EVALUATION OF ENVIRONMENTAL EFFECTS ON POLYMER MATRIX COMPOSITES BY MICROMECHANICAL AND MACROMECHANICAL TESTS

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ABSTRACT

Degradation of the mechanical performance of carbon/vinylester, carbon/epoxy, E-glass/vinylester, and E-glass/epoxy composites subject to water exposure (distilled water at RT and seawater at RT, 40, and 60°C) has been experimentally investigated. Water absorption behavior of neat resins and composites was studied by monitoring their weight gain. Resins and fibers were characterized by mechanical testing at dry and wet conditions. To monitor the fiber/matrix (F/M) interface degradation, the single fiber fragmentation test was used. The F/M interface shear strength was reduced and extensive F/M debonding was found after water exposure. Transverse flexure tests of dry and wet composites were also conducted. Transverse strength was substantially reduced after water exposure implying that the severe F/M interface degradation found by micromechanical testing also influenced the macroscopic behavior of the composite. The tests results evidence water degradation of the F/M interface as a major strength limiting mechanism.

1. INTRODUCTION

Fiber reinforced polymer matrix composites are established structural materials in marine applications as they offer several advantages over monolithic materials such as metals, ceramics, and plastics. Such advantages include low density, high specific stiffness and strength, and lack of corrosion. However, moisture absorption is a common scenario in composite materials which may lead to a number of undesirable effects, such as degradation of the matrix, fiber, and fiber/matrix (F/M) interface.

The structural integrity of fibrous polymer composites is critically dependent on the stability of the fiber, matrix, and fiber/matrix interface [1]. A strong adhesion between fiber and matrix assures efficient load transfer; it delays the onset of microstructural damage formation and reduces the rate of damage accumulation, which is necessary for material long-term property retention [2]. Absorption of moisture may degrade the fiber/matrix interface resulting in a reduction of the adhesion between fiber and matrix. Therefore, the analysis of the environmental effects in the fiber/matrix interface region becomes extremely important.

The aim of this work is to experimentally investigate the degradation of polymer matrix composites subject to water. The single fiber fragmentation test (SFFT) is used to determine the fiber/matrix interface shear strength and extent of fiber debonding. Transverse flexural tests are performed on composite test specimens to examine the influence of the integrity of the matrix and fiber/matrix interface on the macroscopic response. In addition, flexure and tensile tests are performed on the matrix materials, and the tensile strength reduction of the fibers is monitored using the single filament test (SFT).

2. MATERIALS AND SPECIMENS

The fibers used in this project are T700 carbon fibers from Toray with "F" sizing which is a sizing especially designed by the manufacturer to be compatible with vinylester resins, AS4 unsized carbon fibers from Hexcel, and E-glass fibers from 3TEX with silane sizing. The fibers are combined with the following resins: MAS epoxy, Ashland Derakane 411-350 vinylester (VE D411), Ashland Derakane 8084 elastomer modified vinylester (VE D8084), and Hetron 922L pre-promoted vinylester (VE H922L).

2.1 Single Fiber Fragmentation Test Specimens

The single fiber fragmentation test (SFFT) employs a single fiber embedded in a resin matrix which is molded into a dog-bone specimen as shown in Fig. 1.

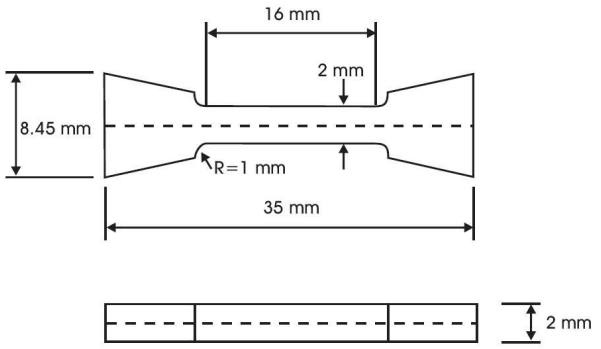


Figure 1: Single fiber fragmentation test (SFFT) specimen [3]

The following fiber and matrix combinations were studied using the SFFT: T700/VE D411, T700/VE D8084, T700/MAS epoxy, AS4/VE H922L, E-glass/ VED8084, and E-glass/MAS epoxy. The preparation of the SFFT specimen and processing of the resin are detailed in a paper to be submitted [4].

