

Effects of Environmental Aging on the Properties of Pultruded GFRP

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Abstract

Pultruded glass-fiber-reinforced vinyl ester matrix composite coupons were subjected to environmental aging in order to study their durability since such composites are of interest for infrastructure applications. Specimens were tested as received and after aging in water or salt solutions at room temperature (25 °C) or in water at 75 °C for various times. The flexural properties (strength and modulus) were determined for bending perpendicular to the 0° orientations (0° being the pull direction) for all aging conditions. In addition, flexural properties in the 90° orientation and tensile properties in the 0° orientation were also measured for as-received specimens and specimens exposed to selected aging conditions. Both strengths and moduli were generally found to decrease with environmental aging. Comparing fracture mirrors on the broken ends of the fibers in aged and un-aged samples suggested that environmental aging decreased the *in situ* fiber strength. In addition, examination of the failure surfaces and comparisons between the strength of 90° specimens suggested that degradation of the fiber/matrix interface region also occurred during the aging process.

Keywords: composites; environmental aging; fatigue; fiber/matrix interphase; glass fiber; modulus; strength; vinyl ester; water

1. Introduction

Glass-fiber-reinforced composites (or glass-fiber-reinforced plastics, GFRP) have seen limited use in the building and construction industry for decades. Because of the need to repair and retrofit rapidly deteriorating infrastructure in recent years, the potential for using fiber-reinforced composites in a wider range of applications is now being realized [1-4]. Fiber-reinforced composites offer better resistance to environmental agents and the advantages of high stiffness-to-weight and strength-to-weight ratios when compared to conventional construction materials. One of the obstacles preventing the extensive use of composites, however, has been a lack of long-term durability data. New studies and data pertaining to infrastructure applications are in great demand, especially for composites produced by low-cost, large-volume processing methods such as pultrusion.

In the present study, pultruded GFRP coupons were aged in several different conditions that simulate common outdoor environments. The tensile and flexural properties were determined after these exposures. The effects of environmental aging on each of the constituents (the fiber, the matrix, and the fiber/matrix interface region) were studied in pultruded GFRP samples were studied by measuring the tensile and flexural properties.

2. Material and Method¹

The material under study is pultruded E-glass fiber-reinforced vinyl ester composite provided by Strongwell, Bristol Division (formerly known as Morrison Molded Fiber

¹Certain commercial materials and equipment 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, nor does it imply necessarily that the items are the best available for the purpose.

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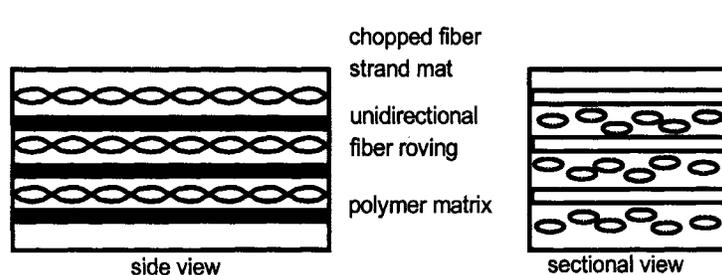


Figure 1: Schematic of the structure of the pultruded composite material being studied.

Glass). This material is designated EXTREN[®] 625. Structurally, this material consists of alternating layers of unidirectional fiber roving and chopped fiber strand mat embedded in vinyl ester matrix, shown schematically in Fig. 1. The fiber volume fraction determined from burn-off experiments is about 0.34 with a standard uncertainty of 0.02. 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 cm² nominal cross sectional area), some specimens may contain more fiber roving than others, and this produces considerable scattering in mechanical properties data.

The as-received materials were 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 four-point bend test. Strength and modulus were determined as outlined in D790-92. The strength corresponded to the maximum stress in the surface of the tension side of the four-point bend specimen. Coupons with dimensions 25.4 cm x 1.3 cm x 0.64 cm (10.0 in x 0.5 in x 0.25 in) were also cut for tensile tests. Composite end tabs were bonded to the tensile specimens as outlined in the ASTM specification D3039/D3039M. The strength and modulus were calculated as outlined in that specification. Specimens with fiber roving parallel to the longitudinal axis (hereafter referred to as 0° specimens) and with fiber roving perpendicular to the longitudinal axis (hereafter referred to as 90° specimens) were cut for flexural tests; only 0° specimens were cut for tensile tests.

