Short-Term Effects of Sea Water on E-Glass/Vinylester Composites

LIXIN WU, KAREN MURPHY, VISTASP M. KARBHARI, JAMES S. ZHANG

Department of Structural Engineering, MC – 0085, Building 409 University Center, University of California, San Diego, La Jolla, California 92093-0085

ABSTRACT: The use of ambient cured E-glass/vinylester composites is increasingly being considered for infrastructure applications both along the shore and offshore, thereby exposing the composite to a marine aqueous environment. The use of ambient cure potentially results in incomplete polymerization and susceptibility for degradation early in life. This study characterizes the mechanical response of E-glass/vinylester quadriaxial composites immersed in deionized water, sea water, and synthetic sea water. It is seen that there are substantial differences based on the solution type, with deionized water immersion causing the maximum drop in interlaminar shear performance and sea water causing the maximum reduction in tensile performance. The effect of cycling, simulating the tidal zone or the splash zone, is seen to be more pronounced in a resin-dominated response. Drying of specimens, even over prolonged periods of time, is not seen to result in complete regain of performance degradation due to sorption processes. A clear competition is seen between the phenomena of moisture-induced residual cure/postcure and physical (fiber-matrix debonding, microcracking, plasticization) and chemical (hydrolysis) aging. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 2760–2767, 2002

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INTRODUCTION

Vinylester resins, produced from various epoxides and ethylenically unsaturated monocarboxylic acids, in general, show superior mechanical properties and resistance to chemicals and various solvents to those of most unsaturated polyesters and are, hence, increasingly being used in applications in civil infrastructure where longevity and durability are critical. However, research on the characterization of durability of these resins and their composites has largely been overshadowed by the emphasis on polyesters and epoxies, result-

ing in critical gaps in the database of these materials, which is only recently being addressed. Due to the inherent susceptibility of steel to corrosion, which is aggravated in a marine environment, E-glass composites are increasingly being considered for use in structural applications ranging from jackets for strengthening of existing piers and external strengthening of deteriorating beams and slabs on wharves and jetties to their use as deck systems for new elements adjacent to the shoreline and even offshore.

Although there is a substantial body of literature related to aspects of moisture absorption in composites[1–4] and there have been extensive studies of effects due to saltwater and marine environments,[5–9] with the exception of a few recent studies such as refs. 10 and 11, there is a lack

of information related to sea-water effects on vi-nylesters and E-glass/vinylester composites,[12] with most previous efforts being restricted to ep-oxy and unsaturated polyester-based systems. The increasing consideration of E-glass/vinylester composites in civil infrastructure systems, such as in piling, decking for piers and wharves, and fender systems and in offshore applications such as risers, downhole tubing, and subsea flowlines, makes the lack of this information a severe draw-back. It is also known that, although moisture absorption in itself causes mechanisms of degra-dation, reversible and irreversible, in polymers and composites at the level of the constituents and the interface the actual effects are largely dependent on the type of aqueous solution being considered, with the presence of salts such as NaCl reducing the saturation moisture content in some cases[13,14] and even causing substantial de-viation from Fickian behavior in others[5] includ-ing the early onset of irreversibility.[15] In the present article, the effect of actual and simulated sea water on properties of an E-glass/vinylester composite were assessed through tensile and in-terlaminar shear testing, moisture-absorption ki-netics, and dynamic mechanical thermal analysis (DMTA) techniques.

EXPERIMENTAL

Composite specimens were fabricated using wet layup with the application of a vacuum through-out the cure. The vinylester resin used was an Interplastics CoRezyn® CORVE 8121, which is a bisphenol A epichlorohydrin-based vinylester, having a nominal viscosity of 600 cps at 23°C. The cure was conducted under ambient conditions of 22–24°C and 50% RH using 1.2% methyl ethyl ketone peroxide (MEKP). The reinforcement con-sisted of two layers of a quadriaxial fabric, QM-5708, laid up symmetrically about the midplane with the bias (±45) plies toward the center, with a resulting fiber weight fraction of between 68 and 69%. Specimens were exposed to the follow-ing environments for periods up to 12 months:

1. 23°C and 55% RH conditions;
2. Synthetic sea water prepared following ASTM D1141 and stored at 23°C (having a pH of 8.24);
3. Sea water collected from La Jolla shores at some distance away from the shore and stored at 23°C (and having a pH of 8.24);

4. Deionized water at 23°C (having a pH of 6.95).

In addition, a set of samples was cycled in sea water through immersion for 12 h, followed by drying in air at 23°C for 12 h, so as to ascertain the effects of continuous wet and dry regimes as would be seen in the area between high and low tide levels. To assess the effectiveness of sealing edges with resin after the cure was completed, as would be the case with a cut edge in a structural component, a set of specimens exposed to sea water was also coated on all edges with a thin layer of the same resin. This coating was applied after conditioning of the samples and was allowed to cure for 24 h prior to the initiation of immer-sion.