2.2 Composite Specimens

Unidirectional composites were made from T700/VE D411, T700/VE D8084, and T700/epoxy. Laminates consisting of four plies were fabricated using vacuum assisted resin transfer molding (VARTM) at room temperature (RT) and cured for 24 hours (RT). Then, post-cure was performed as specified for the resin used [4]. The panel thickness after post-cure was 1.2mm. Transverse flexure test specimens, 50.8 mm long and 12.7mm wide, were cut from the unidirectional composite plates.

2.3 Resin and Fiber Test Specimens

1.2mm thick resin panels were cast at room temperature between two glass plates (treated with release agent) and cured for 24 hours (RT) followed by post cure as specified for the resin used [4]. Then the panels were cut into straight-edge coupons 50.8mm long and 12.7mm wide for flexure testing. Dog-bone specimens with a gage length of 50mm and gage section dimensions of 12mm by 3.5mm were fabricated for tensile testing by pouring the resin into silicone rubber molds. For the single filament test (SFT), a single fiber was separated from a tow of fibers and mounted on a cardboard tab according to ASTM D3379 [5]

3. TEST PROCEDURES

3.1 Environmental Exposure

Selected specimens were immersed in water (distilled water at RT and seawater at RT, 40, and 60°C). The weight change was periodically monitored. Each time a specimen was removed from an immersion tank, it was carefully dried with a paper towel. Then, weight measurement was done using a precision balance. The moisture content, M, (in percent) is calculating using

$$M\% = \frac{W_t - W_o}{W_o} \times 100 \qquad (1)$$

where W_t is the measured weight of the specimen at time t and W_o is the specimen initial dry weight.

3.2 Material Characterization

Flexure tests on dry and wet neat resin specimens were conducted according to ASTM D790-03 [6]. The tests were conducted in a small three-point bending stage equipped with a 200N load cell at a cross head rate of 1mm/min, and support span of 23mm. The maximum flexural stress, σ_f, obtained from classical beam theory is

$$\sigma_f = \frac{3PL}{2wt^2} \qquad (2)$$

where P is the applied load, L is the support span, t is the thickness, and w is the specimen width. In addition, standard tensile tests were conducted on dry neat resin dog-bone specimens according to ASTM D638 [7]. The tensile failure strain is extremely important since the SFFT requires a ductile matrix in order to reach saturation of fiber breaks before matrix cracking. The test was performed in a MTS Insight 50 universal testing machine at a cross head speed of 2mm/min. An extensometer with 25.4mm gage length was used to measure the strain.

The single filament test (SFT), ASTM D3379-75 [5], was used to determine the tensile strength of dry and water immersed fibers. Tensile testing was performed at a cross-head speed of 0.5 mm/min in a MTS insight 1 universal testing machine equipped with a 2N capacity load cell.

The fiber volume fraction of composites was determined by hot nitric acid digestion of the matrix according to ASTM Standard D3171 [8] and the photomicrographic technique [9].

3.3 Single Fiber Fragmentation (SFFT) and Composite Tests

The single fiber fragmentation test was conducted on dry and moisture saturated specimens. The SFFT specimen was loaded in tension using a small hand-operated tensile stage. In the SFFT, the fiber axial stress is introduced through interfacial shear stresses acting parallel to the fiber [10]. The axial fiber stress increases from zero at the ends and assumes constant stress over most of its length. At a certain level of applied load, the fiber will fracture. If the loading is continued, shear stresses at the fiber/matrix interface will transfer load into the broken fiber and repetition of the failure process will occur until the remaining fiber fragments are so short that the shear stress transfer becomes insufficient to build up enough tensile stress in the fiber to cause any further break. This state is called break saturation, and the final fragmentation length is referred