The flexural properties (strength and modulus) were measured to 0° specimens as received and after aging in fluids. The fluids included water and two salt solutions, one containing a mass fraction of 5 % NaCl and the other containing a mass fraction of 10 % NaCl. For the remainder of the paper, the terms 5 % salt solution and 10 % salt solution will be used to designate the particular fluid involved. The aging conditions are:

- a. de-ionized water for up to 3900 h at room temperature,
- b. 5 % salt solution for up to 3980 h at room temperature,
- c. 10 % salt solution for up to 6570 h at room temperature,

and

- d. de-ionized water for 2400 h at 75 °C.

The flexural properties (strength and modulus) were measured for 90° specimens as received and after aging in the following conditions.

- e. de-ionized water for up to 7940 h at room temperature, and
- f. de-ionized water for up to 1360 h at 75 °C.

The tensile properties (strength and modulus) were measured for 0° specimens as received and after aging in the following conditions.

- g. de-ionized water for up to 9120 h at room temperature.

The conditions, water and salt solutions were chosen to simulate rain and salt spray, two commonly encountered outdoor environments. Samples aged at elevated temperature were tested since high temperature is often used as a way to shorten the conditioning time and accelerated the testing. To study sorption behavior, mass changes for the specimens during aging were recorded at regular time intervals using an electronic balance. Tensile and flexural tests were conducted in a servo-hydraulic test frame with an extensometer used to record the strain during a tensile test, and a displacement gage was used to measure the mid-span deflection under four-point bend load.

3. Results

3.1 Sorption behavior

The amount of fluid absorbed by both the 0° and 90° specimens during aging was closely followed. Results are presented in Fig. 2. Each data point in the figure represents the average value of 5 to 10 specimens. Sorption behavior in conditions a, b, c, and e all follow Fickian behavior: a rapid initial mass gain which slows and approaches saturation after prolonged immersion. Mass increase in the coupons depends on the concentration of salt, the higher salt concentration produces a lower change in mass. For instance, average mass increase after 3,900 h of immersion in water, 5 % salt solution,

and 10 % salt solution are 0.64 %, 0.52 %, and 0.45 %, respectively. The mass increase during room temperature aging also seems to depend on fiber orientation: the percent increase for 90° coupons is higher than that of 0° coupons.

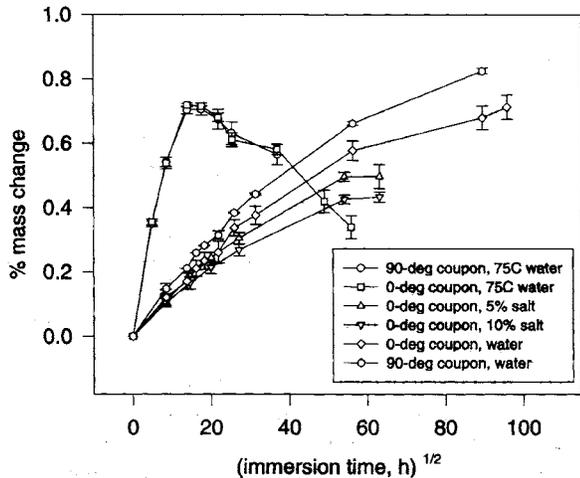


Figure 2: Sorption behavior of pultruded composite coupons under various aging conditions. The percent mass change is calculated as $100(m - m_0)/m_0$, where m_0 is the initial mass and m is the current sample mass. The standard uncertainty in the measurement of the mass fraction of sorbed fluid is estimated as 0.01 %.

