

Low-Temperature Hygrothermal Degradation of Ambient Cured E-Glass/Vinylester Composites

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ABSTRACT: Freeze and freeze-thaw durability characteristics of fiber reinforced polymer (FRP) composites, especially in the presence of moisture, need to be investigated prior to the widespread implementation of these materials in civil, polar, and offshore structural components and systems. The hygrothermal degradation characteristics of an ambient cure E-glass/vinylester system due to exposure to -10°C conditions and conditions of freeze-thaw, including in the presence of water and seawater, was investigated. Changes in mechanical characteristics such as strength and modulus, and thermo-mechanical dynamic characteristics such as storage and loss moduli, and glass-transition tem-

perature were measured, and short-term effects of environmental exposure were assessed. It is seen that the presence of moisture/solution has a significant effect; both in terms of physical and chemical aging, and in terms of microcracking and fiber-matrix debond initiation. Results indicate the critical importance of cure characteristics and diffusion related phenomena. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2255–2260, 2002

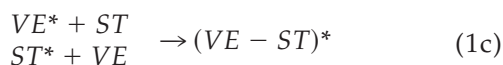
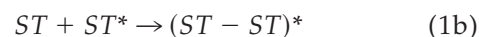
Key words: aging; composites; degradation; mechanical properties; resins

INTRODUCTION

FRP Composites based on a nonautoclave-based process and fabricated using ambient or moderate-temperature cure regimes are increasingly being considered for use in civil infrastructure renewal applications, off-shore platforms, oil development-related structural facilities, and marine terminal infrastructure. The use of these materials as replacements for conventional materials such as steel, concrete, and timber is based on considerations of weight savings, tailored performance characteristics, and potential increases in overall durability and longevity. E-glass/vinylester systems are often chosen due to cost, processing, and potential durability considerations. However, an uncertainty that is providing a major challenge to the widespread implementation of these materials is the lack of a comprehensive database for these materials in the environments and life expectations under consideration and the lack of the fundamental understanding of aging and degradation mechanisms.

Vinylester resin systems are combinations of methacrylated epoxy compounds and styrene, wherein styrene is used as a reactive diluent and the vinylester serves as the crosslinking agent. Cure is achieved by free radical bulk polymerization, with

rates and degree of cure being highly dependent on actual system formulation and cure regime used. Typical vinylester systems contain 30–60% styrene monomer by weight, which both increases overall hydrophobicity and decreases overall homogeneity. The generic network formation process can be considered as a combination of three ongoing processes with propagation taking place in the same time frame through three ongoing reactions between the vinylester (VE) and styrene (ST) monomers, namely



wherein the first two equations represent homopolymerization of vinylester and styrene, respectively, and the third represents their copolymerization. Although the rate of fractional conversion of styrene double bonds is initially less than that of the vinyl esters, the styrene monomer may continue reacting after the vinylester double bond conversion has stopped. This difference in rates can result in the formation of microgel structures with domains of high crosslink density in a pool of unreacted monomers, leading to distinct heterogeneities. It is known that the presence of morphologic heterogeneities, especially as related to levels of fractional conversion, can lead to moisture-associated degradation.^{1,2}

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TABLE I
Constituent Material Characteristics

Property	E-Glass fiber in stabilized unidirectional fabric form	VE 8117 vinylester resin
Tensile modulus (GPa)	73	3.6
Tensile strength (MPa)	1520	82
Elongation (%)	2.1	4.5
Density (g/cc)	2.55	1.12
Layer thickness (mm)	0.125	—

In addition to the effects of moisture uptake on the durability of these materials there is a level of concern for effects of freeze and freeze-thaw response with previous research,^{3–6} indicating the potential for matrix microcracking, fiber–matrix debonding, and change in mechanical characteristics. The potential for accelerated degradation mechanisms due to synergy between the effects of moisture uptake and freeze and freeze-thaw phenomena lead to a level of concern with the use of heterogeneity containing systems such as vinylesters, which exhibit levels of fractional conversions lower than 100% and sometimes as low as 0.60, especially when cured under ambient conditions.^{2,7,8} This article investigates the response of ambient cure E-glass/vinylester composites after short-term exposure to freeze (-10°C) and freeze-thaw (-10 to 22.5°C) conditions, both with and without immersion in aqueous environments.