to as the *critical length,* l_c. A stronger bond between fiber and matrix increases the transfer rate of load and results in a shorter critical fragment length.
Based on the measured lengths of the fiber fragments, it is possible to estimate the shear strength, τ, of the fiber/matrix interface. It is realized that a fiber may be considered as consisting of several links, each containing a flaw of varying severity. The fragment length is a statistical quantity described by Drzal and co-workers [11] by a two-parameter Weibull distribution analysis which leads to the following expression for the F/M interface shear strength

$$\tau = \frac{\sigma_f}{2\beta}\Gamma\left(1-\frac{1}{\alpha}\right) \qquad (3)$$

where α and β are the Weibull shape and scale parameters respectively, and Γ is the Gamma function. A long fiber has a higher probability of encountering a more severe flaw along the fiber length and should be weaker than a short fiber. To determine the fiber strength at the critical fragment length, which is usually less than 1mm, using the single filament test [5] is virtually impossible; therefore, fibers with larger gage lengths, l_o, are tested and the results are subsequently extrapolated to the critical length, l_c, using the Weibull weakest link theory [12]

$$\sigma_f = \overline{\sigma}_o\left(\frac{l_c}{l_o}\right)^{-1/w} \qquad (4)$$

where $\overline{\sigma}_o$ and σ_f are the fiber tensile strength at gage lengths, l_o, and l_c, respectively, and w is the Weibull shape parameter.

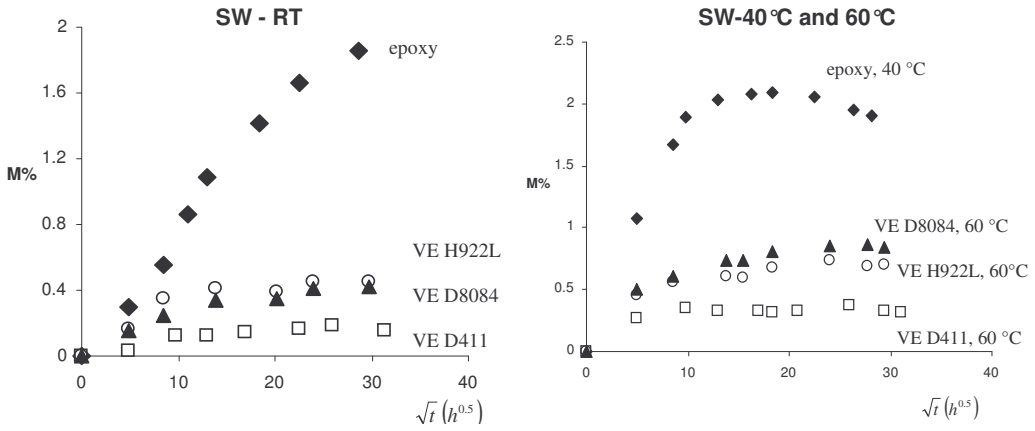
In addition to fiber fractures, debonding between fiber and matrix typically occurs when the fiber breaks. Fiber breaks and F/M debonding were examined during SFFT testing using photoelastic patterns observed in optical transmission microscopy (Olympus BX41 with a QICAM-FAST 1394 camera). The region around a fiber break exhibits a colored pattern called birefringence. This phenomenon is caused by shear stresses in the matrix [13]. Theoretically, the highest shear stress in the fiber should occur near the end of the fragment, however, as mentioned before, debonding between fiber and matrix typically accompanies a fiber break reducing the shear stress transfer at the interface.

The composite test specimens were tested in transverse flexure. The flexure test was conducted in a three-point fixture at a support span of 23mm in a small loading stage (Gatan, microtest 200) with a 200N load cell at a cross head rate of 1mm/min. The flexural strength is calculated from eq. (2)

4. RESULTS AND DISCUSSION

4.1 Water Absorption

Figure 2 illustrates curves of weight change of the neat resin specimens in seawater (at RT and elevated temperatures) vs. square root of immersion time. In general, the epoxy specimens absorb much more moisture than the vinylester specimens.