For specimens aged in 75 °C water, the maximum percent mass increase was about 0.75 % in 200 h and started to decrease afterwards. The mass increase dropped to 0.34 % in 2,400 h. The 0° and 90° specimens show similar mass change at this temperature. This is consistent with results at elevated temperatures for other types of polymeric composites discussed in a comprehensive review by Weitsman [5]. Usually, weight loss at elevated temperatures is closely associated with hydrolysis, or the separation of side groups from the polymer chain, or the dissociation of matter located around the fiber/matrix interphase region [5].

3.2 Flexural properties of 0° and 90° specimens

Results of the flexural tests for 0° specimens are summarized in Figs. 3 and 4. Compared to the as-received specimens, the flexural modulus of 0° specimens aged in conditions a, b, and c remains essentially the same (Fig. 3). The effects of salt concentration on flexural modulus cannot be differentiated for up to 6,570 h. The aging time for specimens in condition c (10 % salt solution) is 65 % longer than those in condition b (5 % salt solution). Since condition c might be considered the most savier, this implies that significant modulus drop is not expected for specimens in conditions a and b, for at least up to 6570 h. No significant modulus drop was seen for 0° specimens aged in condition d (75 °C water for

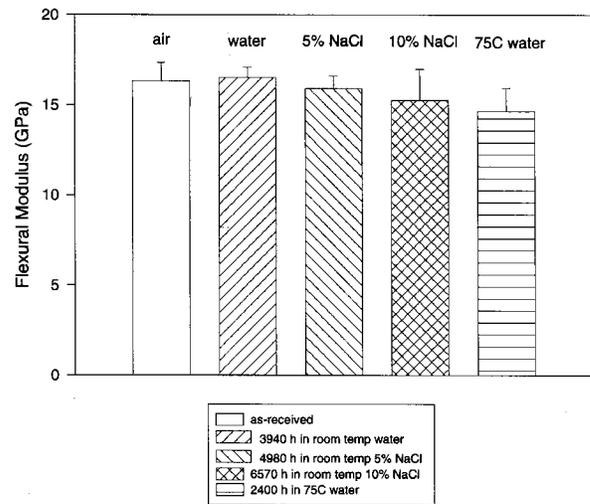


Figure 3: Flexural modulus for 0° specimens of pultruded composite coupons before and after environmental aging. Error bars represent the standard uncertainty in the experimental data.

2,400 h) either. As indicated in Fig. 3, even the drop of 10 % for the mean flexural modulus for this group of hot-water aged specimens is not clearly outside the experimental uncertainty.

The flexural strength after aging, however, showed some degree of degradation (Fig.4). The mean flexural strength for 0° specimens aged in conditions a, b, and c showed a 4.8 %, 12 %, and 13 % decrease, respectively. It seems that aging in salt solutions resulted in a larger decrease in flexural strength. The failure strains also decreased for the aged specimens. The average failure strain for as-received and those aged in conditions a, b, and c are 2.14 %, 1.90 %, 1.97 %, and 1.94 %, respectively. A more significant drop in flexural strength was seen in specimens aged in condition d where an average 40 % drop in flexural strength was seen (Fig.4). The failure strains was 1.34 %.

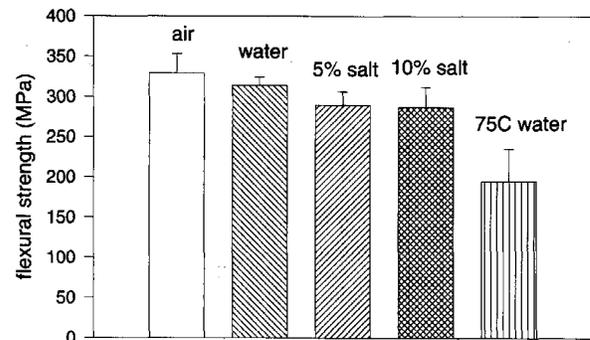


Figure 4: Flexural strength for 0° specimens of pultruded composite coupons before and after environmental aging. Error bars represent the standard uncertainty in the experimental data.

