7.1 INTRODUCTION

The vulnerability of steel to environmental degradation has led many transportation agencies to investigate advanced polymer matrix composites (PMCs) as alternative materials for infrastructure applications. The polymers are quite popular due their non-corrosive and non-metallic properties. In addition, PMCs can have ultimate strength and stiffness similar to those of metals while still being at less weight. This system offers great promise in repair and retrofit of existing structures. Though these materials do not rust in the conventional sense, the mechanical properties of composites can be degraded over time by various environmental factors including moisture, chemicals, light, ultraviolet radiation, wind conditions, freezing and elevated temperatures [35,62,108].

Environmental testing of composite materials is an essential part of the certification process for any application, because the environmental factors can combine to degrade the composite material over the long term altering the durability of the material. Hence, it is vital to assess the degradation which may be occurring in typical service [176]. This degradation can be quite severe in some cases. The greatest effect on composite materials is due to moisture. The epoxy matrix of most composite materials can pick up moisture at faster rate and resulting in the degradation of mechanical properties. The effects of moisture can be reasonably well simulated in the laboratory using environmental conditioning chambers in a short period of time, the effects of long-term exposure cannot be predicted reliably [8,34,55,176].

Glass fibers are the reinforcement of choice for many commercial composites. The strength degradation of the glass fiber under environmental exposure depends on the presence of moisture, stress, time, compositions of the glass, and the presence of sub-or post-critical flaws. The moisture causes change in the polymer through diffusion of the water, engendering a distribution of swelling stresses, hydrolysis and physical aging. While swelling and plasticizing are reversible, an excess amount of moisture absorption may lead to micro-cracking, which is an irreversible process. Finally, exposure to water decreases the effective interfacial strength. The mechanism of degradation of a glass
fabric reinforced composites is more complex, since each of the above mentioned components has the capability of being the weak-link in the structure at different stages. In addition, the rate of degradation of the mechanical properties of a composite laminate could be higher than that of the individual components due to the synergy among the different degradation mechanisms. This implies that the effect of environment is critically dependent upon the specific material system [121].

So therefore it becomes necessary to quantify the effects of moisture by exposing the composite laminates to various adverse environments and to know the rate of degradation of polymer composites with the mechanism driving the degradation. As the expected service life of the FRP reinforcement is several decades it is impractical to expose laminates to real working conditions. So to predict the strength retention properties of the composite laminates under working conditions, the laminates are subjected to aggressive accelerated ageing conditions for shorter time periods. Therefore in this chapter with an aim to study the strength degradation of composite laminates when exposed to various adverse environments that cause the degradation.

7.2 OBJECTIVES

- To examine the moisture absorption properties of the GSFRP laminates.
- To examine the strength degradation of composite laminates due to various environments like moisture, acidic, alkalinity, organic fuel and freezing environments.
- To investigate the residual strength of GSFRP laminates as a function of exposure to adverse environment.
- To determine the diffusivity as a function of fiber percentage.
- To find the changes in the performance of the material against impact loads as a function of time when exposed to degrading environments.
- To predict the service life of GSFRP laminates under exposed conditions.
- To use the Fickian Model for moisture absorption and to compare with the experimental results.
7.3 ENVIRONMENTAL FACTORS AFFECTING COMPOSITES
The use of any material in structural applications needs a detailed study of the effect of environmental conditions on its properties. The environmental factors that cause the degradation of composite structures are temperature, moisture, alkalinity, freeze-thaw, ultraviolet rays and others. The environmental factors for GFRP are 0.7-0.8 as per their exposure conditions. In this study, the investigations were conducted only for the conditions of moisture, acidic, alkalinity (saline), freezing and organic fuels.

7.3.1 Moisture Absorption
The objective of the moisture absorption study was to determine the weight gain of the GSFPR laminates as a function of time. FRP reinforcements are not recommended for use in structures that are exposed to high temperature, as the modulus is reduced after being exposed to temperature in excess of the glass transition temperature. Similarly, on exposure to moisture their will be drastic reduction in mechanical strengths. The strength reduction with respect to time indicates that there are two mechanisms driving the degradation. The mechanisms may be fiber degradation and resin or fiber interface degradation [175]. Specimens used for the weight gain measurements were initially subjected to dimension and weight measurement and then immersed in the solution. The moisture uptake was recorded at the specified time by taking out the specimens from the tank, then surface dried and weighed.

