Hygrothermic Behaviour of Carbon/Vinylester, Glass/Vinylester, Carbon/Epoxy and Glass/Epoxy Composites

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ABSTRACT

Moisture absorption behaviour of polymer matrix composites (PMCs) in humid and tropical environments is a complex phenomenon. Moisture diffusion weakens the fibre/matrix interface which leads to deterioration of mechanical properties. Hygrothermic ageing of carbon/vinylester, glass/vinylester, carbon/epoxy and glass/epoxy composites were studied for their suitability in marine applications. The specimens were exposed to 50°C, 60°C and 70°C temperatures and humidity of 95% RH for a maximum duration of 170 days. The specimens were periodically weighed for moisture absorption and tested for mechanical properties (ultimate tensile strength, flexural strength and interlaminar shear strength) degradations. The maximum moisture absorption was observed for epoxy/glass composite and the minimum for vinylester/carbon composite. Diffusion mechanism was studied on the basis of the Fick’s law of diffusion. It was found that diffusion coefficient (D) is at highest for epoxy/glass composite and at the lowest for vinylester/carbon composite. Diffusion coefficient increased with increase in temperature for all the specimens. Comparing vinylester/carbon and epoxy/carbon samples data, although both lowered in properties, the former showed still better results in flexural strength (FS), ultimate tensile strength (UTS) and interlaminar shear strength (ILSS) values than the latter. As a whole, Vinylester/glass has behaved superior to epoxy/glass with respect to changes in their mechanical properties. The experimental observations are confirmed by SEM. Vinylester based specimens showed greater chemical stability than the epoxy based specimens. Even after 170 days of hygrothermic exposure, vinylester/carbon showed lower degree of fibre pulls out compared to other three specimens tested.

INTRODUCTION

High strength-to-weight ratio, corrosion resistance, good chemical stability, easy processing, and outstanding insulating properties enable polymer matrix composites (PMCs) behave as advanced materials for marine, aerospace, automotive, and other high end applications. Their drawback is the moisture absorption which is more pronounced in marine environment. Hence, research works have been focused on identifying the matrix, reinforcement materials and their characterization for hygrothermic ageing. In humid temperature the water absorption rate increases with increase in temperature. In hot humid exposure, moisture diffuses through the fibre, matrix and fibre-matrix interface. The absorbed moisture
has plasticization effect on the matrix phase and reduces its glass transition temperature [1-3]. The moisture absorption leads to impairment of mechanical properties of the composites by damaging the fibre/matrix interfacial bond [4-6]. The synergistic effect between matrix and reinforcement will decide the physical and the mechanical performance of the composite. The fibre/matrix interface region is also important in determining the properties of the composite.

Moisture diffusion in polymers is both Fickian and non-Fickian in nature. The viscoelastic nature of polymer and resulting cracks show the non-Fickian type of diffusion. The parameters such as volume fraction of the fibre, nature of resin system, temperature, additives, humidity, orientations of the fibre, fibre surface coating, sizing and void volume affect the water diffusion in polymer matrix composites. The moisture absorption of composites is mainly related to the matrix resin, whereas the permeable fibres absorb very little moisture. Carbon is more resistant towards moisture compared to glass. Vinylester has superior chemical stability especially in moisture and hence it is the best choice for marine applications [7-9]. The factors inducing the water penetrations to the composites are: (1) swelling of the matrix phase and residual stresses at and near the interfaces, (2) weakening or breaking of adhesion bond between matrix and reinforcement through external substrate, (3) formation of micro-cracks due to environmental stress free volume, (4) osmotic phenomenon, and (5) polymer-solvent interactions as the main mechanisms governing the water diffusion in the polymer composite system [10-12]. Although there are several works which have focused on the hygrothermic behaviour of polymer matrix composites, a comprehensive study and comparative results on the hygrothermic behaviour of the material systems and mechanical properties is not reported.