Macroscopic failure modes under flexural loading for the as-received and room-temperature-aged specimens closely resemble each other. Typical load-displacement curves are shown in Fig. 5. These curves remain quite linear prior to failure. Failure process under quasi-static flexural loading begins with the development of parallel matrix cracks transverse to the longitudinal direction on the lower surface sustaining tensile stress; followed by failure of the unidirectional fiber roving, and initiation and propagation of a “delamination”, longitudinal through-the-width cracks between fiber roving and the layers of fiber strand mats, or between the fiber strand mats themselves.

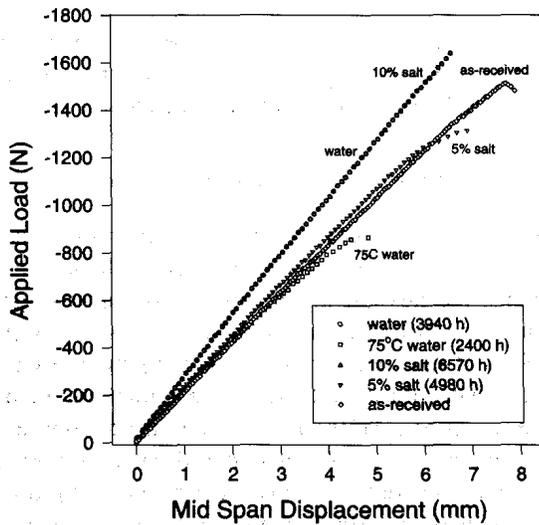


Figure 5: Typical load versus mid-span displacement curves under four-point-bending loading. Data for the specimen labeled “water” are hidden behind the data labeled “10 % salt.” The standard uncertainty in the experimental data is 5 N.

Results of flexural tests on 90° specimens are summarized in Figs. 6-7. Compared to those without aging, the flexural modulus for coupons aged in conditions e (room temperature water for 7,940 h) and f (75 °C water for 1,700 h) showed a 13 % and 19 % drop, respectively. Significant flexural strength degradation was seen for the 90° specimens. Those aged in conditions e and f showed a 21 % and 54 % drop in flexural strength, respectively. The failure strains for the as-received samples and those aged in conditions e and f are 2.0 %, 1.9 %, and 1.0 %, respectively.

3.3 Tensile Properties of 0° specimens

A group of specimens were also aged in room temperature water for 9,120 h before tested to failure in tension. The mean tensile modulus after aging (14.4 GPa) is 23 % lower than that before aging (18.6 GPa). The mean tensile strength after aging

(227 MPa) was dropped by 29 % compared to those without aging (160 MPa). The failure strain for the as-received and the aged specimens are 2.1 % and 1.4 %, respectively.

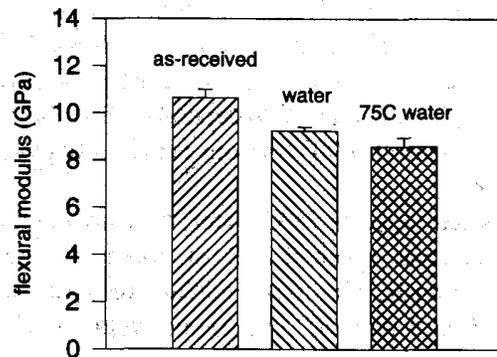


Figure 6: Flexural modulus for 90° specimens of pultruded composite coupons before and after environmental aging. Error bars represent the standard uncertainty in the experimental data.

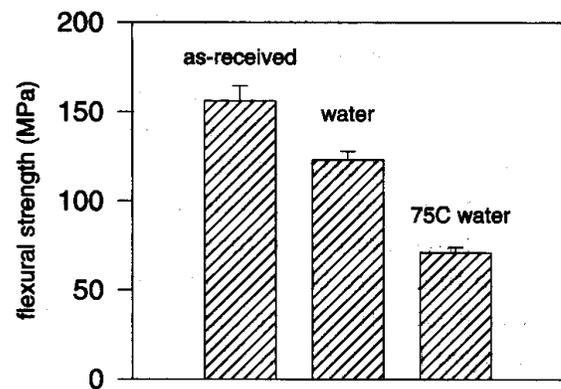


Figure 7: Flexural strength for 90° specimens of pultruded composite coupons before and after environmental aging. Error bars represent the standard uncertainty in the experimental data.

