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THE EFFECT OF WATER ON THE FATIGUE BEHAVIOR FOR A PULTRUDED GLASS-REINFORCED COMPOSITE

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Abstract

Pultruded composites are finding increasing use in infrastructure and marine applications where they see prolonged exposure to environmental factors such as moisture. This work examines the fatigue behavior (4 point bending) in air and water for pultruded materials. Some specimens were preconditioned in water for 6 months (room temperature) before testing in water. The results show that water significantly reduces the fatigue life at low loads but not high loads. Moreover, preconditioning had no effect on fatigue life in water. Consequently, using higher loads or preconditioning to accelerate fatigue tests in water is not a useful approach.

Background

Composites have seen limited use in construction over the past few decades, but the urgent need to repair and retrofit much of the Nation's rapidly-deteriorating infrastructure has generated considerable interest in the potential for greatly expanded applications of composites [1-6]. The need for low costs in such structures has focused attention on glass reinforcement and economical fabrication methods like pultrusion. In addition to low cost, infrastructure applications generally have a long service life--some bridges are designed to last 50 years or more. Composites generally have very good environmental durability. Many studies have been conducted with carbon or short glass fibers [7-9], but the data on very long term behavior of continuous-fiber, glass-reinforced composites are limited. The work that does exist has shown that fluids, like moisture, can attack both glass fibers and the fiber-matrix interface [10-17] which greatly complicates the behavior.

The work here seeks to help address this deficiency by studying the environmental fatigue of pultruded materials. Since many infrastructure applications involve beams loaded in bending, the primary tool for these studies is the 4-point bend experiment. The work will be extended beyond 10 million cycles where little data currently exists. The variables often used to accelerate such tests (higher loads, and preconditioning) will also be examined.

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Material and Method[b]

The material studied here is pultruded, E-glass fiber-reinforced vinyl ester (Strongwell EXTREN® 625). This composite is typical of the type being considered for some infrastructure applications. The sample was provided by MMFG as 30.5 cm x 122 cm x 0.64 cm (12 in x 48 in x 0.25 in) plates. Bar specimens of dimensions 12.7 cm x 1.3 cm x 0.64 cm (5.0 in x 0.5 in x 0.25 in) were cut from the plates according to the ASTM standard (D790-92) for the four-point bend test. Structurally, the material consists of unidirectional fiber rovings and layers of chopped fiber strand mat embedded in vinyl ester matrix, shown schematically in Fig. 1. The fiber volume fraction, determined by burn-off experiments is 34 % with a standard uncertainty of 2 %. As a result of the pultrusion process, the fiber roving are not uniformly distributed locally. Also, because of the relatively small size of the test specimens (0.83 cm^2 cross sectional area), some specimens may contain more fiber roving than others, which gives rise to considerable data scattering in mechanical properties.

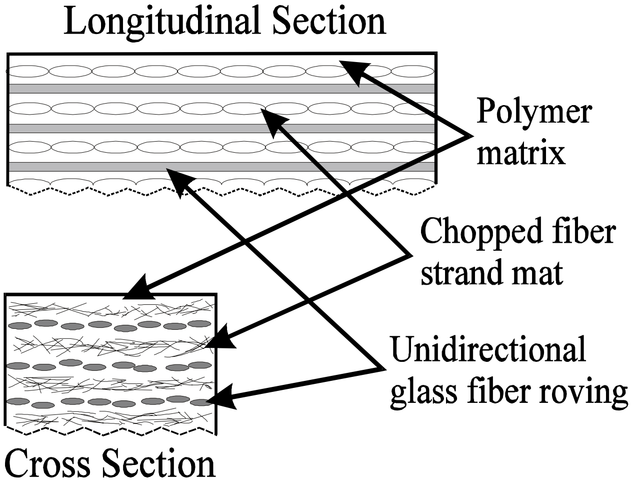

***Figure 1**: Schematic microstructure in pultruded material.*

Specimens were preconditioned by immersing in three different fluid environments:

a. de-ionized water for 5 months at room temperature,
b. 5 % (by mass) NaC1 solution for 6 months at room temperature, and
c. 10 % (by mass) NaC1 solution for 6 months at room temperature.