All samples were preconditioned by storage at 23°C and 55% RH for 3 months prior to the initi-ation of the exposure. Mechanical testing in the form of tensile tests (ASTM D3039) and inter-laminar shear tests (ASTM D790) in the weft, or 0° direction, were conducted on a minimum of five specimens for each condition and time period (0-, 1-, 3-, 6-, 9-, and 12-month exposure) with speci-mens being dried with a paper towel prior to testing to remove surface moisture. Penetrant up-take, in terms of weight gain, was determined through gravimetric means with precautions taken to remove surface moisture by carefully wiping each specimen before weighing. The per-centage change in weight was determined as

$$M = \left(\frac{\begin{array}{c}\text{weight of specimen} \\ - \text{ weight of unexposed control}\end{array}}{\text{weight of unexposed control}} \right) \times 100$$

Thermal analysis of the sample to determine the glass transition temperature and viscoelastic re-sponse was conducted using dynamic mechanical thermal analysis (DMTA) between 23 and 250°C at a rate of 10°C/min and at a frequency of 1 Hz. The DMTA results, however, should be consid-ered as relative indicators since the heating pro-cess during the temperature ramp causes a loss of moisture, which could result in the actual T_g be-ing lower than that which is measured.

RESULTS AND DISCUSSION

Moisture Absorption

The results of the gravimetric measurements show that the composite samples displayed a

Fickian response in all solutions for which continuous immersion was considered. The initial rate of weight gain over the first 25 days was the highest in synthetic sea water and the lowest in deionized water, after which there was very little discernible difference among the three environments. The levels of maximum weight gain recorded in deionized water, synthetic sea water, and natural sea water were 0.182, 0.185, and 0.182%, respectively, with a leveling off in weight gain occurring between 150 and 175 days after exposure initiation. It is noted that the samples with sealed edges initially showed a 15% lower rate of weight gain than that of the unsealed ones in natural sea water, but continued to gain weight over a longer period of time, 240 days, resulting in the highest overall level of weight gain of 0.2%. Whereas this may not appear intuitive, it must be remembered that the edges were sealed with the same resin as used in the composite and it was only allowed to cure for 24 h prior to immersion. The level of cure in the unreinforced resin, used for sealing, after this period was estimated to be just 78% through differential scanning calorimetry (DSC). In a styrene-based system, such as in the resin under consideration, this results in residual curing in a solution,[16,17] with a greater propensity for weight gain after completion of the residual cure.

The values of diffusivity determined using the sorption rate equation in ref. 18 for levels of M_t/M_m being greater than 0.4 were 4.83×10^{-7}, 4.29×10^{-7}, and 4.98×10^{-7} mm^2/s for composites immersed in deionized water, synthetic sea water, and sea water, respectively, indicating that sea-water solutions do not seem to appreciably change the solubility of water in this resin system. Some samples were dried after completion of the 1-year immersion period, under conditions of 23°C and 55% RH. It was noted that samples immersed in deionized water showed a slightly lower retention of weight, 0.03%, than that of samples immersed in sea water and synthetic sea water, 0.05–0.06%. Thus, all samples showed retention, resulting in final masses, after drying, higher than their initial, unexposed masses, suggesting irreversible changes at both the physical and chemical levels due to sorption of the aqueous solutions. The higher mass retention in samples immersed in sea water and synthetic sea water is thought to be due to the sorption of salts into the resin by diffusion and along fiber–matrix interface debonds and bulk material cracks by wicking.
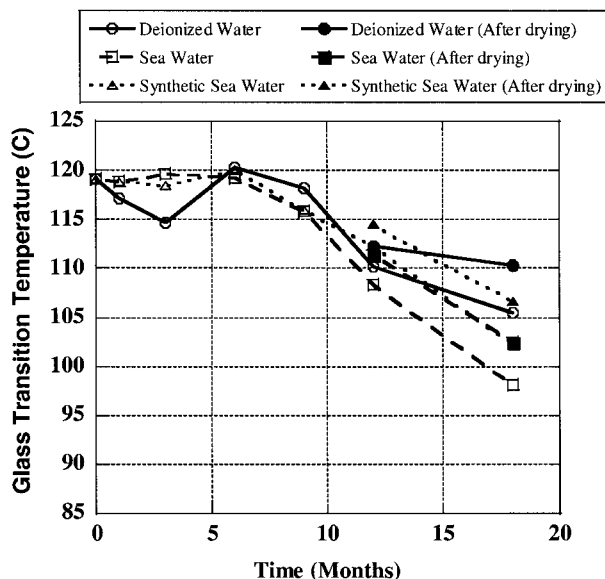

