Durability Study of Hygro-Thermal Effects on Epoxy and Wet Layup Carbon/Epoxy Composites

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Fiber reinforced polymers (FRPs) are finding increasing use in civil engineering areas because of their high strength, light weight, and good corrosion resistance. However, the durability data of FRPs are far from complete compared with traditional construction materials such as steel. This situation prevents FRPs from being used to their full potential. In this paper, the durability of epoxy and carbon fiber reinforced epoxy manufactured by wet lay-up is studied via immersion in deionized water of different temperatures (73 F, 100 F and 140 F), as well as alkali and salt solutions up to two years. The study of epoxy under the same situations is conducted for comparison purpose. Performed tests include moisture absorption, tension, flexural, short-beam shear, and dynamic mechanical thermal analysis (DMTA). These durability data can provide useful degradation information of these materials. The durability data are also useful for creating numerical models to predict the long-term durability behavior of FRPs.

Key words: durability, FRP, materials property, degradation

Introduction

Now, a lot of civil infrastructures in the U.S. need to be repaired. For example, according to a report from American Society of Civil Engineering (ASCE)[1], 27.5% of the current bridges in U.S. are deficient and need to be rehabilitated. Due to their intrinsic merits of easy handling, light weight, corrosion resistant, and high strength to weight ratio, the use of fiber reinforced polymers (FRPs) as a means of rehabilitation of deteriorating and understrength concrete structures is rapidly increasing.

However, despite the increasing FRPs application in civil engineering, the durability of FRPs remains a concern. The lack of an easily accessible, well documented durability database[2] is preventing FRPs from being used to their full potential. Considering the working conditions of FRPs, the durability study usually includes monitoring moisture absorption, and relating it to the corresponding materials properties (strength, Young's modulus, etc.). The moisture absorption behavior of FRP is affected by factors such as temperature, stoichiometry, and interface etc. VanLandingham et. al.[3] studied the moisture diffusion in epoxy systems, and they found that differences in

diffusion behavior are related to the relative importance of diffusion through the low-density and high-density microstructural phases for different stoichiometries. For FRPs, the presence of interfaces sometimes causes a stepped behavior in moisture absorption at higher temperature[4], possibly due to deterioration at the level of the interface resulting in a sudden increase in moisture uptake due to wicking. The effects of moisture and temperature on ultimate tensile strength of graphite epoxy composites were studied by Shen and Springer[5]. They found that for 0° and $\pi/4$ laminates, the changes in temperature (in the range 200 K to 380 K) and moisture content of the composites (<1%) have negligible effects on the ultimate tensile strength, while for 90° laminates, the increase of temperature and moisture content affect significantly the ultimate tensile strength. Kennedy et. al.[6] characterized interfacial bond strength of FRPs via short beam shear, double cantilever beam, and torsional dynamic mechanical (DMA) tests. They found that the DMA test was superior to the short beam shear and double cantilever beam test for measuring fiber/matrix bonding. Dynamic Mechanical Thermal Analysis (DMTA) has become a powerful tool for developing insight into structure and viscoelastic response of polymeric composites, as well as detecting the changes in internal molecular mobility in recent years. Glass transition temperature, T_g, can be determined accurately through DMTA by monitoring changes in the storage modulus, E', loss modulus, E'', or the loss tangent, tan δ, as a function of temperature. T_g usually changes based on the frequency used in testing and the rate of heating used. In general, an increase in the heating rate is known to shift T_g to a higher temperature[7] whereas an increase in test frequency for a constant heating rate also increases T_g[7, 8]. DMTA has been used as a means of monitoring changes in post-cure in air and in water[9, 10], as well as the influence of moisture and sizing on fiber–matrix interface response [11,12].

In this paper, results from durability study of epoxy and carbon fiber reinforced epoxy manufactured by wet lay-up will be presented and analyzed with regard to moisture absorption, tension, flexural, short-beam shear, and glass transition temperature.

Experimental Procedure

The epoxy resin used in this study is mixed at a ratio of 2 parts resin and 1 part of hardener by volume. The composite consists of a primarily unidirectional fabric of 600 gsm (18 oz./sq. yd) basis weight formed using T700 carbon fibers in untwisted 24k tow form, and was fabricated as unidirectional composites using the wet layup process at thickness of 2 layer.