7.4 EXPERIMENTATION
7.4.1 Sample Preparation
The matrix material was medium viscosity epoxy resin with a room temperature curing hardener. The glass and textile satin fabrics as reinforcements were used. The details of material selection, their properties and the conditions under which specimen were fabricated are discussed in chapter- 4. The bidirectional glass and satin fabric laminates used for the investigation has the same stacking sequence, number of plies and orientation (0/90°) for all the laminates. The volume fraction of epoxy matrix for all the laminates was 40%, while the reinforcement fabric accounts for 60% of the volume. Three different combinations of glass and satin fabric were selected for composite preparation by varying the volume fraction of glass in steps of 15%.
7.4.2 Environmental Selection

Considering the adverse environments which degrade the material strength, the following five types of environments have been selected for the present investigation:

**Water:** Pure distilled water has been used.

**Saline water:** 200 mg of NaCl has been mixed in 1000ml of distilled water to prepare the saline water.

**Acidic water:** Sulphuric acid of strength N/100 has been taken as acidic water. Here, distilled water has been used to prepare N/100 strength from concentrated H₂SO₄.

**Organic fuel:** Commercially available kerosene oil has been used.

**Freezing temperature:** Ice crystals made of distilled water were used to obtain freezing temperature.

7.4.3 Conditioning Tanks

Glass tanks with approximately ten liters capacity were selected and placed on thick plywood. The tanks were maintained at room temperature and to avoid the variations in temperature from the bottom, plywood is used and it acts as heat insulator. Before putting the specimens in the tank, each tank was filled with the prepared solution and checked to ensure it against any leakages. A glass partitions in the tank was prepared in such a way that laminates to be tested on the prescribed day could be removed as one layer. After putting the laminates in the partition of the tank, the top of each tank was covered with the lid of the tank, so as to minimize the moisture loss from the top. The pH of the solution and water level in each of the tanks was checked periodically.

7.4.4 Environmental Exposure

The moisture uptake was measured through mass gain of specimens weighed periodically by an electronic balance with ±0.001g precision. The initial mass of the specimens were recorded and mass gain in percent of the initial mass or increase in moisture content versus time were plotted to observe the moisture uptake process. Specimens in a group are exposed to selected environments for different duration, i.e. 50, 100, 150, 200 and 250 hrs. The rate of environmental effect has been calculated for each exposed specimen in the form of percentage of weight gain and strength loss.
7.4.5 Experimental Setup
Among the different testing devices, the instrumented Charpy test is very attractive since it is one of the most commonly used testing procedures. ASTM D256 standards define test conditions and a series of medium velocity impact tests were performed on the composite specimen using single-blow pendulum type impact setup. The specimens after exposing to respective environments were mounted in such a way that the pendulum strikes at the opposite end of the notch.

7.5 RESULTS AND DISCUSSION
The composite laminates were immersed in different liquids to suit the selected environment and after exposing for the desired duration the laminates were analyzed for moisture absorption, swelling of laminates, their performance and strength retention. The discussion is categorized into the following sections.

7.5.1 Moisture Absorption Characteristics
The moisture content of materials immersed in liquids are sensitive to both time and temperature [31], therefore all environmental liquids are maintained at room temperature for the analysis. The results of the moisture absorption tests for the laminates with three percentages of glass content and immersed at various durations are shown in Fig. 7.1, each point in these figures is the average of three data points. The results show that the laminates immersed in water based solutions have absorbed more moisture than others.

A weight gain of 2.27% has been recorded as the maximum gain in case of laminates immersed in distilled water. The penetration of water molecules in the interface region through the voids of the composite may be the reason of weight gain. The osmotic pressure of the water molecule might have facilitated the entrance of water molecules into matrix phase, and may have expanded its boundary in due course resulting into maximum absorption. Whereas the minimum weight gain with 0.5% was observed in case of laminates exposed to organic fuel (kerosene), this may be attributed to the absorption of aromatic constituents of liquid fuel that might have caused marginal weight gain.
Fig. 7.1 Weight Change as a function of Immersion Time of Laminate in various Environments.