Water and NaCl solutions were chosen to simulate rain and salt spray, two commonly encountered outdoor conditions. Mass changes for the specimens during preconditioning were recorded at regular time intervals using an electronic balance.

A 4-point bend experiment (ASTM D790-92) was used to determine the quasi-static flexural strength (FS) and flexural modulus for as received specimens as well as for preconditioned with conditions **a**, **b**, and **c**. Flexural fatigue experiments were then conducted using a sinusoidal wave function at 10 Hz, with R=10 (where R is the ratio of the maximum to the minimum cyclic load). These conditions avoid macroscopic heating in the sample while minimizing the time required for long term tests. The experiments were performed at room temperature in five different conditions:

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[b] Certain commercial materials and equipments are identified in this paper in order to specify adequately the experimental procedure. In no case does such information imply endorsement by the National Institute of Standards and Technology and Northwestern University, nor does it imply necessarily that the items are the best available for the purpose.

A. air (dry),
B. water without prior preconditioning of the sample,
C. water with sample preconditioned using condition **a**,
D. 5 % (by mass) NaC1 solution with sample preconditioned using condition **b** (5 % NaCl solution),
E. 10 % (by mass) NaC1 solution with sample preconditioned using condition **c** (10 % NaCl solution).

When testing under conditions **B** to **E**, the specimens were sealed in nylon bags filled with deionized water or NaCl solution.

The cyclic tests were carried out under load control with maximum loads at 85 %, 65 %, 45 %, and 30 % of the mean flexural strength of dry samples tested in air at room temperature (DFS). Since the primary interest here is long term behavior, not all load levels were tested for each conditions. Only specimens from conditions **A**, **B**, and **C** were tested at 85 % DFS. Specimens from condition **E** (10 % NaCl solution) were only tested at 30 % DFS in order to compare to those tested under condition **D** (5 % NaCl solution). For selected samples, the cyclic testing was periodically interrupted to measure the flexural modulus by means of a displacement gage (MTS® model 632.06H-20) and to record mass change of the specimen using an electronic balance. Surface-related damage during fatigue was also examined and recorded using optical and scanning electron microscopies.

Results and Discussion

Quasi-static flexural strength and modulus and sorption behavior

The flexural modulus and quasi-static flexural strength were determined for as-received specimens and those preconditioned with conditions **a** (water), **b** (5 % NaCl solution), and **c** (10 % NaCl solution). Flexural strength, *FS,* is determined as the maximum tensile stress on the lower outer surface:

$$FS = P_f L / b d^2 \qquad \textbf{(1)}$$

where P_f is the failure load, L, b, and d are the length, width, and thickness of the specimen, respectively. Compared to the as-received specimens, the flexural modulus for those after preconditioning remains essentially the same. The mean flexural strength for specimens preconditioned in conditions **a**, **b**, and **c** showed a 4.8 %, 12 %, and 13 % decrease, respectively, relative to that for the dry specimens. Although these changes are not outside the experimental uncertainty for the tests performed here, the trends are consistent with degradation results seen in previous studies [10-15].

The amount of fluid absorbed by samples during preconditioning and cyclic loading was periodically monitored by measuring mass gain. Preconditioning in water or NaCl solution for (5 or 6) months gave moisture contents of about 0.5 % by mass. The addition of NaCl to the water slows the pickup rate or reduces the saturation level or both. Some typical results are presented in Fig. 2. When these data are compared to sorption results for dry specimen fatigued in water, it is clear that loading accelerates the moisture pickup. Even at the lowest load tested (30 % of the flexural strength), the failure point is reached well before the moisture content approaches the levels generated by preconditioning.