Figure 1 Change in T_g as a function of the aqueous solution and period of immersion.

Thermal Analysis

Penetration of aqueous solutions into thermoset composites is known to cause both plasticization over the short term and hydrolysis through attack of the ester linkages. The chemical attack, hydrolysis, although primarily a phenomenon associated with long periods of exposure, is also initiated by incomplete cure of the vinylester. Both plasticization and hydrolysis induce higher levels of molecular mobility, resulting in a consequent decrease in the T_g, although the decrease could be partially offset through the residual curing of the vinylester itself in the aqueous solution. Levels of T_g recorded after each of the exposure periods, including data taken after 18 months, and after drying at levels of 12 and 18 months are shown in Figure 1. It can be seen that the maximum decrease in T_g, 14%, was seen after immersion in sea water for 18 months, whereas the minimum, 11.4%, was recorded for deionized water over the same period of time, which is in congruence with the results from thermal analysis. It is also seen that, initially, until the 6-month level, there is very little change in the T_g for specimens immersed in sea water and synthetic sea water, although results of the DSC analysis conducted on the specimens shows a substantial decrease in levels of residual heat and, hence, an increase in the degree of polymerization over the same period of time. This competition between two phenom-

Table I   Levels of Tensile Strength (MPa) as a Function of Exposure Type and Time

Exposure Type	Time of Exposure					
	Unexposed	1 Month	3 Months	6 Months	9 Months	12 Months
	363 [4.21]	—	—	—	—	—
Deionized water	—	355 [9.65]	349 [4.48]	341 [1.31]	335 [2.83]	322 [12.48]
Sea water	—	354 [14.82]	360 [9.10]	341 [7.65]	322 [11.10]	314 [11.45]
Sea water (sealed edges)	—	360 [16.62]	352 [6.76]	350 [11.03]	345 [3.72]	315 [8.34]
Sea water (cycling)	—	338 [7.93]	363 [25.86]	339 [19.03]	336 [18.55]	333 [18.13]
Synthetic sea water	—	343 [11.03]	351 [5.31]	340 [15.03]	341 [16.13]	316 [15.44]

ena related to moisture sorption, hydrolysis causing an increase in molecular mobility resulting in a decrease in T_g and residual curing causing an increase in crosslink density resulting in an increase in T_g, follows the trends identified in refs. 16, 17, and 19. It should be noted that increases in T_g could also be due to the leaching of low molecular weight flexibilizing segments, leading to embrittlement of the network. Samples removed after 12 and 18 months of immersion and then dried for 1 year at 23 and 55% RH do show some regain in the T_g, but the levels, as shown in Figure 1, do not return to those prior to exposure, emphasizing irreversible changes due to chemical degradation. It is noted that the levels of decrease in the T_g, as well as those of regain after drying, were different for the three solutions, although, as reported earlier, the levels of weight gain were comparable, pointing out the difference in degradation due to the salts carried by the aqueous solutions into the bulk resin and the composite.