When the laminates are exposed to saline water, 1.54% weight gain has been recorded after 250 hrs duration of exposure. The higher density of the liquid may be held
responsible for lower penetration of the saline water as compared to pure water. At the
same time laminates on exposure to acidic water, 2.11% weight gain has been recorded
after 250-hrs duration of exposure. A marginal weight gain with 0.52% was also
observed in freezing environment, as expected the moisture uptake is quite less and is
mainly due to the solid ice crystals used in the study. The authors at references [31,43]
have also reported the similar trends when laminates are exposed to acidic, saline and
freezing environments.

The investigation has been carried out in three groups of volume fractions of
glass, 15%, 30% and 45%. At the higher percentage of glass content, a notable reduction
in the moisture uptake was observed. The presence of more satin content has shown
greater affinity for moisture uptake and this is might be because the satin fabric
comprises of some percentage of cotton and hence resulting into higher absorption
capacity. In almost all the adverse environments, the rate of moisture absorption was
very high for first 100 hrs, thereafter rate of absorption observed to be bit less, and it is
found to be true for all the percentages of glass content. Therefore a well balance in glass
transition temperature for the laminates is maintained upto 100 hrs of exposure, there
onwards the glass transition temperature drastically reduces because more the moisture
absorption smaller will be the glass transition temperature [111].

7.5.2 Effect of Moisture on Physical Properties
The laminates after analyzing for moisture absorption were used for the analysis of the
physical properties, the dimensional variations due to moisture (swelling of laminates)
and the changes in density were selected for the study. The swelling of the laminates
were investigated by measuring the volume change percentage with respect to the
duration exposed in various environments that is as shown in Fig. 7.2.

The laminates which were immersed in distilled water are the severely affected
category with approximately 25% of swelling, similar behaviour was recorded in case of
saline and acidic solution also. Swelling in case of saline environment is high in
comparison to acidic, may be due to the presence of sodium content in the solution.
Fig. 7.2 Change in volume as a function of immersion time in various environments.
The laminates exposed to the fuel kerosene have also indicated significant increase in volume by swelling approximately 20% of its size. However only a marginal swelling was reported in case of laminates exposed to freezing environments, this difference in the swelling behaviour may be due to that all other environments except freezing are in the liquid form. The test coupons are immersed in liquids to obtain the desired environment, whereas in case of freezing environment the freezing temperature is obtained by using ice crystals and these are in the solid form, hence liquid penetration is marginal and the change in volume is marginal.

Comparing the laminates with respect to the presence of the glass content, it was observed that the severity of swelling is very high as percentage of glass increases, it is found to be true for all the environments except the freezing environment. This is might be due to the fact that the glass fibers are more sensitive to moisture absorption and in case of freezing environments only a small quantity of moisture was absorbed and hence quite a less swelling. It was also seen that the rate of swelling is quite high for the first 100hrs and thereon swelling rate reduces to a great extent in all the environments.

The density variation of the laminates was also recorded and found that the density as a function of the duration of exposure, the environment and also the percentage of glass content in the laminates. For the analysis purpose the results are shown in Fig. 7.3, significant variations in density were recorded in case of laminate with 45% glass content. The distilled water has affected the laminates density severely, whereas less variations were observed in case of freezing environments. Since the glass is very sensitive to moisture, the laminates with higher glass percentages have indicated greater variation in density.
Fig. 7.3 Change in density as a function of immersion time in various environments.
7.5.3 Impact Strength Degradation

The penetration of water molecules in the interface region through the voids of the composite may be the reason of weight gain. The osmotic pressure of the water molecule might have facilitated the entrance of water molecules into matrix phase, and may have expanded its boundary in due course. As a result, the bond strength of the fiber and matrix has been weakened and load-bearing strength of the composite has been reduced and this caused the reduction in impact strength of laminates.

From the Fig.7.4 the impact strength degradation has been found to be significant in almost all the environments, lower degradation was recorded in the laminates with lower percentages of glass content. A strength degradation upto 85% was observed in the 45% glass content laminates immersed in adverse environments, however for the same duration of exposure the degradation level is approximately 45% for laminates with 15% glass content. The reduction in impact strength should be taken as a simultaneous effect of corrosive environment and liquid penetration into the material.

The reduction in impact strength in acidic solution has been found to be at a higher level of approximately 85% as compared to distilled water and saline environments for the duration of exposure, although the liquid penetration is observed to be less than water and more than saline water. This high value of degradation on impact strength may be attributed to the reaction of acid on composites. Concentrated H₂SO₄ acid would digest the binder material and debond the fibers from the matrix. When the concentration decreases to N/100, these effects would substantially decrease. However, prolonged exposure of composite may be taken to cause a slow reaction of acid and matrix, and developed debonding, delamination and micro-cracking in composite phases. Thus, there is a high amount of strength degradation.

