ageing using Arrhenius rate model. The specimens were exposed to 30 °C, 50 °C and 60 °C and 95% relative humidity for 75 days and tested for tensile strength retention as a function of duration of exposure. The predicted tensile strength retentions for one year of ageing of vinylester/glass at 30 °C, 50 °C and 60 °C using Arrhenius rate model were 59%, 48% and 43% respectively. The corresponding strength retentions predicted for 4 wt.% nanoclay/vinylester/glass were 81.1%, 77.9% and 76.4%. Strength retentions for ten years were predicted using the analytical model to assess their long-term performance.

1. Introduction

Hygrothermal ageing of Polymer Matrix Composites (PMCs) causes degradation of mechanical properties due to the combined effect of moisture and temperature. Plasticization and hydrolysis are the two main causes of degradation in hygrothermal ageing [1]. PMCs used in aerospace or marine structures are exposed to environment which involves high temperature and humidity and hence their durability and performance have become a primary concern for composite designers [2]. Given the strong correlation between the rate of deterioration and moisture uptake, it is crucial that the diffusion process in such materials be understood as a step towards prediction of long-term durability [3–6]. Moisture diffusion through polymer or Fibre Reinforced Plastic (FRP) is intrinsically related to its molecular structure, water–polymer interaction, and the degradation processes resulting thereof. The swelling due to moisture absorption leads to weakening of the fibre/polymer interface and hence affects the long-term durability of the composites [7–11].

Globally research is concentrated on developing PMCs with superior moisture barrier properties. Nanoclay as a filler material in polymers has shown great promise to improve such properties due to increased diffusion path based on tortuosity [12] which is dependent on the degree of exfoliation in polymers [13]. Improvement in mechanical, thermal and moisture barrier properties due to the incorporation of organomodified nanoclay (OMMT) in polymers is documented in recent studies [14–17]. Although nanofillers show such improvements, their addition in excess leads to agglomeration in polymeric resins resulting in diminution of mechanical properties. Several researchers [18–26] reported diminution in tensile strength, impact strength, fracture toughness as well as strain at break in FRP nanocomposites which can hamper their service life.

Monitoring real life of an in-service structure might take several years and it is impractical to wait such long periods of time to determine its service life and performance. Therefore, accelerated ageing tests are performed and durability of the structures is predicted by using analytical models. Chu et al. [27] performed durability and deterioration evaluation of glass/vinylester specimens immersed in deionized water and alkaline solution at temperatures ranging from 23 °C to 80 °C using Arrhenius rate model which complied well with the experimental results. Similar durability predictions of wet lay-up unidirectional carbon/epoxy laminates were made by Karbhari et al. [28]. Several authors also adopted such analytical models for predicting the durability of materials exposed to different media such as [29] for epoxy–polyurethane and aluminum composites in 3 wt.% NaCl solution, [30] for steel/CFRP double strap joints in alkaline medium, [31] for bond between GFRP and steel bars to concrete under acid environment and also [32] for hygrothermal ageing behaviour of carbon/bismaleimide FRP at elevated temperatures.

Review of literature [1–26] outline the experimental investigation of the effects of hygrothermal ageing on FRP and the influence of nanoclay addition on improved mechanical/moisture barrier

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properties. Refs. [27–32] outline the short-term and long-term durability predictions of FRP composites immersed in different media using analytical models in general and Arrhenius rate model in particular. However, such durability studies of nanoclay based FRP nanocomposites exposed to hygrothermal ageing is not yet attempted. Hence, the primary objective of this research was to study the effect of hygrothermic ageing on nanoclay/vinylester/glass nanocomposites exposed to 30 °C, 50 °C and 60 °C and 95% RH. Based on the experimental results of tensile strength degradation, glass transition temperature and void content, long term durability of the nanocomposites was predicted using Arrhenius rate model.

2. Experimental study

2.1. Materials and processes

Specifications of the materials for specimen preparation are presented in Table 1.

Nanoclay, C-15A (0–5) wt.% was dispersed in vinylester using tip type sonicator of 37 kHz frequency for 20 min and further processed in a co-rotating twin screw extruder (Fig. 1, Steer Engineering Pvt. Ltd., Bangalore, India). Extrusion was carried out at 200 rpm screw speed and 5 °C. The extrudant was mixed with curing agents 2 wt.% each of promoter, accelerator and catalyst at room temperature to activate the cross-linking process. C-15A/VE/ GF laminates with fibre:resin of 35:65 wt.% were fabricated to $(250 \times 250 \times 3)\ mm^3$ dimensions by wet hand lay-up and cured in a Hot press at room temperature for 24 h as per the curing schedule for Polyflex GR 200-65 based on manufacturer recommendations. The GFRP tensile test specimens were prepared as per ASTM D638 $(216 \times 19 \times 3)\ mm^3$ [33] and divided into two series: (1) unconditioned reference or "Control" (18 specimens); and (2) aged samples in hygrothermal chamber at 30 °C, 50 °C and 60 °C and 95% RH (54 specimens).