Hygrothermic behaviour in hot and humid conditions especially in long durations of exposure is vital for the selection of composites in marine applications. The primary goal of this research was to determine the effects of temperature and moisture on the flexural strength (FS), ultimate tensile strength (UTS) and interlaminar shear strength (ILSS) of the polymer matrix composites using glass or carbon fibres as reinforcements and epoxy or vinylester as resin systems. The secondary goal was to correlate the moisture absorption with the failure mode of the laminate demonstrating the severe effect of moisture on the matrix/fibre interfacial strength using scanning electron microscopy. The specimens were exposed to hygrothermic conditions of 50°C, 60°C and 70°C and 95% RH in a maximum duration of 170 days.

**EXPERIMENTAL**

**Materials and Processing**

The composites used in the study were virtually identical in every aspect (e.g., fabrication technique, type of fibre, fibre volume content). The employed glass fibre (vetrotex, Saint Gobain) and carbon fibre (CS inter glass, Germany) were plain-woven fabric type. The glass fibre was coated with an emulsion based sizing agent and the PAN based carbon fibre sized with epoxy to promote good chemical adhesion with the resin matrix. The two-resins used in this study were epoxy (Ciba-Geigy, Araldite-LY 556 and Amine Hardener HY 951 - The resin hardener ratio- 100:10) and vinylester (Ecmalon 9911, Ecmas Hyderabad, with 2% cobalt accelerator, catalyst 50% methyl ethyl ketone peroxide (MEKP) in 10% DMA solution, ratio of resin/accelerator/catalyst/promoter: 100/2/2/2). The specimens were fabricated using wet hand lay-up process. Woven mat 2-D fibres [0/90] were used in the specimens. 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 two weeks, as most of the materials for marine applications are naturally cured, before exposing to hygrothermic conditions. The edges of the panels were sealed using the matrix resin.

**Hygrothermic Tests**

The cut and edge sealed specimens (vinylester/carbon, vinylester/glass, epoxy/carbon and epoxy/glass) of dimensions 127×12.5×3 mm (flexural test; ASTM D 790), 24×6.35×3 mm (interlaminar shear strength test: ASTM D2344) and 216×19×3 mm (tensile test: ASTM D 638) were kept in the instrumented environmental chamber (M/s CM Envoron systems,
Bangalore) at 95% RH and 50°C, 60°C, and 70°C, respectively. The tests were conducted in a maximum duration of 170 days. The specifications of the chamber are: temperature: 20°C to 200°C, humidity: 0-95% RH with provision for salt spray.

The specimens were taken at regular intervals, wiped dry to remove the surface moisture and then weighed by an electronic balance to monitor the mass change behaviour or moisture diffusion. The percentage mass change (M) of the composite panel was computed by the expression, according to Manfredi et al. [13]:

\[ M = \left( \frac{m_s - m_d}{m_d} \right) \times 100 \]  

where, \( m_s \) is the mass of the panel after a given immersion time and \( m_d \) is the original panel mass. The hygrothermic exposure is very critical for marine grade polymer composites because it is an irreversible process. The moisture which is absorbed by the composite causes degradation in the composites in a manner similar to that of accelerated ageing.

Degradation Studies
The flexural strengths of the specimens were determined at different hygrothermic exposure durations by the three-point bending test with a span length of 90 mm, using an instrumented 10 ton capacity UTM (M/s Kalpak, Pune). The flexural strengths of the composites were determined using the formula according to Paiva et al. [14]:

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

where,
- \( P \) : peak load (N),
- \( L \) : support span length (mm),
- \( b \) : width of specimen (mm),
- \( d \) : thickness of the specimen (mm).