Samples were exposed to 6 different environments as listed in Table 1. Condition 1 is employed to determine a general characterization of the response when specimens are unexposed. Conditions 2-6 were determined to obtain data for accelerated aging tests under different conditions. Samples were placed in environments for periods of time up to 2 years, and were removed for characterization through moisture uptake, tension, three-point flexure, short beam shear, and DMTA at intermediate periods.

Moisture absorption measurements were done with reference to ASTM D5229. Tension tests of epoxy samples were done according to ASTM D638, while tension tests of composite samples were done according to ASTM D3039. Flexural properties were measured according to ASTM D790, and short beam shear tests were done according to ASTM D2344. DMTA tests were done with reference to ASTM E 1640. Multiple specimens were used for each set of measurements.

Table 1 Environmental experiment conditions

No.	*Temperature (F)*	*Condition*	*Note*
1	73	30% R. H.	Ambient
2	73	Deionized (DI) water	Full immersion
3	100	Deionized (DI) water	Full immersion
4	140	Deionized (DI) water	Full immersion
5	73	Alkali solution pH = 12	Full immersion
6	73	Salt solution 5% NaCl solution	Full immersion

Results and Discussion

Moisture Absorption Kinetics

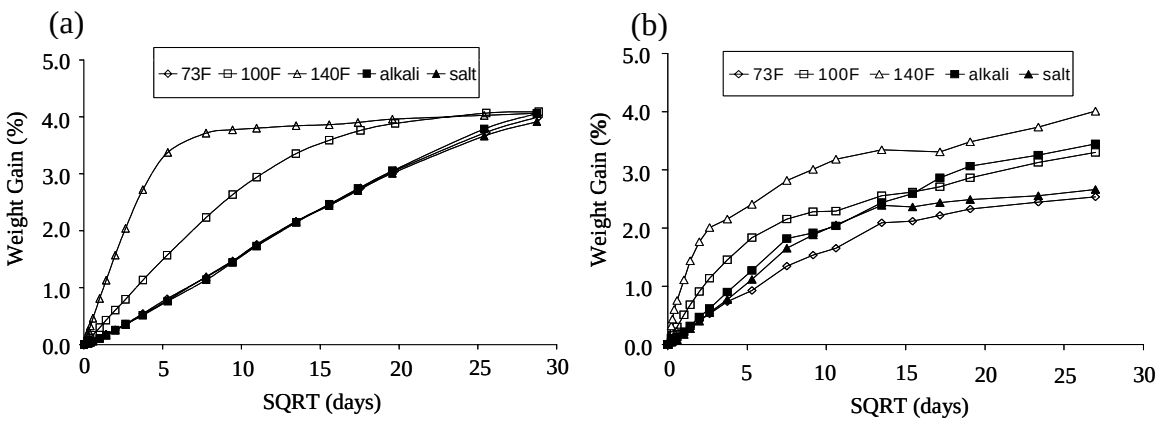

Figure 1 Moisture absorption kinetics of epoxy resin and wet layup samples

The moisture absorption behaviors of epoxy resin and wet layup samples are different. For epoxy resin samples, as seen in Figure 1a, the moisture absorption kinetics is roughly Fickian in nature. The moisture absorption of samples immersed in 140F DI water reached equilibrium first, while the moisture absorption of samples immersed in 100F DI water reached equilibrium after about 21 months immersion. One phenomenon worth notice is that the moisture absorption of samples immersed in lower temperature water caught up with those of samples immersed in higher temperature water after some time, and exceeded/or will exceed in the long term. For wet layup samples, stepped behaviors are observed for samples immersed in 140F DI water and alkali solution (Figure 1b). It is noted that such behavior was not observed in pure epoxy samples under the same immersion conditions. These stepped behaviors are probably caused by the deterioration at the composite's interfaces where an abrupt increase in moisture happened due to wicking.

Maximum moisture uptake and diffusion coefficient calculated from experiment are listed in **Table 2**. The lower level of moisture uptake in wet layup samples is probably caused by the occupation of carbon fibers, where no or little moisture absorption happened. For both epoxy resin and wet layup samples, there is very little difference in response due to immersion in 73 F deionized water and salt solution which

is in consistent with the results reported early on similar systems. For samples immersed in DI water, the diffusion coefficient of both epoxy resin and wet layup samples increases with the increase of immersion temperature. However, it must be noticed that the diffusion coefficients were calculated by assuming Fickian diffusion, which should have no stepped behavior in moisture absorption curve.