2.2. X-ray Diffraction (XRD), Differential Scanning Calorimetry (DSC) and density characterization

Dispersion of nanoclay in vinylester was evaluated using X-ray Diffractometer (Shimadzu XRD-7000, Japan) in the low angle of 2θ at room temperature. The X-ray beam was CuKα radiation (λ = 1.540598 Å) using 45 kV voltage generator and 40 mA current, scanning speed of $2^\circ\ min^{-1}$ and 0.15 mm receiving slit width. The d-spacing between the clay layers and degree of dispersion of nano-platelets in the polymer was determined using Bragg's law ($d = \lambda/2\sin\theta_{max}$).

Glass transition temperature (T_g) of nanocomposites as per ASTM E1356 was obtained using Differential Scanning Calorimetry (DSC 823^e METTLER TOLEDO, Switzerland). Measurements were made at a constant heat rate of 10 °C/min. from 30 °C to 200 °C in Nitrogen atmosphere with a purge rate of 20 ml/min. Each sample was scanned twice and T_g was determined from the second scan or run.

Density (ρ_{ce}) of C-15A/VE/GF was determined as per ASTM D792 using Archimedes principle for the specimens of size $5 \times 5 \times 3\ mm^3$. Void content was determined by burn-off test (700 °C for 3 h) using an ageing bath furnace (Dexter Batteries, Bangalore) with specimens of size $20 \times 5 \times 3\ mm^3$ as per ASTM D2584-94. The theoretical density (ρ_{ct}) of FRP nanocomposites was computed as per [34] using Eq. (1):

$$\rho_{ct} = \frac{1}{(W_f/\rho_f) + (W_m/\rho_m) + (W_p/\rho_p)} \quad (1)$$

where ρ and W represent the density and weight fraction of the constituents respectively. The suffix m, f and ct stand for matrix, fibre and composite respectively. The suffix 'p' indicates the nanoclay filler. However, actual density (ρ_{ce}) of the composite was determined experimentally by Archimedes principle. Percentage volume fraction of voids (V_v) in the composite was computed using Eq. (2):

$$V_v = \left(\frac{\rho_{ct} - \rho_{ce}}{\rho_{ct}}\right) \times 100 \quad (2)$$

2.3. Hygrothermal ageing

An Environmental chamber (CM Environ systems, Bangalore) was used for hygrothermal ageing of C-15A/VE/GF specimens prepared as per ASTM D638 at 30 °C, 50 °C and 60 °C and 95% RH for 75 days.

2.4. Tensile tests and fractography

Tensile test was performed on the specimens using a ten ton capacity UTM (Kalpak Instruments, Pune, India) at a cross head speed of 1 mm/min and gauge length of 105 mm as per ASTM D638. Three identical specimens were tested for each condition and mean strength was considered. Tensile fractured specimens were studied using Scanning-electron-microscope (SEM), Hitachi

Table 2
Relationship between UTS retention (%) and ageing duration generated from Fig. 3.

Temperature (°C)	Linear relationship	R^2
30	$y(t) = -4.421 * \ln(t) + 104.13$	0.95
50	$y(t) = -4.655 * \ln(t) + 104.16$	0.93
60	$y(t) = -5.590 * \ln(t) + 104.97$	0.97

Table 1
Specifications of the materials used in the present research.

Materials	Specifications
E-Glass fibre (GF), 360 gsm (Plain 2D woven, [0°/90°]), Suntech Fibres and Polymer, Bangalore, India	Density: 2.5 g/cc UTS: 3400–3500 MPa Young's modulus:70–75 GPa
Cloisite-15A (C-15A) nanoclay, Southern Clay Products, USA	Bulk density: 1.66 g/cc Platelet size: 150–250 nm D-spacing: 31.5 Å
Vinylester resin (VE), (Polyflex GR 200-65 superior), Naptha Resins & Chemicals (p), Bangalore, India	Density: 1.05 g/cc, UTS: 60 MPa, flexural strength: 130 MPa, heat distortion temperature: 125 °C
Di-Methyl acetamide (DMA) as promoter	Density: 0.94 g/cm^3
Cobalt napthalate as accelerator	Density: 0.98 g/cm^3
Methyl Ethyl Ketone peroxide (MEKP) as catalyst	Density: 1.17 g/cm^3