The specimens were loaded in tension at a crosshead speed of 1 mm/min to determine their tensile behaviour. Three-point bend test was carried out to determine the ILSS of the specimens as per ASTM D2344. The testing was performed on short beams of 24×6.35×3 mm at a crosshead speed of 1 mm/min maintaining a sample size of three for each experiment and the average values have been reported. The interlaminar shear strength (ILSS) was determined using the equation according to Ray [15]:

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

where,
- \( ILSS \) : interlaminar shear strength (MPa),
- \( P \) : peak load (N),
- \( b \) : width (mm),
- \( t \) : the thickness of the specimen (mm).

Scanning Electron Microscopy
Scanning electron microscope (Jeol, JSM 840A, Japan) was employed to characterize the tensile fractured specimens before and after hygrothermic exposure. The effect of moisture diffusion on the interface region and the matrix plasticization due to hygrothermic conditioning in short and long durations and the modes of failure as a function of temperature and duration of exposure were studied using SEM.

RESULTS AND DISCUSSION

Hygrothermic Behaviour
Moisture absorption as a function of duration of exposure is presented in Figure 1. The maximum moisture absorption (M∞) at three temperatures is shown in Table 1. Epoxy/glass absorbed the highest amount of moisture, i.e., 0.95 wt% at 70°C and 95% RH and 0.87 wt% at 50°C and 95% RH. The least was in the case of vinylester/carbon as 0.55 wt% at 70°C and 95% RH and 0.5 wt% at 50°C and 95% RH.

The saturation in moisture uptake was observed by the asymptotic nature of the curves. Vinylester/carbon stabilized at much lower values of moisture uptake at all the three temperatures. Since the saturation levels of moisture uptake dictates the property of degradation in the materials employed for underwater applications, vinylester based composites proved superior to epoxy based specimens.

Several authors have studied the influence of fibre orientation on the moisture diffusion phenomenon in polymer matrix composites. Boukhoulda et al. [18]
have reported that specimens with 90° oriented fibres absorbed lower levels of moisture and with 0° oriented fibres distinctly absorbed higher levels. Hence, higher angles of orientation are preferred to lower ones for lowering the moisture absorption levels. The specimens used in the present study comprised of 2D woven mat, which have 0/90 orientations for bidirectional strength as these novel structures experience buckling due to hydrostatic pressure and are analyzed as plane strain problems. Thus, moisture absorption levels of the composites are expected to be at moderate levels.

**Diffusion Studies**
The Fick's second law of diffusion can be used to study the diffusion mechanism in polymer

![Table 1. Maximum moisture absorption and diffusion coefficient of the composites at 50°C, 60°C and 70°C.](image)

![Figure 1. Percentage of moisture absorption due to hygrothermic exposure of 50°C, 60°C, 70°C and 95% RH.](image)
composites. The diffusion coefficient $D$ can be computed using the formula as per Gopalan et al. [16]:

$$D = \pi \left( \frac{h}{4M_\infty} \right)^2 \left( \frac{M_2 - M_1}{\sqrt{(t_2 - t_1)}} \right)^2 \tag{4}$$

where, $M_1$ and $M_2$ are the moisture contents at time $t_1$ and $t_2$, respectively, $h$ is the thickness of the specimen in mm and $M_\infty$ is the maximum moisture uptake. The fibres absorb less moisture than the polymeric matrix. The fibres may change the diffusion path of water molecules in an anisotropic fashion by hindering them from straight diffusion. $D$ parameter varies with temperature according to the Arrhenius equation as per Karbhari et al. [17]:

$$D = D_0 \exp \left( -\frac{E_d}{RT} \right) \tag{5}$$

where, $D_0$ is the coefficient of diffusion at temperature $T_0$, $E_d$ is the activation energy of diffusion, and $R$ is gas constant (8.3143 J/mol.K). $E_d$ is the energy barrier the composite has to overcome against diffusion of moisture. Water molecules have higher probability to reach the activation energy necessary to initiate diffusion. $E_d$ values can be obtained by plotting $\ln D$ versus $1/T$ as shown in Figure 2 for different specimens. They are found to be