4. Discussion

Changes in mechanical properties of the composite material as a consequence of fluid ingress may be reversible, partially reversible, irreversible, or a combination of these types depending on the exposure time and conditions [6]. For the reversible process which involves plasticization and swelling of the polymer matrix, the mechanical properties can usually be restored by drying [Antoon,1980]. In the case of irreversible processes resulting in damage to the fibers, matrix cracking, debonding of the fiber/matrix interphase region, and delamination caused by swelling and/or internal stress generation, the mechanical properties are permanently altered [6-8].

Damage of glass fibers by fluids is initiated by physical or chemical reactions between the two. The extent of damage depends on fluid type, fluid concentration, as well as the composition of the fibers under attack. Numerous studies have proven that the fiber/matrix interphase region plays a crucial role in durability of composites in aqueous environment [9-13]. Fibers may be left debonded from the matrix as a consequence of fluid attack on the fiber/matrix interphase region. Improved bonding between the fiber and the matrix, particularly chemical bonding (i.e., the use of coupling agents), tends to delay the corrosion process and minimize loss in mechanical properties. The detrimental effects of fluid absorption on the matrix of the composites seem to be only secondary compared to the damage in the fibers and the fiber/matrix interphase region [6]. In general, the higher the temperature of the environment and the longer the exposure time, the larger the decrease in strength and modulus of GFRP. Compared to aging at lower temperatures, significant degradation for GFRP occurs at temperatures above 70 °C, a consequence of fiber/matrix debonding leading to delamination and cracking combined with plasticization of the matrix [14]. In the light of previous studies, we will discuss the effects of environmental aging on strength and stiffness degradation by focusing on the fiber and the fiber/matrix interphase region.

4.1 *In situ* fiber strength degradation

It is now well understood that the strength of glass fiber degrades upon exposure to corrosive fluids [15-17]. Metcalfe and Schmitz suggested that the underlying mechanisms of stress corrosion is driven by the exchange of alkali metal ions (Na⁺ and K⁺) in the glass and hydrogen ions (H⁺) of the attacking fluid [16]. Michalske and Frieman have proposed a molecular model for stress corrosion of glasses and ceramics in which the silicate network (Si-O-Si bond) is destroyed by water molecules [17]. Vauthier, *et al.* showed that more broken fibers were found in environmentally aged GFRP samples than those without aging, implying degraded *in situ* fiber strength by aging [18].

It has been shown by many studies that the morphology of the fracture surface of glass or ceramics can be related to the its breaking stress [19-21]. A typical broken fiber showing a distinct pattern of mirror, mist, and hackle is shown in Fig. 8. The relationship between the breaking stress, σ , and the radius of fracture mirror, r , is

$$\sigma \sqrt{r} = A \quad (1)$$

where A is a constant. To evaluate the *in situ* fiber strength in different groups of 0° specimen (as-received, conditions **a**, **b**, and **d**), one specimen from each of these groups with the flexural strength close to the mean flexural strength of their respective groups was selected. Fifteen to twenty individual

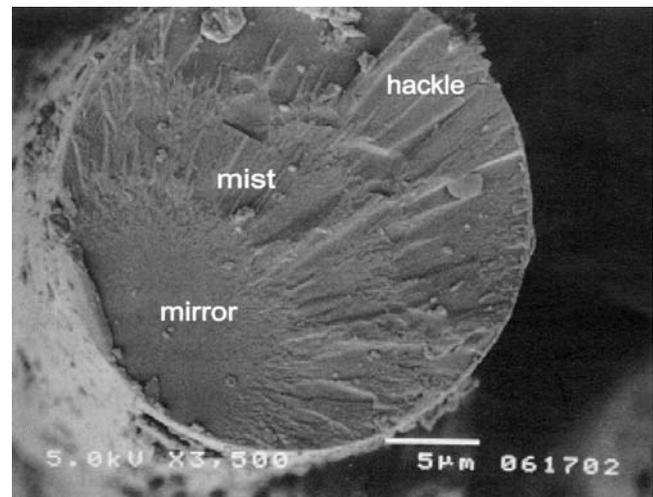


Figure 8: Scanning electron micrograph of fiber end produced by failure showing typical surface features: mirror, mist, and heckle pattern.