Fatigue Behavior

Fatigue is often characterized by monitoring the change in modulus that occurs as damage builds up in the specimen during cyclic loading [18,19]. Although a wide variety of conditions were tested here, all samples exhibited a pattern which is typical of that seen in other composites [19]. During the first 10 % of the sample's fatigue life, the flexural modulus often exhibits a small drop. This is followed by a region where the modulus is relatively constant. At about 85 % of the fatigue life, the modulus begins to drop again, and the rate accelerates until final failure.

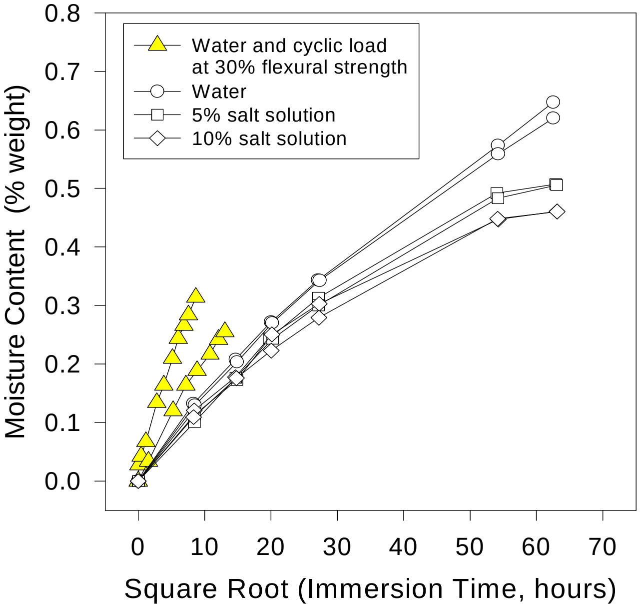

Figure 2: *Moisture Pickup for four different conditions. Two samples were measured for each condition to get an indication of the uncertainty in the data.*

Optical and scanning electron microscopies were used to examine the growth of damage as a function of fatigue cycles. The damage patterns are similar for all the specimens tested here. The first indication of damage is the appearance of transverse matrix cracks which initiate from the edge of the specimen on the lower (tensile) surface. During the middle of the fatigue life, these cracks become more regularly spaced and extend all the way across the lower surface. Further fatigue causes the cracks to deepen until they go through the layer of fiber strand mat on the surface and reach the first layer of unidirectional fibers underneath. Toward the end of the fatigue life, longitudinal cracks and debonds develop at this layer of unidirectional fibers. These cracks grow and combine until they form a "delamination" between the fiber strand mat and unidirectional fiber roving. This delamination grows more and more quickly causing a significant drop in flexural modulus. This is soon followed by catastrophic failure involving complete delamination of the layer and failure in the unidirectional layer. Although the general chain of events during the failure process is the same for all of the samples, the timing of the events and the loads at which they occur are different for the various conditions. These differences are discussed below.

SN Behavior

The SN curves were determined for the various conditions. In an SN curve the abscissa represents the number of cycles to failure on a logarithmic scale while the ordinate represents maximum tensile stress on the specimen. The maximum tensile stress, σ, is equal to PL/bd^2 where P is the peak of the cyclic load while L, b, and d are the same as in Eq. 1. The general trends observed here, see Fig. 3, are typical of behavior seen for composites; i.e., as the maximum tensile stress goes up, the fatigue life decreases.

All of the fatigue data in Fig. 3 can be divided into two regimes, a regime where performance depends on stress but not environment, and a regime where performance depends on both stress and environment. The first regime is defined by cyclic loading above 45 % of the DFS. Under these conditions, the SN data are indistinguishable among conditions **A** through **D** (specimens from condition **E** were only tested at 30 % DFS). Although the flexural strengths are decreased slightly after preconditioning in water and NaCl solutions, no differences are seen in the fatigue life. Of course, there is significant scatter in the results which could mask any smaller differences in behavior that might be present. One factor contributing to the scatter is material variability which is generally higher for pultruded materials than for hand lay-up, autoclave-cured samples. This regime where fatigue is dependent on load but not environment is characterized not only by high cyclic load levels but also by low cycles to failure (short loading time).