Table 2 Moisture Absorption Characteristics Determined by Experiment

Materials	Epoxy Resin		Wet Layup	
Immersion Solution	Maximum moisture uptake (%)	Diffusion Coefficient (mm^2/s)	Maximum moisture uptake (%)	Diffusion Coefficient (mm^2/s)
73F DI water	4.00	2.11E-07	2.56	5.13E-08
100 F DI water	4.09	3.37E-07	3.30	1.55E-07
140 F DI water	4.06	1.92E-06	4.01	4.18E-07
Salt	3.92	2.15E-07	2.66	6.02E-08
Alkali	4.06	2.07E-07	3.44	5.22E-08

Tension Tests

Tension test results of epoxy resin are plotted in Figure 2. Obvious degcrease in strength and Young's modulus was seen for immersion samples. For samples immersed in deionized water, the decrease increases with the water temperature (Figure 2a, b). However, there was little difference in strength and Young's modulus between samples immersed in salt, alkali solution, and 73 F deionized water (Figure 2c, d), which suggests that salt and alkali may not affect the tensile strength and Yong's modulus of epoxy more than deionized water.

For tension tests of wet layup samples, no clear decrease in strength and Young's modulus was observed for immersion samples (Figure 3). This observation is in consistent with the experiment results from Shen and Springer. However, no significant drop in strength and Young's modulus does not necessarily implicate that degradation does not happen in immersion samples. The reason why the degradation did not show via the strength and Young's modulus of materials is that the test samples were cut along the unidirectional carbon fibers. In this direction, the mechanical properties are dominated by carbon fibers. Since strength and Young's modulus of carbon fibers are much higher than those of epoxy matrix, and carbon fibers are little affected by water absorption.

Flexure and Short Beam Shear

Flexural tests are often used to determine flexural strength of layered materials such as wet layup polymeric composite. The results can provide useful information on the deterioration of layered fabric based composites. In this study, flexural tests were done on wet layup samples. The results show that there was a substantial drop in flexural strength in the first 2 months for all the samples including ambient samples (unexposed). After that, the flexural strength of ambient samples leveled out. The flexural strength of immersion samples continued to decrease until it eventually leveled out after about 6 months immersion (Figure 4a, Figure 4b).