fibers with distinctive fracture mirror near the tensile failure surface were randomly selected, and the size of the fracture mirrors was measured from SEM images. To compare the *in situ* fiber strength between selected specimens, the mirror sizes measured from selected fibers of each specimen are ranked in descending order (such that the breaking stress is in ascending order) and a probability of failure is assigned to each of these broken fibers using a median rank method. By doing so it is assumed that the strength of selected fibers is representative of the specimen group. It should be mentioned that not every individual broken fiber exhibits a distinct fracture mirror. Eckel and Bradt suggested that fibers without a distinctive fracture mirror are results of low stress fracture [22]. Here low stress fractures are not taken into account in determining the fiber strength distribution. Although by excluding low stress fractures the fiber strength distribution may not represent the actual distribution, it nevertheless represents an upper limit [22], and therefore a comparison between different groups is viable in revealing the effect of aging on fiber strength.

Results for fracture mirror measurements from 0° specimens are shown in Fig. 9. Noticeable difference in probability of failure is seen between the aged and as-received specimens. The as-received specimen has stronger fibers and displayed a broader fiber strength distribution while the aged specimens have weaker fibers and showed a narrower distribution. At this point, the cause for the apparent change in the strength distribution is unclear. However, a strong link between fiber strength degradation and observed in flexural strength degradation is suggested by the results of fracture mirror measurements.

If the data in Figure 9 are taken as an indication of relative fiber strengths, it is worth noting that the strengths of fibers in specimens aged for 2400 h in 75 °C water are not significantly

different than those of fibers in specimens aged in water at room temperature for 3900 h. In contrast, the flexural strength of composites aged in hot water dropped by 40 % while the samples aged in water at room temperature decreased by a few percent. This discrepancy implies that the fiber/matrix interphase region and/or the matrix also played an important role in the accelerated degradation process.

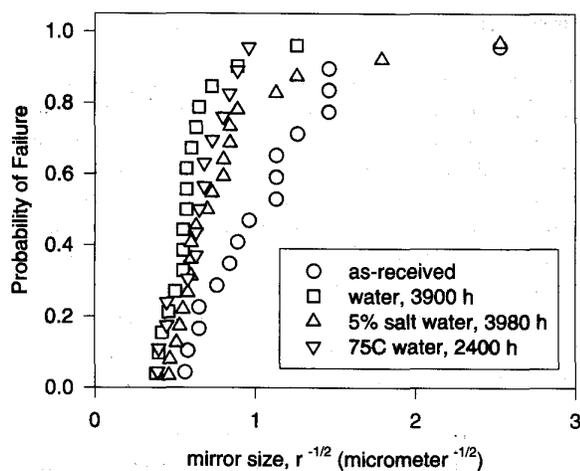


Figure 9: Relationship between the mirror size and the probability of failure based on a ranging of fiber strengths predicted from the radius of the fracture mirrors.

4.2 Degradation of the Fiber/Matrix Interphase Region

Failure of the 90° specimens were accompanied by through-the-width matrix cracks transverse to the loading direction on the tensile failure surfaces. These cracks were recorded for as-received 90° specimens and 90° specimens aged under conditions e and f. The average crack density (in number of cracks per cm) within the load points for as-received, water-aged (condition e), and hot-water aged (condition f) specimens are 1.7 cm⁻¹, 1.1 cm⁻¹, and 1.0 cm⁻¹, respectively. The decrease in transverse crack density after aging could be attributed to either the degradation of the fiber/matrix interface region or the matrix plasticization, or both. If the matrix interface region was weakened, transverse surface crack may grow more quickly into the thickness of the specimen, and this might reduce the stress levels at the surface. A more likely explanation, however, is that the matrix is plasticized by water which makes the resin more resistant to cracking.