MATERIALS AND TEST METHODS

E-glass reinforced vinylester composites were fabricated by the wet layup process using a VE-8117 Vinylester resin catalyzed with 1.5% organic peroxide (Cadox 50) and cured under conditions of 22.5°C and 50% RH. (Commercial designations are identified in this article to specify the experiment adequately. Such identification is not intended to imply recommendation or endorsement.) Fabrication was conducted on concrete surfaces, to simulate field conditions associated with infrastructure rehabilitation, with the addition of a peel ply at the composite–concrete interface to enable separation from the concrete substrate. Wet layup procedures followed those specified by a commercial concrete rehabilitation firm to again simulate, as closely as possible, field conditions in the application area under consideration. Both flat panels and hollow cylindrical specimens, of 150 mm internal diameter, were fabricated using three layers of stabilized unidirectional fabric. The nominal properties of the constituents are given in Table I. Gel time for the system was in the range of 20–25 min, with a peak exotherm of 120°C .

The specimens were subjected to five exposure conditions for a total period of 2400 h, namely (a) storage at 22.5°C and 50% RH (serving as the unexposed ambient condition); (b) constant temperature level of -10°C (representative of the “freeze” condition); (c) freeze-thaw cycling at 20% RH; (d) freeze-thaw cycling with immersion in deionized water at 22.5°C ; (e) freeze-thaw cycling with immersion in a 5% NaCl solution at 22.5°C (representative of a salt water solution).

Freeze-thaw was conducted between -10 and 22.5°C with an 8-h dwell at each extreme and with the cycle being repeated every 24 h. Response of the composites to each of the exposure conditions was characterized through gravimetric moisture uptake measurements, tensile tests following ASTM D3039, compression tests using the modified Wyoming compression fixture and protocol, split-D ring tests following ASTM D2290, Dynamic Mechanical Thermal Analysis (DMTA), and Differential Scanning Calorimetry (DSC). The Split-D test was used as a means of evaluating both materials and process implications in a configuration that approximately simulates the confining action of FRP composite jackets used in seismic retrofit. The test, in this investigation, is not expected to be used for determination of materials allowables, and is preferred for simplicity, in this case, over the more rigorous ring burst test.⁹ DMTA was conducted at a frequency of 1 Hertz, with two temperature sweeps of 25 to 200°C and -10 to 30°C at a rate of $5^{\circ}\text{C}/\text{min}$. The second sweep was intended to capture and characterize low temperature effects. Tests within each category and exposure level were conducted on a minimum of five replicates an over exposure periods up to 2400 h (100 days).

RESULTS AND DISCUSSION

Fiber volume fractions for the specimens were determined using burn-off procedures and were found to be 45 and 38% for the flat-plate and split-D rings, respectively. The lower fiber fraction in the rings shows the effect of configuration on process-related characteristics because it was possible to achieve higher levels of compaction, and hence, higher fiber content and lower void fractions in the flat specimens rather than the curved cylindrical ones. It should be noted that this concern has led to the adoption of the NOL-ring burst test rather than flat tensile coupons for characterization of materials for seismic retrofit of columns.^{9,10}

Moisture uptake

Freeze-thaw exposures, in this study, were conducted both in a nominally “dry” state and in aqueous solutions of deionized water and salt water. It is expected