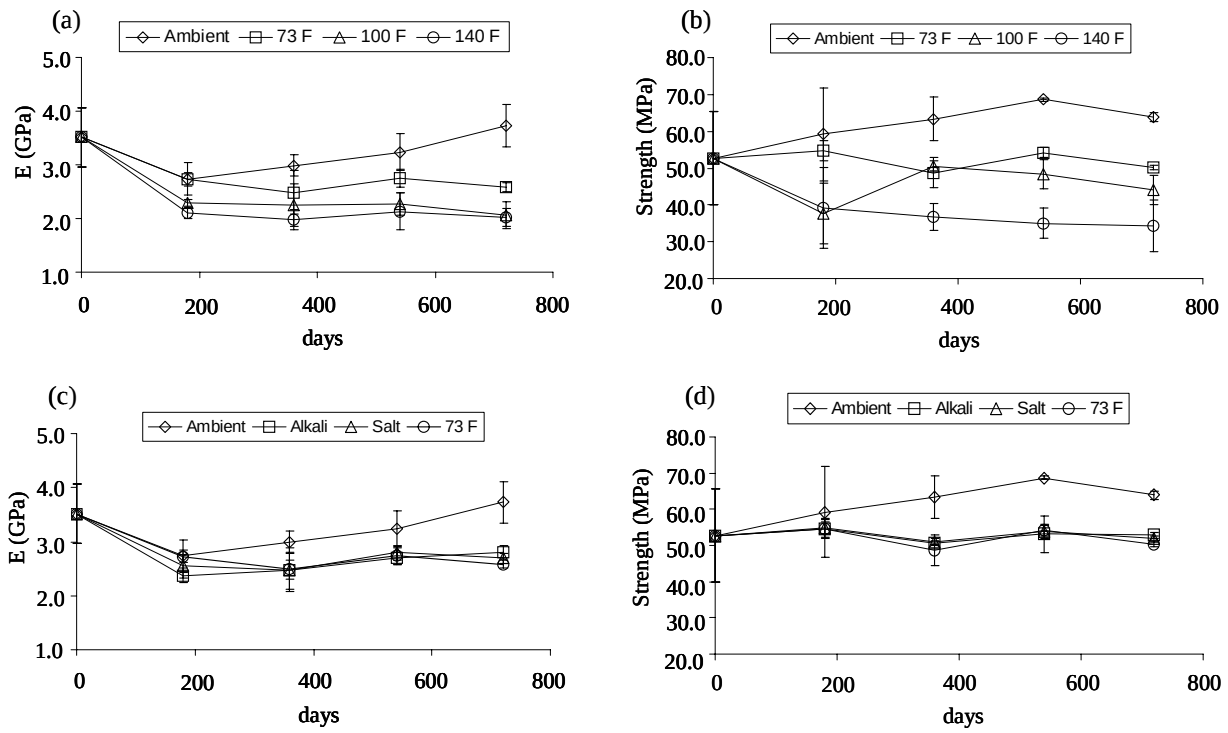

Figure 2 Tension results of epoxy resin

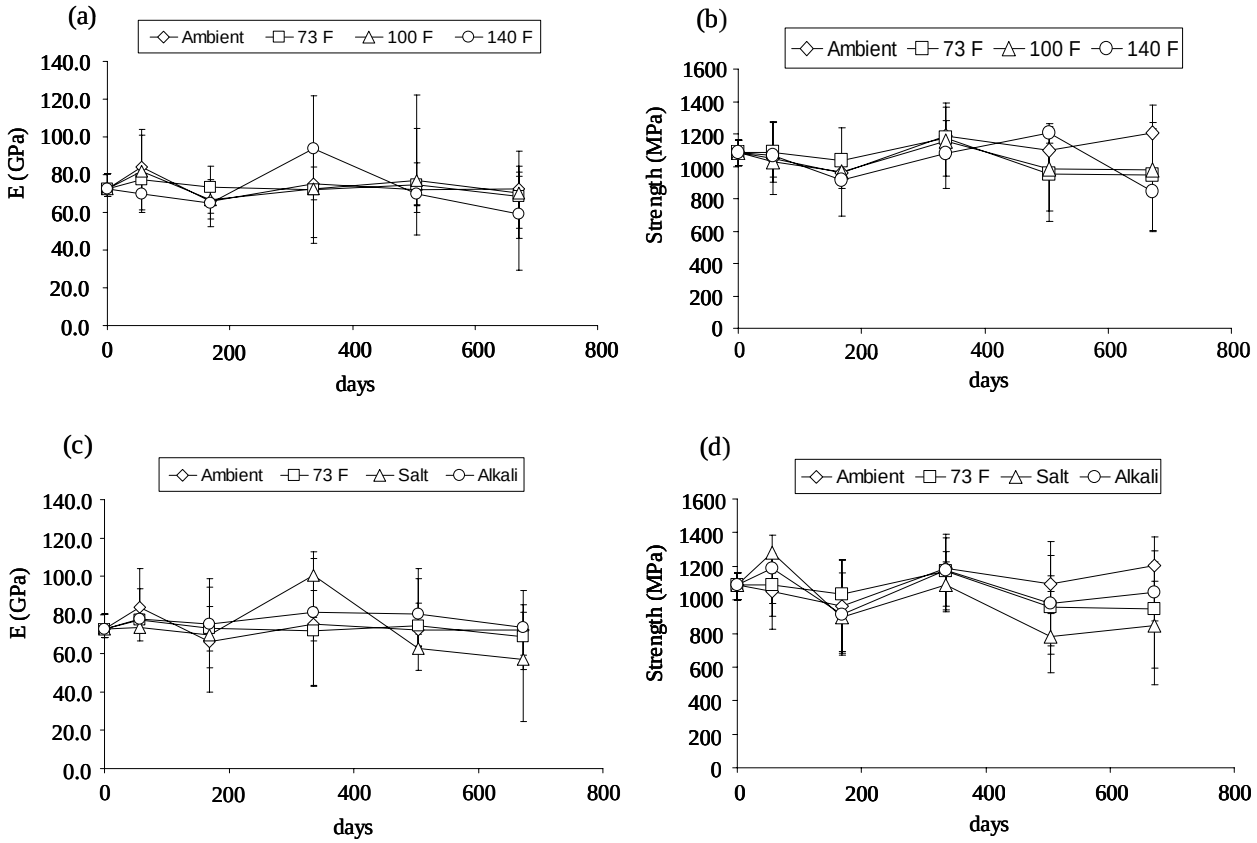

Figure 3 Tension results of wey layup composite

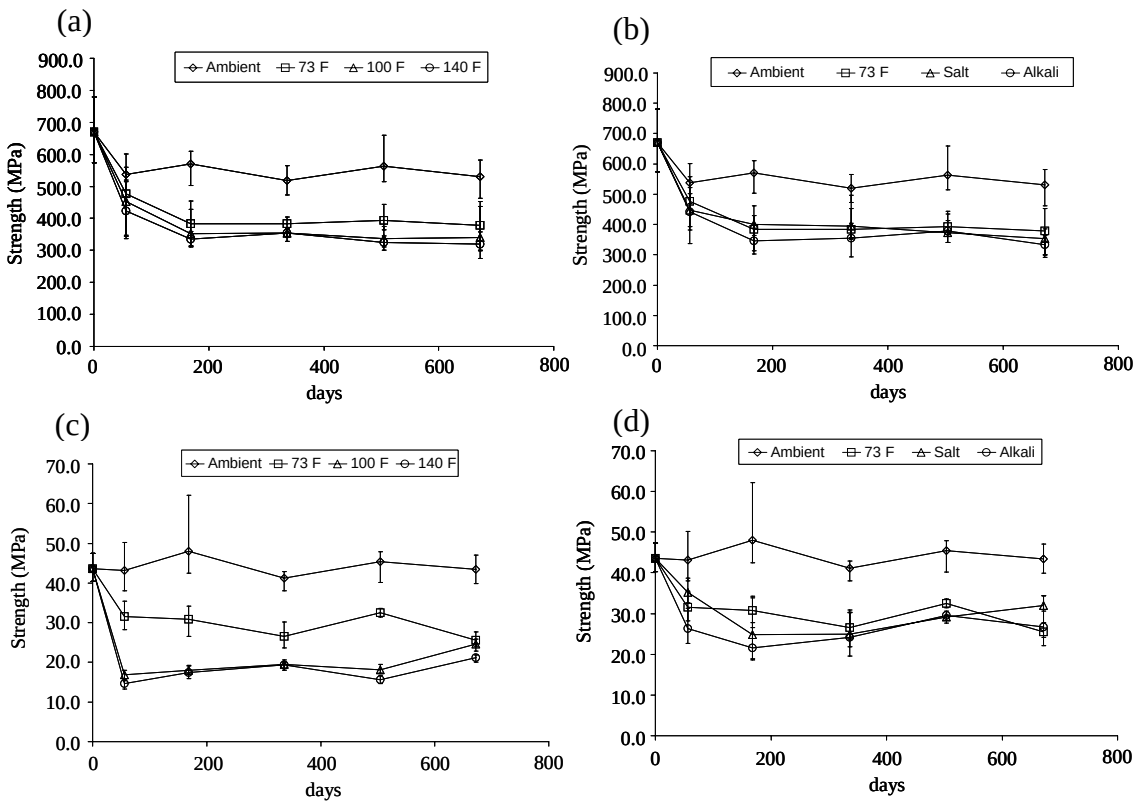

Figure 4 Flexural strength (a), (b), and short beam strength (c), (d), of wet layup composites

Short beam shear is used to get interlaminar shear strength of layered materials. Although short beam strength is not directly related to any one material property, it can qualitatively reflect how well the layers are connected to each other. Short beam shear results of wet layup samples are plotted in Figure 4c and Figure 4d. The results show that for unexposed ambient samples, the short beam strength was little changed over time, indicating that the fiber-epoxy interface was not degraded. For samples immersed in deionized water, the decrease in strength increases with immersion temperature, indicating degradation at the interface also increases with higher immersion temperature. The degradation at the interface is seen to decrease the short beam strength of samples immersed in 73 F, 100 F, and 140 F deionized water by 41.5%, 43.4%, and 51.5% respectively at the end of 2 years immersion. There is little difference between the short beam strength of samples immersed in 73 F deionized water, alkali solution, and salt solution (Figure 4d). It is noted that there was a substantial drop in strength in the first 2 months for immersion samples, and the short beam strength leveled out after 2 months. This indicates that most degradation at the fiber/epoxy interface happened in the first 2 months.

DMTA

DMTA characterization can provide useful information of polymeric materials such as glass transition temperature, plasticization, cure progression, and cross-link density. Here, focus is given on glass transition temperature from DMTA results. Glass transition temperature T_g was determined as the peak of the tan δ curve to enable ease and

consistency in identification although tan δ peak occurs at the end of the transition region between elastic and viscoelastic regimes.