Appicella, *et al.* suggested that there is a competitive effect between matrix plasticization as a result of water sorption and stiffness increase due to the loss of low molecular weight substances [7]. They showed that, after immersion in 20 °C water for 50 days, vinyl ester resin showed a 10 % increase in stiffness, and 42 % and 57 % drop in ultimate strength and failure strain, respectively. For vinyl ester specimens immersed at 90 °C for 50 days, there was a 6 %

drop in stiffness. The failure stress was increased by 59 % while the failure strain decreased by 60 %. In any case, failure strain of vinyl ester was decreased after the aging processes in water. Supposing that there is no change in the fiber/matrix interphase region, the results of Appicella, *et al.* indicate an increase in crack density at a lower load level because of the decrease in matrix failure strain. However, our observation suggest the opposite.

Previous studies have asserted that the fiber/matrix interphase region has a controlling effect on the environmental aging of GFRP. Gaur, *et al.* showed that the bond strength of E-glass/epoxy microcomposite degraded about 40 % after aging in 88 °C water for an hour using a microbond pull-out technique [11]. Wagner and Lustiger showed that the fiber/matrix interfacial energy (a function of the fiber geometrical and mechanical characteristics) decreased after immersion in 95 °C water for up to 336 h [12]. Schultheisz, *et al.* showed, using a single-fiber fragmentation test of E-glass/epoxy model composites, that both the strength of the fiber and the strength of the interface degraded after immersion in water at 25 °C and 75 °C for 4000 h [24]. Pritchard and Taneja observed debonded fiber-resin interface of glass/polyester composites aged in water for up to 1500 h in the temperature range from 35 °C to 80 °C, even without externally applied load [23]. Bradley, *et al.* observed fiber/matrix interfacial failure in transverse glass/vinyl ester composites as a result of aging in sea water for up to 90 days [25].

When the failed specimens were examined under SEM, fiber surfaces with adhered residue were seen in as-received specimens while smooth fiber surfaces with much less residue were seen in aged specimens, indicating degraded interfacial bonding by environmental aging. Typical SEM images are shown in Figs. 10-11. Similar observations were also given by Watanabe [26], Sekine, *et al.* [27], and Komai, *et al.* [28].

Decreased strength and modulus of 90° specimens are indications of degraded fiber/matrix interphase region. Carlsson and Pomies reported that the transverse modulus and strength of E-glass/epoxy were reduced to less than 50 % of its dry value after 4800 h immersion in water at 35 °C [29]. Similar findings are also provided by Bradley, *et al.* [25]. Compared to 0° specimens, 90° specimens showed more significant drops in flexural strength and modulus, which is attributed to the degraded interphase region. After aged in room temperature water for 7940 h, the flexural modulus and strength of the 90° coupons were decreased by 13 % and 21 %, respectively. For approximately the same amount of degradation, an additional 1200 h was required for the 0° specimens. Also, compared to a 40 % drop in strength of the 0° specimens after 2400 h aging in 75 °C water, the strength degradation for 90° specimens was 54 % after only 1360 h. Thus interfacial degradation is evident.

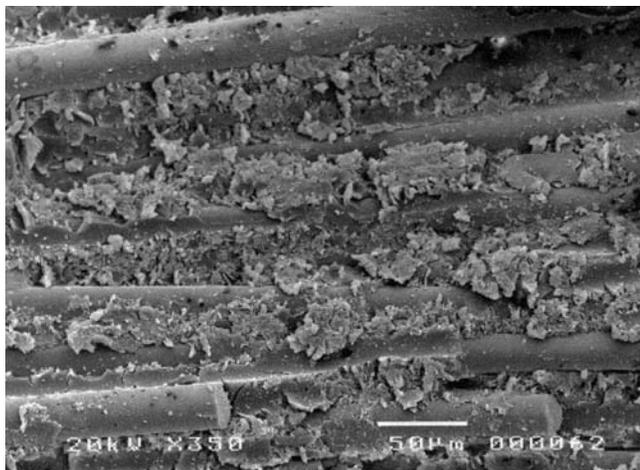


Figure 10: Failure surface of 90° flexural specimens tested before environmental aging showing significant matrix resin adhering to the fiber surfaces.