Effects on Tensile Properties

As can be seen from Table I, exposure to all conditions results in a decrease in tensile strength, and although the absolute difference in response between the various exposures is small, some trends can be highlighted. The maximum reduction in tensile strength after 12 months of exposure was in sea water at a level of 13.5%, whereas the minimum, 8.26%, was recorded for the case of cycling in sea water. It is noted that, although the sealing of edges resulted in a slower degradation of strength up to a period of 9 months, at the 12 month level, there was virtually no difference of results between the sealed and unsealed samples immersed in sea water, indicating that the use of the same resin as a sealant did serve as a diffusion, and perhaps osmotic, barrier for a period of time. After immersion in sea water, the surfaces of all the specimens showed discoloration with the initiation of blistering at areas where fibers were close to the surface, suggesting both effects of salts on the fiber–matrix integrity and the existence of osmotic processes. In contrast, specimens immersed in deionized water and synthetic sea water did not show discoloration and blistering. The process of cycling resulted in the lowest overall loss in strength but also the highest level in scatter, perhaps due, in part, to the increased level of longitudinal microcracking noticeable in these samples. The microcracking is thought to be a result of the continuous change from a wet to a dry regime and back again, resulting in a swelling variation. Swelling is constrained in the direction of the fibers, which are significantly stiffer than is the bulk resin, and this, in conjunction with slowly evolving crosslinking due to a moisture-initiated residual cure and flexibilizing of the fiber–matrix bond, can result in these microcracks, which were not seen to the same extent in any of the other specimens. It is noted that, over the time period of study, degradation was not seen to achieve an asymptotic level and, in fact, was seen to continuously increase between the 6- and 12-month levels in all cases except for the cycling regime, suggesting that short-term studies of such systems are unlikely to yield full behavioral characteristics developed over extended periods of time.

In a number of previous studies on unidirectional materials, it was shown that, although degradation is seen in levels of tensile strength due to aqueous immersion, there is only a very slow reduction in the modulus. In the present case, the decrease in the modulus of specimens tested in the warp direction (i.e., along the 0° direction of the quadriaxial fabric) over a period of 12 months is somewhat less than that of the strength. The maximum degradation at the 12-month level is

that of 12% for samples immersed in sea water, whereas the least, 6.2%, is for samples immersed in deionized water. In contrast, levels of degradation in strength over the same time period are 13.5 and 11.3% for sea water and deionized water, respectively. The more comparable levels of degradation in the strength and modulus are because the fabric has a quadriaxial architecture with a chopped strand region in the center. The diffusion of moisture and salts through the resin and by wicking along cracks and fiber–matrix debonds causes degradation in resin regions between layers, resulting in a decrease in modulus as well as in strength. Examination of interface regions after 12 months of immersion shows the initiation of damage at the fiber level through localized pitting and circumferential cracking, with damage being more pronounced in samples immersed in deionized water rather than in sea water. It is likely that further exposure would result in more significant decreases in strength due to this fiber level of degradation.

As shown in Figure 2(a,b), the specimens show a rapid decrease in the modulus in the first month, followed by an increase, due to residual curing, until the 6-month level, followed by a decrease again, indicating the dominance of moisture-related degradation over residual cure effects. As seen in Figure 2(a), although there is a reduction in the modulus of 12.8, 14, and 16% after a single month of immersion in deionized water, sea water, and synthetic sea water, respectively, a residual cure that takes place over the next 5 months results in the reduction in the actual level of degradation due to deionized water to 4.8%. In comparison, samples immersed in sea water and synthetic sea water both showed increases in the modulus back to the initial level of the unexposed specimens. Figure 2(b) shows that, of the three cases involving sea water, the maximum level of residual cure was seen by direct immersion, with the least being due to cycling. Over the 12-month period of exposure, the ultimate degradation for samples immersed in sea water both without sealed edges and with sealed edges and as a result of cycling was 12, 7.8, and 10.9%. As with the strength, the presence of the additional resin used as a sealant does tend to retard degradation, although it does not stop it. However, as remarked earlier, once residual cure has reached its peak effect, in this case at the 6-month level of immersion, the rate of degradation increases and approaches that of the samples with unsealed edges. The samples with sealed
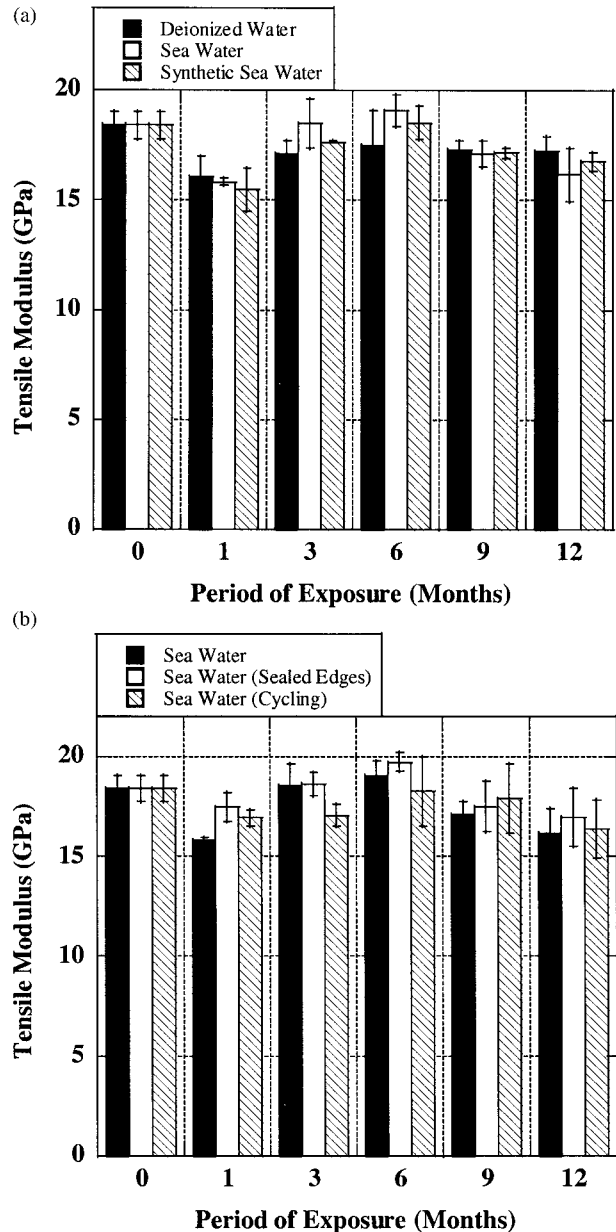