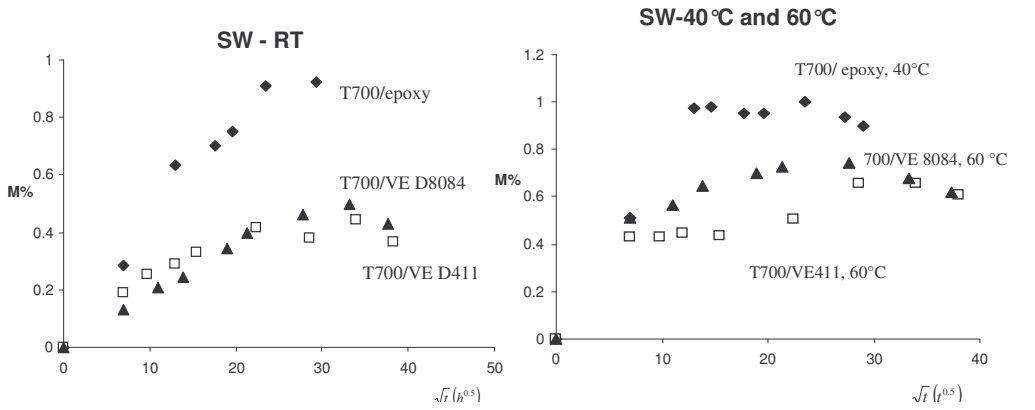


(a) (b)

Figure 2: Weight change for neat resin specimens in seawater as function of square root of immersion time. (a) RT and (b) 40 °C and 60 °C

For the vinylester resins, the pre-promoted (VE H922l) and rubber-modified (VE D8084) vinylesters absorbed about twice as much moisture as VE D411. It can be also noticed that exposure to water at higher temperatures leads to higher slopes of the initially linear portion of the curve indicating a higher rate of moisture transport. This phenomenon occurs since water diffusion is a thermally activated process [14].

Figure 3 illustrates curves of weight change of the composite specimens after immersion in seawater (at RT and elevated temperatures) as function of square root of time.



(a) (b)

Figure 3: Weight change of composite specimens after immersion in seawater as function of square root of immersion time (a) RT and (b) 40 °C and 60 °C

The T700/VE D411 composite specimens absorbed more moisture than the VE D411 neat resin specimens, T700/VE D8084 composite specimens absorbed about the same amount of moisture as VE D8084 neat resin specimens, while T700/epoxy composite specimens absorbed less moisture than the epoxy neat resin specimens. Taking into account the fact that the composites contain only about 36% resin (see section 4.3) and

that carbon fibers do not absorb water, moisture absorption along the F/M interface (wicking) and possibly through cracks and voids in the material becomes evident.

4.2 Material Mechanical Behavior

Figure 4 presents typical stress-strain curves of the various resins at dry conditions. Vinylester D411 and pre-promoted VE H922L resins present extremely similar stress-strain curves and high strength (around 76MPa), but their strain to failure (4.6%) is too low to be an effective resin for the SFFT. On the other hand, the elastomer modified vinylester (VE D8084) and the epoxy resins present lower strengths but higher ductility which should make them suitable for the SFFT.