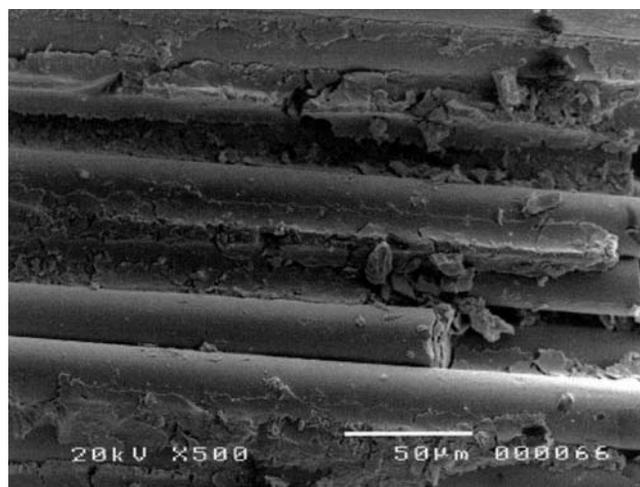


Figure 11: Failure surface of 90° specimens tested after environmental aging showing smooth fiber surfaces with relatively little matrix attached.

4.3 Is there a stress-corrosion knee ?

The substantial tensile strength and modulus degradation of 0° specimens after 9120 h of aging in room temperature water (23 % drop in tensile modulus and a 29 % drop in tensile strength) is worth noticing. Compared to only a 4.8 % drop in flexural strength and essentially no modulus drop in condition **c** after 6570 h, these degradations were abrupt. It has been well-established now that glass fibers exhibit a non-linear behavior under stress corrosion and zero-stress aging where an abrupt drop in strength occurs after exposure to corrosive environment for a certain period of time. The mechanism,

suggested by Matthewson, is the initiation of new surface flaws by surface dissolution [30]. Similar findings were also reported by Cuellar, *et al.* [31]. Metcalfe and Schmitz also reported some earlier work showing similar result on E-glass filaments aged in water and 100 % relative humidity [16]. For composites, Hojo and Tsuda showed that sudden decrease of tensile strength happened for E-glass/vinyl ester composite in NaOH and HCl [32], and Phillips showed a stress-corrosion knee exists in environmental stress corrosion of glass/polyester composites [33]. Although our data did not conclusively indicate such a nonlinear effect for pultruded GFRP, further long-term aging experiments need to be conducted for clarification.

4.4. On Accelerated Testing

It is clear now that different sorption behavior for aging in elevated temperatures indicates a different aging mechanism. From fracture mirror measurements, it is shown that fiber strength degradation in 75 °C water for 2400 h is comparable to aging in room-temperature water for 3900 h. As a result, the higher percentage of strength and modulus drop in hot-water aged coupons implies severe degradation in matrix and the interphase region. Therefore, when correlating results from accelerated aging to normal aging process, all of the aforementioned factors must be accounted for in an appropriate way.

5. Conclusions

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

- Aging in water and salt solutions results in degraded flexural and tensile properties of pultruded E-glass fiber reinforced vinyl ester matrix composite.
- Salt concentration does not seem to affect flexural properties in a noticeable way.
- Degradation of glass fibers is evident by fracture mirror measurements.
- Evidence of matrix and interphase contribution in environmental degradation is shown by crack density measurements, transverse strength degradation, and fiber surface morphology.
- Accelerated aging can produce changes in constituents at different rates as compared to the normal aging process. As a result, caution should be exercised when correlating accelerated aging to normal aging process.

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