![Figure 2. Plots of $\ln D$ vs. $1/T$ for: (a) vinylester/carbon, (b) vinylester/glass, (c) epoxy/carbon and (d) epoxy/glass composite systems.](image-url)
Figure 3. Flexural strength variation due to hygrothermic exposure at 50°C, 60°C, 70°C and 95% RH for four composite samples.
5 kJ/mol.K for epoxy/glass, 6.1 kJ/mol.K for vinylester/glass, 7.24 kJ/mol.K for epoxy/carbon and 11 kJ/mol.K for vinylester/carbon. The values of $E_d$ showed that vinylester/carbon possessed highest activation energy and hence, the water permeation was at its minimum in this case. The experimental value of the maximum moisture absorbed was the least in this system at all the experimental conditions.

**Flexural Strength, Ultimate Tensile Strength and Interlaminar Shear Strength Analyses**

All the four composites samples showed decrease in flexural strength, ultimate tensile strength and interlaminar shear strength due to hygrothermic conditioning (Figures 3-5). The percentage of degradations of each mechanical properties at 50°C, 60°C and 70°C after 25 and 170 days are shown in Tables 2-4, respectively. Epoxy/carbon composite

**Figure 4.** Ultimate tensile strength variation due to hygrothermic exposure at 50°C, 60°C, 70°C and 95% RH for four composite samples.
showed greater degradation than vinylester/carbon in ultimate tensile strength, flexural strength and ultimate tensile strength. Similar behaviour was observed in epoxy/glass and vinylester/glass composites, as well. The degradation increased with increase in temperature.

Water penetrates into the interface through the microvoids and microcracks and the trapped water damages the interface region. In longer duration of exposure, water diffusion would be slow because of the water saturation in the matrix phase. The property degradation in the post saturation period is
considerably less than that of the pre-saturation period. By comparison, vinylester/carbon composites saturate much faster than epoxy/carbon ones and it is similarly the same for vinylester/glass and epoxy/glass composites when compared to each other. The degree of plasticization in the matrix phase is more critical for mechanical properties. Due to its superior chemical stability [7] vinylester shows lower degradation in the matrix phase than epoxy. Also, the superior mechanical properties of carbon fibres compared to glass fibres give good mechanical stability to the former systems even after the hygrothermic conditioning.

Hygrothermic effects and interlaminar shear strength degradations have been reported by Ray [15], as well. It is reported that carbon/epoxy samples absorbed 1.2 wt% moisture at 70°C and 95% RH resulting in interlaminar shear strength drop of 30 MPa, after 1200 h. For the same material moisture absorption was 0.9 wt% at 60°C and 95 % RH and interlaminar shear strength drop was 20 MPa after the same duration of exposure. Glass/epoxy composite samples after 260 h of exposure at 70°C and 95% RH have absorbed 2.5 wt% moisture and shown interlaminar shear strength drop of 10 MPa. The same material showed a drop of 5 MPa at 50°C and 95% RH after the same duration of exposure. All the four types of specimens showed reduction in Young's modulus with respect to increased duration and temperature of exposure. The drop in $E_d$ after 170

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<th>Flexural strength</th>
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<td>25 days</td>
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<td>Epoxy/glass</td>
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Table 2. Percentage drop in mechanical properties (MPa) at 50°C.

Table 3. Percentage drop in mechanical properties (MPa) at 60°C.