Figure 2 (a) Comparison of change in tensile modulus due to immersion in different aqueous solutions. (b) Comparison of change in tensile modulus due to seawater immersion conditions

edges showed a decrease of 14% over the last 6 months, whereas the decrease in samples with unsealed edges was 15.1% and that for the cycled specimens was only 7.8%.

Effect of Interlaminar Shear

Although interlaminar shear strength cannot rigorously be assessed through the use of the short-
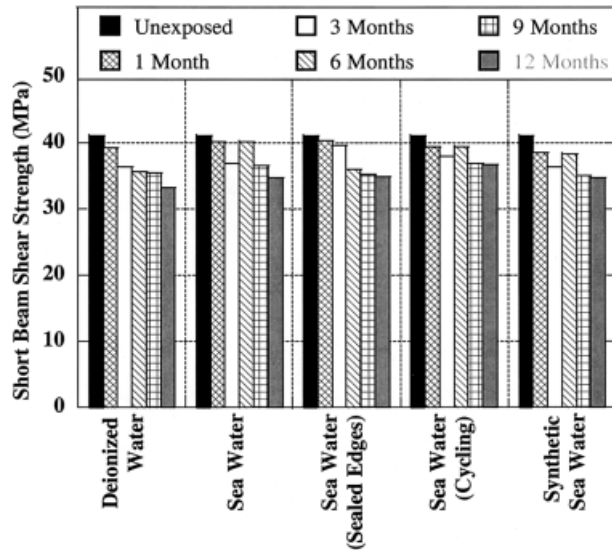
Figure 3 Effect of immersion on short-beam shear strength. Bars represent a progression of time of immersion: 0, 1, 3, 6, 9, and 12 months from left to right in each case.

beam shear test for nonunidirectional tests, the procedure does present a useful and efficient means of assessing relative degradation in composite performance through changes in the resin region between layers. As seen in Figure 3, short-beam shear strength is seen to decrease over the 12-month period of exposure for all conditions considered, with the maximum overall decrease at the 12-month level being 19.3% for samples in deionized water and the minimum being 10.9% for samples subject to the cycling regime in sea water. The overall decrease for the other three conditions was roughly equivalent to 15.6, 15.2, and 15.4% for samples immersed in sea water, sea water with sealed edges, and synthetic sea water, respectively. The increased level of degradation in deionized water can be correlated to the reasoning that, in a short-beam shear test, the highest level of shear stress is attained at the midplane and therefore degradation due to moisture sorption will be dependent on the level of moisture diffusion. Deionized water, being free of solute ions, diffuses to the center faster than does sea water or synthetic sea water and, hence, the highest level of shear-strength degradation is realized in this case. In contrast in the case of cycling, the diffusion through the thickness is retarded at each step in addition to the total period of immersion being shorter and, hence, this intuitively and in reality shows the least degradation. As dis-