As can be seen from Figure 5, T_g of unexposed samples (ambient) is almost unchanged over time. For immersion samples, moisture uptake causes the depression of T_g. There was a substantial decrease in T_g after the first 6 months of immersion, and T_g leveled out after that. It is noted that the average decrease of T_g is about 14.0% and 29.7% for epoxy resin and wet layup samples respectively at the end of 2 years immersion. The larger amount of decrease in T_g for wet layup immersion samples is probably caused by more severe degradation in these samples due to the fiber/matrix interface.

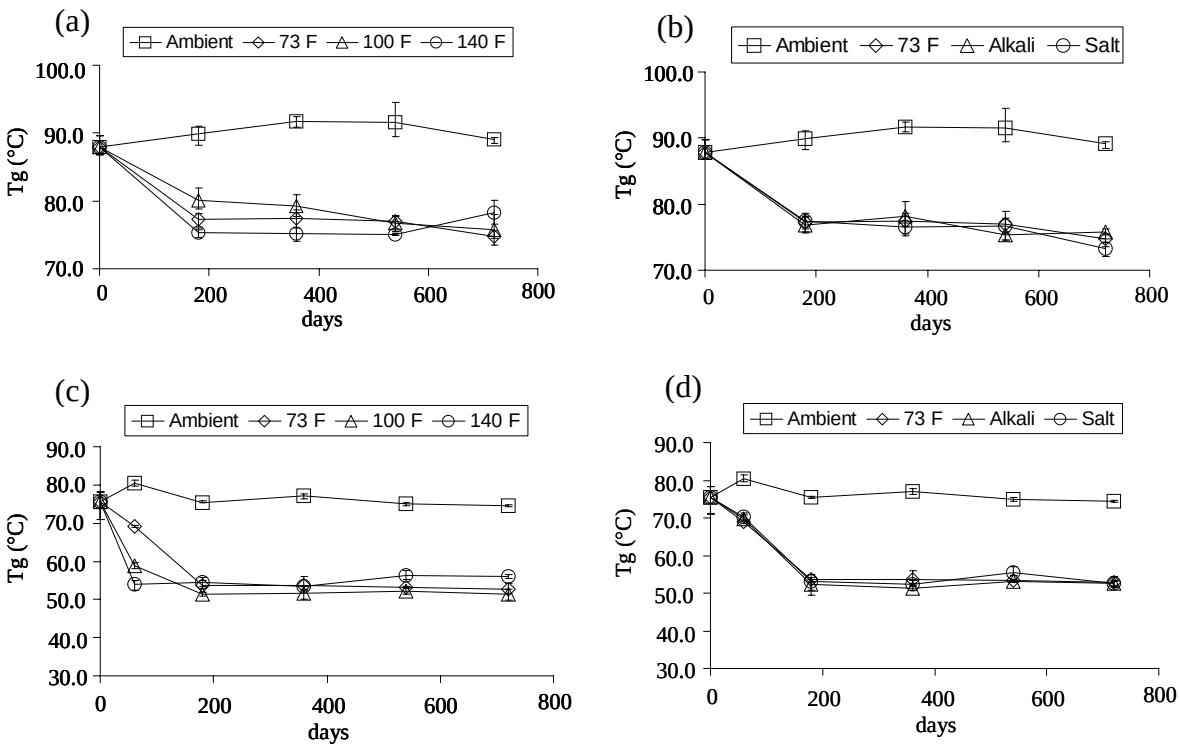

Figure 5 T_g of epoxy resin (a), (b), and wet layup composites (c), (d)

Summary and Conclusions

Durability of epoxy resin and its wet layup composite was studied via moisture absorption, tension, flexural, short-beam shear, and glass transition temperature (T_g) measurements. Results showed degradation of wet layup composites is different from that of epoxy resin due to the presence of fiber/matrix interface. The moisture uptake of epoxy resin is Fickian in general, while there were stepped behaviors for moisture absorption of composites under some situations. Flexural, short beam shear, and DMTA results all indicated most degradation happened in wet layup composite during early time (2-6 months) of immersion, and the degradation became much slower after that. No significant drop in strength and Young's modulus for immersion composite samples is due to the test method that could not reflect the actual degradation.

The results presented here are part of Highway Innovative Technology Evaluation Center (HITEC) project. The objective of this project is to evaluate the durability of FRP materials for rehabilitation of civil infrastructures in the U.S. This research will benefit Caltrans by repairing the damage to bridges and highways at a fraction of current cost.

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