When the laminates were exposed to organic fuel (kerosene), the reduction in impact strength has been found to be high and approximately same as that of the previous cases, that is, water, saline water, and acidic water for the same duration of exposure, although the liquid penetration is marginal and quite less than other liquid based environments. The absorption of aromatic constituents of liquid fuel may be considered to be a cause for marginal weight gain. The apparent cause of strength degradation may be due to fuel absorption, which may corrode the fibers exposed.
Loosely bonded carbon particles may be detached from fiber by chemical reaction resulting in a rough surface. Thus, there is a reduction in fiber strength and hence the probable impact strength degradation.

![Graphs showing strength degradation for different environments and exposure durations.](image)

**Fig. 7.4** Strength degradation due to adverse environments for different exposure durations.
Similarly, under freezing temperature, the water is in the state of transition phase and temperature is about 0°C. The low temperature of the environment will cause the shrinkage of the constituent phases of the epoxy composite and transition pressure will increase water absorption capabilities. This may be due to dissimilar contraction of matrix and fiber in low temperature. In consequence, detachment between the fiber and matrix interface occurs resulting into the development of microcracks, debonding and delamination in the interface region of fiber and matrix. The process will be further aggravated by formation of more cracks and more detachment at the interface when there is a prolonged exposure. Therefore, the impact strength degradation is found to be quite large in comparison to the percentage of moisture absorbed. The overall results obtained from various adverse environments have shown the rate of reduction in impact strength, and it depends on reaction of constituent phases towards the exposed environments, duration of exposure and type of environment.

7.5.4 Moisture Absorption and Strength Retention

In order to establish a relation between the percentage of moisture absorbed and the strength retention, the analysis is extended to generate equations using graphical package for various percentages of glass content and adverse environments. First the three aqueous based liquid solutions were selected, these represent acidic, saline and pure water environments. In all these environments it was observed that the laminates with higher percentage of glass content degrade at faster rate and it is even for small percentage of moisture absorption. Whereas for laminates with small percentage of glass content, it was seen that the strength retention capability reduces gradually and retains more strength even with large moisture absorptions. The experimental results for moisture absorption and strength retention for acidic, saline and water are illustrated in Fig. 7.5, the equation in the boxes show correlation equation for the respective glass percentage.

Under freezing temperature the dissimilarity in the thermal coefficient behaviour of matrix and fiber causes different expansion and contraction characteristics, resulting into microcracks, debonding and delamination at the interface region. The ablation of matrix may be increased as temperature changes, thermal stress produced within the laminates results into the micro buckling of fiber. This has made the composites to
degrade and resulted into the lower values of impact strength. The strength retention after moisture absorption within freezing temperature is shown in Fig. 7.6, in this environment also the trends are similar, higher the glass content, smaller will be the impact strength retention and more sensitive to moisture absorption and vice versa. The trend line for the correlation is shown in the figure for all the percentages of glass content.

Fig. 7.5 Relation between Moisture absorption and Strength retention for laminates immersed in acidic, saline and distilled water.
Comparing the behaviour of laminates under freezing and kerosene environments, it is quite clear that the behaviour of these environments is almost same. The response of the laminates in kerosene is shown in Fig. 7.7, it is found that for quite a marginal percentage of moisture absorption the strength deterioration is very large. Though these laminates absorb small percentage of moisture, but the margin of degradation and the rate of degradation are quite high. This may be due to the reason of internal stresses in case of freezing environment and micro-cracking due to kerosene. The trend-line for this environment is also shown in the same figure. The R-square value for the above cases is obtained which is known as coefficient of determination, and reveals how closely the estimated data for the trend-line corresponds to the actual data. It is given in the range form 0 to 1, and is most reliable if the R-square value is at or near 1. The R-square value obtained was of the order of 0.9 for acidic environment, whereas for distilled water the value was less and it is 0.74.
7.5.5 Prediction of Service Life