TABLE II
Overall Results for Moisture Uptake

Specimen configuration	Environmental condition	Maximum moisture uptake M_{\max} (%)	Time to reach M_{\max} (h)	Moisture uptake at $t = 2400$ h M_{end} (%)
Flat plate	Immersion in deionized water	1.43	1340	1.07
	Immersion in salt water	0.60	1340	0.43
	Freeze-Thaw in deionized water	0.48	672	0.20
	Freeze-Thaw in salt water	0.40	840	0.21
Split-D rings	Immersion in deionized water	1.67	2400	1.67
	Immersion in salt water	0.37	840	0.21
	Freeze-Thaw in deionized water	0.38	576	0.28
	Freeze-Thaw in salt water	0.25	1008	0.19

that FRP composites subject to freeze-thaw cycling would adsorb moisture during the thawing regime of each cycle, with content increasing if the cycling caused microcrack initiation, or any other form of damage. Table II lists overall results wherein moisture uptake data for the cases of immersion in water and salt water at 22.5°C are also given for purposes of comparison. It is seen that the attainment of peak moisture content is followed in all cases, except the rings in water, by a loss of weight that is attributable to a combination of ester hydrolysis and loss of material from the resin phase, especially along the fiber-matrix interface. The FTIR spectrum from the solution also appear to show traces of unbound material such as residual monomer, providing further evidence for leaching and irreversible degradation at this level being reasons for the anomalous water uptake and loss. Similar molecular extraction was noted for an E-Glass/Vinylester by Ghorbel and Valentin,² who ascribed the phenomena to incomplete cure. It should be noted that DSC thermograms on the unreinforced resin, and the composite showed melt endotherms with the degree of conversion being between 0.70 and 0.75 only. This low level of conversion of double bonds after ambient temperature cure was reconfirmed following FTIR (Fourier Transform Infrared) spectroscopy with isothermal cure at 22.5 and 120°C. The results at 120°C, representing the level of peak exotherm reached during cure, showed a slightly higher conversion of 0.82%.

The obvious loss of material, in addition to the interface debonding seen in samples (as in Fig. 1) will obviously substantially affect retention of prop-

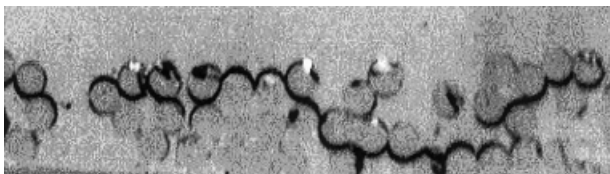


Figure 1 Matrix microcracking and fiber-matrix debonding after 100 freeze-thaw cycles in deionized water.

erties especially in the off-axis direction and in cases wherein fiber-matrix bond integrity is critical to load sharing. Previous studies^{11,12} have reported that the presence of salts such as NaCl in aqueous solutions results in a reduction in saturation, or peak, moisture content, and this trend is clearly followed in the current study. The level of microcracking in the samples subject to freeze-thaw in salt water is higher than that of samples subject to freeze-thaw in deionized water and the surfaces show initiation of blisters. This suggests the existence of osmotic processes as well as the potential role of salt ion migration into the composite itself. As these cracks evolve beyond a critical size they coalesce to form macrocracks in the matrix through which further diffusion and wicking of solution can take place. During the cycling process the condensation within these cracks in addition to expansion due to repeated liquid-solid phase transitions assists in the development of further damage. The degradation in the composite includes that between individual fabric layers and within the incompletely cured and inhomogeneity containing resin itself due to hydrolysis and other irreversible moisture driven processes.

Dynamic mechanical thermal analysis (DMTA)-based characterization

DMTA is used in this investigation to characterize the thermoelastic and viscoelastic transition response and effect of environmental exposure on glass transition temperature. Figure 2 shows the difference in dynamic storage modulus response, E' , with temperature, as a function of the different exposure conditions after 2400 h of exposure. As can be seen, exposure to -10°C conditions result in an increase in E' compared to the unexposed ambient specimen, whereas exposure to freeze-thaw results in a decrease. The maximum decrease is in specimens that underwent a "wet" freeze-thaw with the presence of salt water causing the maximum degradation.