When the samples are tested at loads of 45 % DFS and lower, some differences start to emerge for the various conditions, **A** through **E.** At 45 % DFS, more dry specimens survived longer life (number of cycles to failure), although some overlap in the data still exists. This represents a transition to the second regime mentioned above. For specimens tested at 30 % DFS, the dry specimens are clearly segregated from those tested under fluid environments. All dry specimen survived beyond 10^7 cycles while specimens tested under environmental conditions **B** through **E** all failed within 10^7 cycles. Most environmental SN data (i.e., specimens tested under conditions **B**, **C**, and **D**) for tests at 30 % DFS are clustered within 10^6 to 10^7 cycles. The flexural moduli all start to show a decreasing trend at around 10^6 cycles. It is clear that water and NaCl solutions did exert a detrimental effect on the fatigue life during long-term loading. This regime of load- and environment-dependence is characterized by low cyclic load levels and high cycles to failure (long loading time). Similar stress-life patterns have been reported by Phillips for stress-rupture of GFRP where he has suggested three distinct regimes, namely, environmental-independence, environmental- and stress-dependence, and stress-independence for the stress versus time-to-failure plot [20]. For the conditions examined in this work, only the first two regimes are seen.

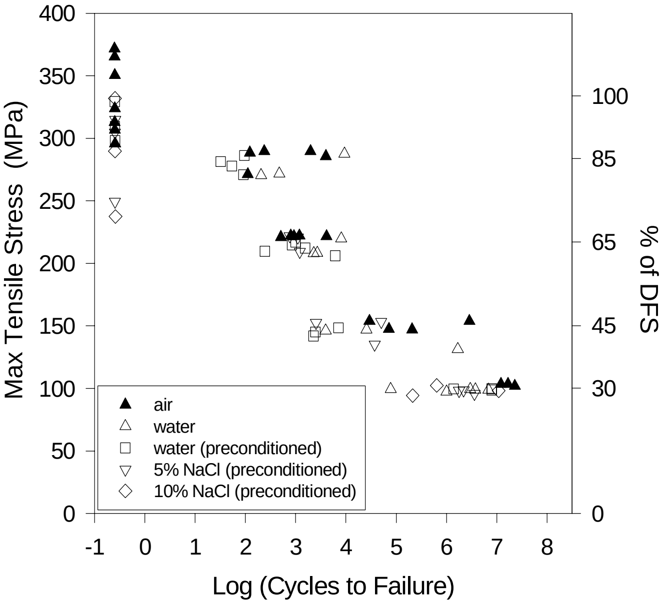

Figure 3: *SN curve for fatigue data on all samples.*

Although previous studies [20] have found that the corrosive effect of a fluid on glass fibers varies depending on factors like fluid pH and absorption level, no differences were found in the work here for any of the fluid exposure conditions, **B** through **E**, and loads, 30 % to 85 % of DFS. It is possible that small differences in response do exist and they are overwhelmed by material variability in the specimens, but major differences were not seen here. This is true even where differences might be expected. Compare, for example, the results for tests under conditions **B** (water, no preconditioning) and **C** (tested in water after preconditioning in water for 5 months). As shown in Fig. 2, even before fatigue testing starts with condition **C**, the water content from preconditioning was over 0.6 % (by mass). For condition **B** samples tested at 30 % DFS, the rate of water absorption was high, but even at failure (top points in Fig. 2), the water content only 0.3 % (by mass). Obviously, water content alone is not the critical factor. Bonniau and Bunsell may have reported a related effect when they observed that damage in their tests was not related to the quantity of water absorbed but to the time of exposure and temperature after the water concentration limit was passed [11]. The results discussed above (conditions **B** and **C**) can also be compared to data for tests at condition **D** (5 % NaCl) and **E** (10 % NaCl). This shows that adding NaCl to the water does not seem to have a significant effect on fatigue life since no differences in life data were found.