From the previous results it was recognized that moisture plays a significant role in influencing the mechanical behaviour, the long term durability of polymer and polymer matrix composites, numerous diffusion models have been proposed over the years for modeling moisture effects in composites [66]. In this work, for predicting the life of the laminates, the corresponding diffusion coefficients and maximum moisture contents are essential hence these were calculated by assuming one-dimensional Fickian absorption. The main assumption involved is that moisture diffusion can be described by Fick’s law. Additionally, diffusivity is assumed to depend on temperature and to be independent of the moisture concentrations or the stress levels inside the material. For a material which is exposed to moisture on all six sides, the moisture absorption is given by the following relation [151].

\[
M = \frac{4 M_n}{h} \left[ \frac{t}{\pi} \right]^{0.5} D^{0.5}
\] (7.1)

Where \( M \) is the moisture content of a material of thickness \( h \) at any given time \( t \), \( M_n \) is the saturation moisture content of the material and \( D \) is the diffusivity. The diffusivity can be solved by finding the initial slope of the moisture uptake curve. Using the weight gain data of the material with respect to time, a graph of percent moisture content of the material Vs square root of time is plotted. Slope of the initial linear part of the graph is found out. Now diffusivity is calculated by using the following formula.

\[
D = \pi \left[ \frac{h}{4 M_n} \right]^2 \left[ \text{slope} \right]^2
\] (7.2)

Therefore to estimate the diffusivity of all the laminates, the plots for square root of time and moisture uptake percentages is generated and are as shown in Fig. 7.8. By using these plots the slopes for all the laminates in different environments and glass percentages are evolved.
To calculate the moisture content of composite using Fick’s Law, knowledge of two parameters, maximum moisture content and diffusivity is a must. The values of maximum moisture content for all the environments and glass percentages are listed in Table 7.1. The diffusivities were calculated according to the method outlined by Shen and Springer [151], the resulting diffusivities are shown in the Fig. 7.9.

Fig. 7.8 Relation between Moisture absorption and Square root of time for different percentages of glass content and environments.
Table 7.1 Summary of the Maximum Moisture Content of the Laminates

<table>
<thead>
<tr>
<th>Glass Content, %</th>
<th>Environment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>water</td>
</tr>
<tr>
<td>15</td>
<td>2.12</td>
</tr>
<tr>
<td>30</td>
<td>2.73</td>
</tr>
<tr>
<td>45</td>
<td>1.83</td>
</tr>
</tbody>
</table>

Fig. 7.9 Diffusivity as function of fiber glass percentage.

Since the time required to reach the maximum moisture content level is insensitive to the moisture content of the environment, it depends on the environmental temperature [32] and hence for estimating the maximum level, room temperature is maintained for all the liquid environments. Using the diffusivity it is possible to estimate the time period for the laminate to attain at least 99.9 percent of its maximum possible moisture content, time $t_m$ for attaining maximum moisture $M_m$ level is shown in Fig. 7.10. This time period was considered as the service life of the laminates under aggressive adverse environments, however the same laminates may last long if used in dry environmental conditions. The life is more in the environments having kerosene and freezing temperature. The percentage of glass fiber will also play significant role in determining the life of the laminates, in the case of laminates in freezing environment, with the increase in glass percentage the life has increased whereas in the case of acidic environment it has reduced the life of laminates.
Fig. 7.10 Predicted Service Life of Laminates on complete Immersion in Adverse Environments.

The Fickian equation is used to compare the experimental results with the Fickian curve fitting, to illustrate the comparison some of the samples are randomly selected and the respective curve fitting is shown in Fig. 7.11. From the trends it is seen that for the laminate with 45% glass content exposed in acidic environment the Fickian fit is almost matches the experimental results, whereas in other cases the curve fitting is approximated indicating a need for further investigation for the exposure durations beyond 250hrs.

Fig. 7.11 Comparing the moisture uptake with Fickian fit for the composite laminates.
7.6 SUMMARY

The goal was to create a better understanding of how moisture may affect impact behavior and service life of hybrid composite materials. This included not only generating and examining experimental evidence, but also considering the existing model for predicting the service life. The laminates which are immersed in distilled water are the severely affected with approximately 25% of swelling, while the impact strength degradation has been found to be significant in almost all the environments, lower degradation was recorded in the laminates with lower percentages of glass content. A strength degradation up to 85% was observed in the 45% glass content laminates immersed in acidic environment. The predicted life is more in the case of environments like kerosene and freezing temperature. Also it was found that with the increase in glass percentage the life has increased whereas in the case of acidic environment the trends are on the other way.