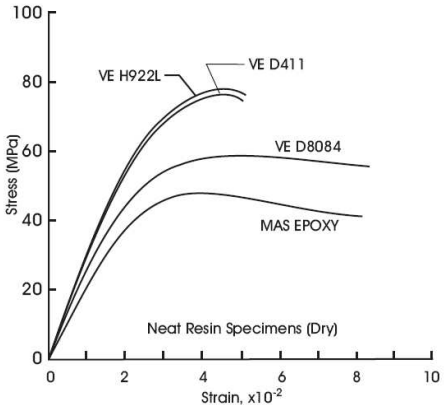


Figure 4: Tensile stress-strain curves for neat resin specimens

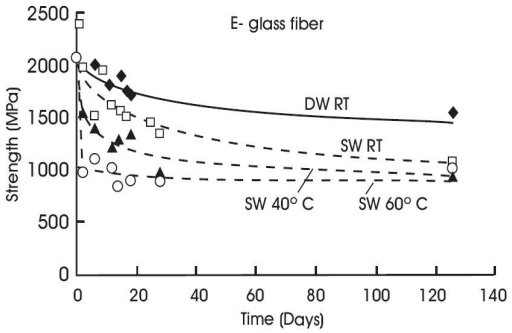


Figure 5: Tensile strength of E-glass fiber after immersion in water

The flexure test results for the resins listed in Table 1 show that the vinylester matrices were not significantly affected by exposure to water; the epoxy, however, presented extensive degradation (i.e. the flexure strength was reduced by a factor of about two after exposure to water at 40°C). This may possibly be related to the high water absorption by the epoxy resin.

Table 1: Flexure strengths of resins at dry and wet conditions.

	MAS EPOXY		**VE D411**		**VE D8084**		**VE H922L**	
	M(%)	σ^F (MPa)	M(%)	σ^F (MPa)	M(%)	σ^F (MPa)	M(%)	σ^F (MPa)
DRY	--	68.5 ± 2.1	--	132 ± 1.3	--	117 ± 1.1		135 ± 4.8
DW RT	1.82	42.5 ± 3.7	0.22	124 ± 0.9	0.40	108 ± 1.5	0.49	128 ± 3.4
SW RT	1.86	38.9 ± 3.6	0.19	126 ± 1.4	0.42	107 ± 0.6	0.45	127 ± 2.3
SW 40C	2.09	31.3 ± 2.1	0.33	132 ± 4.5	0.56	112 ± 1.8	0.60	134 ± 1.1
SW 60C	--	--	0.37	129 ±4.6	0.86	117 ± 1.3	0.73	132 ± 4.5

Table 2: Single fiber strength (at 20mm gage length)

	E-glass	**T700**	**AS4**
Diameter (μm)	14 ± 0.5	6.9 ± 0.3	7.1 ± 0.3
Strength (MPa)	2060 ± 353	4396 ± 905	4559 ± 636
σ_o (MPa)	2204	4756	4819
W	6.85	5.62	9.17

Table 2 summarizes the strength data for carbon and E-glass fibers at dry conditions where σ_o and w are the Weibull scale and shape parameters respectively. A graph of E-

glass fiber strength vs. time of exposure to water is shown in Fig. 5. The E-glass fibers are dramatically weakened by exposure to seawater, especially at elevated temperatures. For instance, E-glass fibers exposed to seawater at 60 °C lost 50% of their strength after two days of exposure. Carbon fibers, on the other hand, were found to be inert to water exposure.

4.3 Single Fiber Fragmentation Test Results

Figure 6 presents typical birefringence patterns at the fiber break saturation state for dry and moisture saturated E-glass/VE D8084 and E-glass/epoxy SFFT specimens. Both systems presented significant decline of the photoelastic pattern intensity after exposure to water showing large extents of F/M debonding.

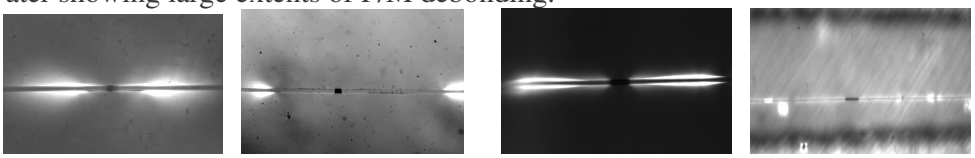


Figure 6: Birefringence patterns for glass fiber SFFT specimens; a) dry E-glass/VE D8084, b) wet E-glass/VE D8084, c) dry E-glass/epoxy, d) wet E-glass/epoxy.

Figure 7 shows typical birefringence patterns for dry and moisture saturated carbon T700/epoxy and AS4/VE H922L SFFT specimens at the fiber break saturation state. For the T700/epoxy SFFT specimens, the birefringence patterns in Figs. 7 (a) and (b) show an extremely large increment of debond length as indicated by the significant decline of photoelastic intensity after exposure to water. Evidently, the F/M interface was severely degraded.