Environmental Fatigue Degradation Mechanism

It has been suggested by a number of previous studies that the fiber/matrix interphase has a controlling effect in the environmental fatigue performance of fiber reinforced composites [21,22]. If the fiber/matrix interphase region is damaged or destroyed during fluid ingression, matrix cracks may propagate more easily because fibers have lost their reinforcing function. This assumption matches well with the fact that small matrix cracks appear earlier on the edge of specimens under environmental fatigue than those tested in air. It seems that the competing effect of matrix plasticization as a result of fluid uptake (which increases the failure strain) is overwhelmed by the environmental damage to the interphase region. Examination of the failure surfaces under SEM revealed a morphological difference on the fiber surface. Typically, more matrix residue adhered to the fiber surface of dry specimens, while "cleaner" fiber surfaces with much less matrix adherent are seen from specimens failed under environmental fatigue. The morphological difference on the fracture surface indeed suggested that fluid action degrades the adhesion between the fibers and the matrix. The same observation is also reported by Sekine et al [14].

The process of environmental fatigue, then, involves coupled interaction between interphase degradation and matrix cracking: once cracks in the matrix are developed, ingress of corrosive fluid into the material is at a much faster rate, which further accelerates the degradation process of the interphase region. Degradation of fiber strength cannot be deduced from data in this paper; however, other studies [14] have shown evidence that glass fibers can degrade when in a composite exposed to water.

Although there isn’t sufficient data to prove a theory that fully explains the observations discussed above, it is interesting to speculate. One step is to recognize that there are three potential factors driving the degradation process and hence dictating the fatigue life: the loading itself, water with no load present (preconditioning experiments), and water in the presence of load or stress concentrations. This concept is similar to the idea proposed by Phillips (24). To explain the results here, however, the three factors must act at different rates depending on the conditions. The rate at which the first factor, loading, degrades the sample depends on the maximum load in the cycle and is fairly rapid at high loads. The second factor, water in the absence of loading, produces a degradation which is so slow that the time scales of the experiments here were not long enough to allow observable effects. The third factor, water attack of the fiber-matrix interface in the presence of loads, apparently gives an intermediate rate of degradation. If high loads are involved, the loading itself produces short fatigue lives so there isn't enough time for water to attack the interface. On the other hand, low loading gives longer fatigue lives, and this allows water attack to occur, to accelerate the interface degradation, and to decrease fatigue life. If this hypothesis is true, it suggests a very interesting experiment. Conducting fatigue tests at lower frequencies would increase the time required to reach the critical cycles to failure at higher loads. This would allow more time for water to attack the interface and decrease the fatigue life. Consequently, the detrimental effect of water on fatigue life should be seen at higher loads.

Concluding Remarks

Based on the findings in this study, the following can be concluded:

- Immersion in water and NaCl solutions results in some degradation of flexural strength for the pultruded glass reinforced composite tested here.

- At cyclic loads above 45 % of the flexural strength (DFS), specimens gave the same behavior when tested in air, in water, or in NaCl solution. In this loading regime, the behavior depends on load but is independent of environment. The fatigue lives were less than 10^7 cycles in all cases.

- At a cyclic load of 30 % DFS, however, results indicate that water and NaCl water have a significant detrimental effect on the life of the coupon, a regime of stress and environment-dependence. This regime is characterized with fatigue life beyond 10^7 cycles.

- The data collected so far indicate that the fatigue lives of specimens preconditioned in water or NaCl solution for about 5 or 6 months did not appear to differ from those for specimens that were not preconditioned.

- Where environmental effects are seen, a major contributor to the reduction in performance appears to be damage of the fiber/matrix interface.

A fatigue limit has not been demonstrated from the data collected thus far. The fatigue behavior still depends on both environment and load at 30 % DFS. If a regime exists where the behavior depends on environment but not load, it must be below 30 % DFS. The concept that the matrix cracking stress in air may be taken as an allowable design stress for environmental fatigue (as matrix cracking allows faster fluid ingression) is inconsistent with the data presented in this paper, because matrix cracking depends on both load and environment [23].

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