Table 4. Percentage drop in mechanical properties (MPa) at 70°C.
Figure 6. SEM micrographs of the tensile fractured epoxy/glass specimens at: (a) 50°C - 25 days, (b) 50°C - 170 days, (c) 60°C - 25 days, (d) 60°C - 170 days, (e) 70°C - 25 days, and (f) 70°C - 170 days of exposure.
Figure 7. SEM micrographs of the tensile fractured vinylester/glass specimens at: (a) 50°C - 25 days, (b) 50°C - 170 days, (c) 60°C - 25 days, (d) 60°C - 170 days, (e) 70°C - 25 days, and (f) 70°C - 170 days of exposure.
Figure 8. SEM micrographs of the tensile fractured epoxy/carbon specimens at: (a) 50°C - 25 days, (b) 50°C - 170 days, (c) 60°C - 25 days, (d) 60°C - 170 days, (e) 70°C - 25 days, and (f) 70°C - 170 days of exposure.
Figure 9. SEM micrographs of the tensile fractured vinylester/carbon specimens at: (a) 50°C - 25 days, (b) 50°C - 170 days, (c) 60°C - 25 days, (d) 60°C - 170 days, (e) 70°C - 25 days, and (f) 70°C - 170 days of exposure.
days at 70°C and 95% RH was 53.4% for epoxy/glass specimens, and under the same conditions, the drop was 37.2% for vinylester/carbon composite samples. These drops were correspondingly lower at 50°C and 60°C for the same specimens. The drop in $E_d$ at 50°C was 47.9% for epoxy/glass composite samples and 31.6% for vinylester/carbon ones.

SEM
SEM analysis provides evidence of the resin/fibre binding in fractured specimens. The degradation in mechanical properties is due to the degradation in fibre/matrix interface bonding. The voids present in the matrix are the main reasons for moisture diffusion. The microcracks formed during the composite preparation or by the service condition can store the trapped water. The voids and microcracks in the specimens can be traced using SEM images. Figures 6-9 show the micrographs of the tensile fractured specimens.

Fibre breaking was the dominant failure mode in the specimens exposed to 50°C, 60°C and 70°C for a period of 25 days and under these conditions only the specimens exposed to 70°C showed slight matrix degradation. Fibre pull-out was the main mode of failure in the specimens after 170 days of exposure at all the three temperatures. The effect of temperature is seen in terms of higher levels of matrix degradation and hence more fibre pull-out as observed in 70°C conditioned specimens.

At all these three temperatures, epoxy/glass showed greater degree of matrix degradation compared to other types of specimens. Even after 170 days of exposure, epoxy/glass showed greater levels of matrix degradation than vinylester/glass and epoxy/carbon composites. Vinylester/carbon samples prove that vinylester is superior to epoxy and carbon fibres to glass composites. Indeed, matrix degradation increased with temperature and exposure time in all the composite specimens.

CONCLUSION
Hygrothermic behaviour of polymer matrix composites (epoxy/glass, epoxy/carbon, vinylester/glass and vinylester/carbon) was studied by exposure at 50°C, 60°C and 70°C and 95% RH in an environmental testing chamber for a maximum duration of 170 days. The maximum moisture uptake and diminished mechanical properties were studied and traced. Diffusion coefficient was evaluated for all the tested specimens. The maximum moisture uptake was the least for vinylester/carbon samples, i.e., 0.42, 0.44 and 0.45 wt% at 50°C, 60°C and 70°C. The same parameter was the highest for epoxy/glass composite samples, i.e., 0.87, 0.90, 0.95 wt% at the same temperatures. It was observed that moisture absorption increased with increase in temperature in all the cases. The composites degradation in the periods subsequent to saturation was much less than that of pre-saturation period. The better performance of vinylester based samples was attributed to its chemical stability and the gel coat effect. Vinylester/carbon samples were found superior to epoxy/carbon ones because of the lower degradation levels exhibited by the former in ultimate tensile strength, flexural strength and interlaminar shear strength in all the test conditions.

Failure modes were studied by SEM. Fibre breaking was the dominant failure mode in shorter durations and only the specimens exposed to 70°C showed slight matrix degradation. Fibre pull out was the main mode of failure in the specimens after 170 days of exposure at all the three temperatures. Temperature increased the matrix degradation and hence more fibre pull-out was observed in 70°C conditioned specimens. The worst affected parameter in all the experimental conditions was ultimate tensile strength, followed by flexural strength and interlaminar shear strength, which was observed commonly in all the four material composite systems.

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