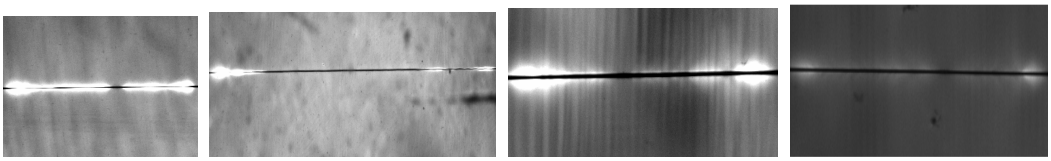


Figure 7: Birefringence patterns for carbon fiber SFFT specimens; a) dry T700/epoxy, b) wet T700/epoxy, c) dry AS4/VE H922L, d) wet AS4/VE H922L.

For the AS4/VE H922L SFFT specimens, Figs. 7(c) and (d), the low intensity of the birefringence patterns shows that the system has a very weak F/M interface even at dry condition. The birefringence patterns for the specimen tested after immersion in water at room temperature were extremely weak making it difficult to identify the fiber breaks. For the AS4/VE H922L SFFT specimens tested after immersion in seawater at elevated temperatures, the photoelastic effects were not detectable implying excessive debonding and therefore it was not possible to identify the fiber breaks and quantify debonds lengths. The weak F/M interface may be attributed to the fact that the AS4 carbon fiber was unsized.

The SFFT results are summarized in Figure 8. The E-glass systems performed better than the carbon systems (using current fiber sizing) in terms of retention of the F/M interface shear strength and debonding. However, it should be kept in mind that E-glass fibers degrade by exposure to water, especially at elevated temperatures, see Fig. 5.

The single fiber fragmentation test was unsuccessful for T700/VE D411 and T700/VE D8084 systems. The T700/VE D411 specimens failed before reaching saturation of fiber breaks due to the brittle nature of this vinylester resin. The few breaks that

occurred before specimen failure presented weak birefringence patterns indicating a poor F/M interface. The T700/VE D8084 specimens presented excessive debonding and extremely weak birefringence patterns making it very difficult to identify and examine fiber breaks (dry conditions); thus, implying that this system has a poor F/M interface.

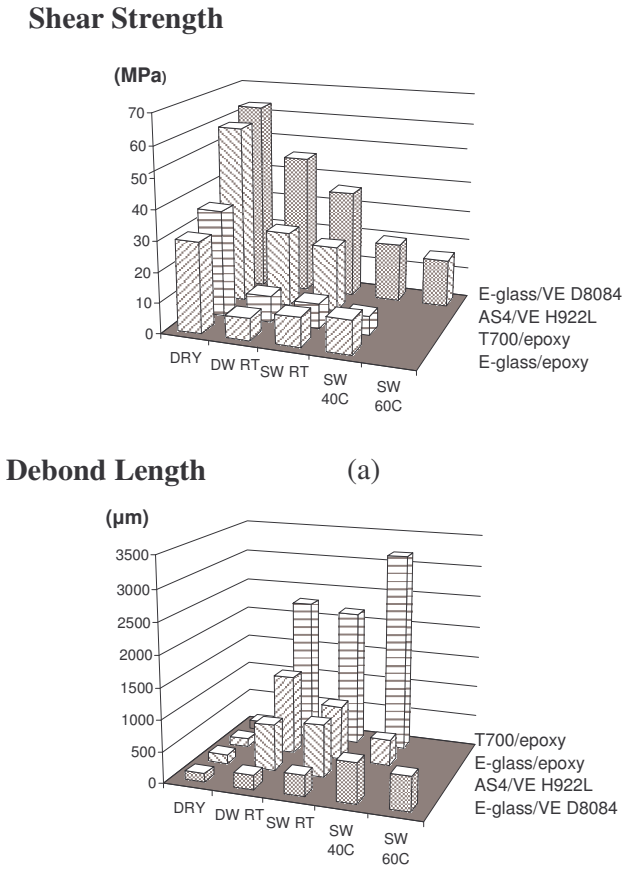


Figure 8: (a) F/M interface shear strength and (b) debond length of various fiber and matrix combinations exposed to water.