cussed previously, the immersion in aqueous solutions causes residual cure (or postcure) and this can clearly be seen at the 6-month level for the samples immersed in sea water and synthetic sea water and for those exposed to a cyclic regime, which compares well with results from both tensile characterization and thermal analysis. In the cases where the effects of residual cure are seen, it is also noted that there is a substantial decrease in the short-beam shear strength immediately after the attainment of higher peak performance, in all cases greater than that recorded in the first month wherein moisture sorption is the fastest, and, therefore, conventionally, degradation has also been taken to be the fastest. In should, however, be remembered that the increase in the crosslink density caused by the residual aqueous solution-initiated cure can result in an anomalous diffusion response, with the formation of a boundary layer between the two outermost swelling layers which can encapsulate the region in between. This core is then subjected to increasing levels of near triaxial stresses, which causes the formation of microcracks that initiate failure in the interlaminar region. As with the tensile results, it is seen that the act of the sealing of edges results in an initial retardation of moisture sorption, followed by a rapid increase once a threshold has been attained, resulting in effects between the sealed and unsealed samples being roughly equivalent at the end of the 12-month time period.

The drying of specimens after completion of periods of exposure is known to result in a partial regain of performance levels, with the final level of loss being due to the levels of chemical change and irreversibility in degradation. A comparison of Figures 3 and 4 clearly shows that although drying does not result in complete recovery in relationship to the unexposed specimens it does cause substantial recovery, with the recovery being the maximum for unsealed specimens immersed in sea water and the minimum for those immersed in deionized water. This trend clearly supports the hypothesis in the previous paragraph related to higher levels of degradation as sorption reaches the center, since desorption would be much slower in those samples, both due to the dimension-constrained reverse-diffusion capacity and the increase in the crosslink density. It is interesting to note that for samples immersed in deionizeed water and synthetic sea water, which did not show a residual cure-related peak during sorption over the 12-month period, a clear peak appears at 6 months after drying. Al-
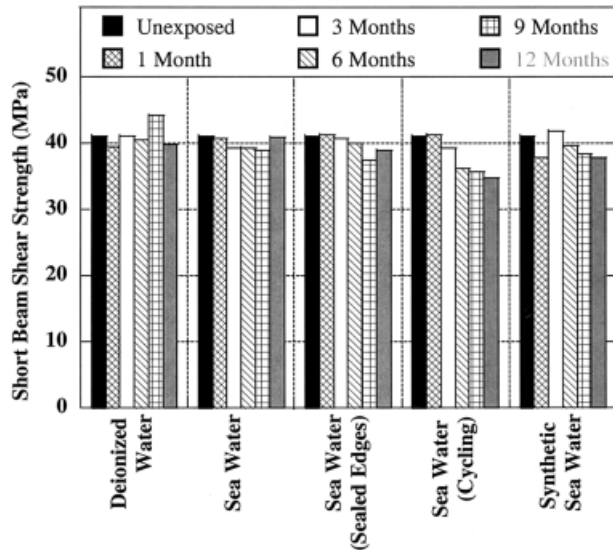
Figure 4 Level of short-beam shear strength after recovery induced by drying for 12 months at 23°C and 55% RH. Bars represent a progression of time of immersion: 0, 1, 3, 6, 9, and 12 months from left to right in each case.

though the reason for this is not entirely clear, it is hypothesized to be due to a combination of resin plasticization, which enables increased elongation and relaxation of residual stresses caused during the initial cure.

CONCLUSIONS

The immersion of E-glass/vinylester composites, fabricated and cured under ambient conditions, in sea water, synthetic sea water, and deionized water for periods up to 12 months, leads to the following conclusions:

1. Immersion in aqueous solutions results in a competition between performance enhancement due to residual cure/postcure initiated by water sorption and degradation due to the same sorption process.
2. There is a discernible difference in response between samples immersed in sea water and deionized water, with the former causing a greater level of fiber–matrix debonding and outer-layer degradation, resulting in increased degradation of the tensile performance, and the latter causing faster diffusion up to the midplane, result-

ing in more severe drops in the interlaminar shear strength.
3. Although the use of the same resin, as used in the composite, as an edge sealant retards the initial rate of sorption and thus results in a lower initial degradation, over a 12-month period, the effect is nullified. This emphasizes the need for use of specialized types of coatings, possibly at greater thicknesses and after longer periods of cure.
4. Although drying results in a partial regain of performance, the environmental conditions considered in this study cause irreversible damage and chemical degradation and aging, resulting in a permanent drop. Initial short-term studies show that cyclic regimes, which already incorporate periods of "wet" and "dry" exposure, result in the greatest permanent drop, emphasizing the need for further study vis-à-vis applications in the tidal and splash zones.

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