4.3 Transverse Flexure Strength

The fiber volume fraction of the composites is about 64%. Transverse flexure tests were performed on dry and moisture saturated specimens. T700/VE D411 and T700/VE D8084 specimens were tested after 900 hours of immersion in water while T700/epoxy specimens were tested after 800 hours of exposure. The transverse flexure strength results of these systems are graphed in Figure 9. At dry conditions, the flexure strength of the composites was much less than that for the neat resins, Table 1. For T700/epoxy and T700/VE D411 the flexure strengths are only about 30% of the flexure strengths of the resins. The transverse flexure strength of T700/VE 8084 is about 42% of the resin flexure strength. The higher transverse strength of this system may be due to the high matrix ductility which would prevent flaw propagation in the composite. The overall low transverse strengths for the systems is attributed to a weak F/M interface.

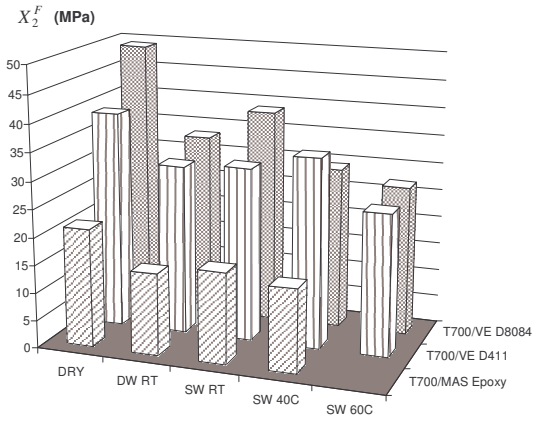


Figure 9: Transverse flexure strength of various composite systems exposed to water

After water immersion, large reductions in transverse strength were found for all composites compared to the strengths at dry conditions. The transverse flexure strengths of T700/epoxy and T700/VE D411 were reduced by approximately 30%, while the strength of T700/VE D8084 composite was reduced by 45%. The composites with vinylester matrices experienced more strength reduction after immersion in water at elevated temperatures. For the epoxy matrix composite, the transverse strength was equally affected by all environments. Recall that the flexure strength of the epoxy resin was degraded by 50% after exposure to seawater at 40°C (Table 1).

5. CONCLUSIONS

The objective of this work was to experimentally investigate mechanisms responsible for water degradation of marine type composites. In general, neat epoxy absorbed much more water than neat vinylester. The vinylester matrix composites absorbed more moisture than the neat resins, which was not expected because the resin volume fraction is only about 36% and the carbon fibers do not absorb water. The epoxy matrix composites, on the other hand, absorbed less moisture than the neat epoxy resin, but more than expected based on the 36% resin volume fraction. The difference in moisture absorption behavior between composites and neat resins are attributed to wicking as a water absorbing mechanism.

The flexure test performed on the neat resins show that the vinylester matrices were not significantly affected by exposure to water while the strength of the epoxy was reduced by a factor of 2. Single fiber fragmentation testing revealed large extents of fiber/matrix (F/M) debonding and substantial reductions in the F/M interface shear strength after exposure to water. The E-glass systems performed better than the carbon systems in terms of retention of the F/M interface shear strength and debonding, but it was found that E-glass fibers degrade by exposure to water, especially at elevated temperatures.

Transverse flexure tests were performed on composite specimens to monitor the influence of fiber/matrix interface on macroscopic behavior. At dry conditions, the composites displayed low transverse flexure strength compared to the flexure strength of the neat resins implying weak F/M interfaces at dry conditions. In addition, large reductions in transverse strength of the water immersed composites were experienced for all systems. The micromechanical and macromechanical tests results are both

supportive of water degradation of the F/M interface as a major mechanism for loss of performance of the composites.

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