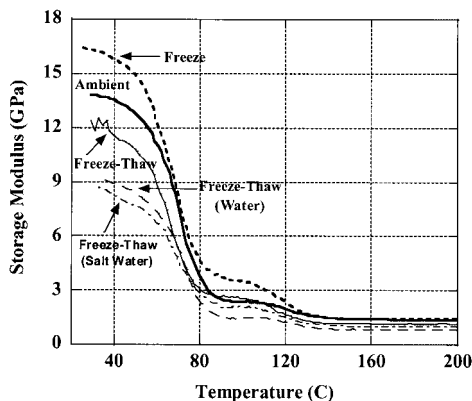


Figure 2 Effect of exposure conditions on the dynamic storage modulus, E' , after 100 days.

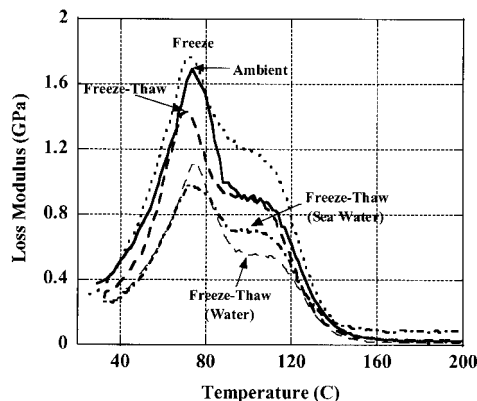


Figure 3 Effect of exposure conditions on the dynamic loss modulus, E'' , after 2400 h of exposure.

The dynamic loss modulus, E'' , can be related to the level of dissipated energy, or that converted to heat through viscous flow. Figure 3 depicts the change in loss modulus as a function of exposure condition and it is clearly seen that exposure to -10°C conditions results in a slight increase in peak loss modulus (4.7% over the ambient unexposed specimens), whereas all freeze-thaw exposures resulted in a greater decrease with the smallest (-15.4%) corresponding to the "dry" freeze-thaw condition and the largest (-42%) corresponding to freeze-thaw in salt water. Exposure to freeze-thaw in deionized water in comparison resulted in a 33.7% decrease in peak loss modulus, emphasizing the higher level of deterioration due to salt water. It is, however, noted that the postpeak saddle or secondary peak region, which may be related to the fiber-matrix interphase level¹³ rather than the bulk composite, is actually higher as a result of sea water exposure compared to that from deionized water. This plateau is noticeable after all freeze-thaw exposure types and test periods.

DMTA tests were conducted on specimens with fibers spanning in the longitudinal direction, and hence, it can be expected that most of the dynamic effects of bending load are initially carried by the fibers resulting in the resin having a delayed transi-

tion. Because the glass transition temperature, T_g , determined from the position of the maximum value of the loss tangent ($\tan \delta$) occurs at the end of the transition region between elastic and viscoelastic regimes, the value is higher than that obtained through the use of the maxima of the loss modulus, E'' , which occurs in the middle. However, the values obtained on the basis of the maxima of the loss modulus are conventionally considered to be more uniform and stable, and hence, it is of interest to compare T_g s determined through both methods as a function of exposure as in Table III. The difference between the two measures is about 9.4% for the unexposed, ambient specimens and between 11 and 15.6% for specimens exposed to freeze and freeze-thaw, with the $\tan \delta$ -based values always being greater than those determined on the basis of the E'' maxima. It is, however, clear that the exposures result in a decrease in T_g , with the maximum decrease being seen in freeze-thaw specimens in aqueous environments, emphasizing the overall effect of moisture in depressing the glass transition temperature. In all cases, it is also seen that the maximum decrease in T_g levels is seen within the first time period of exposure, 720 h, with further exposure resulting in only slight further changes. This is in correspondence with the earlier observations on moisture absorption in the

TABLE III
Effect of Exposure on Glass Transition Temperature

Environmental condition	Time period (h)	Glass transition temperature ($^{\circ}\text{C}$)	
		E'' maxima method	Tan δ method
Unexposed	—	77.63	84.94
Freeze (-10°C)	720	74.19	82.59
	2400	72.57	82.47
Freeze-thaw	720	72.29	83.16
	2400	72.37	81.29
Freeze-thaw in deionized water	720	71.69	82.88
	2400	71.62	82.46
Freeze-thaw in sea water	720	71.79	82.90
	2400	71.50	82.59

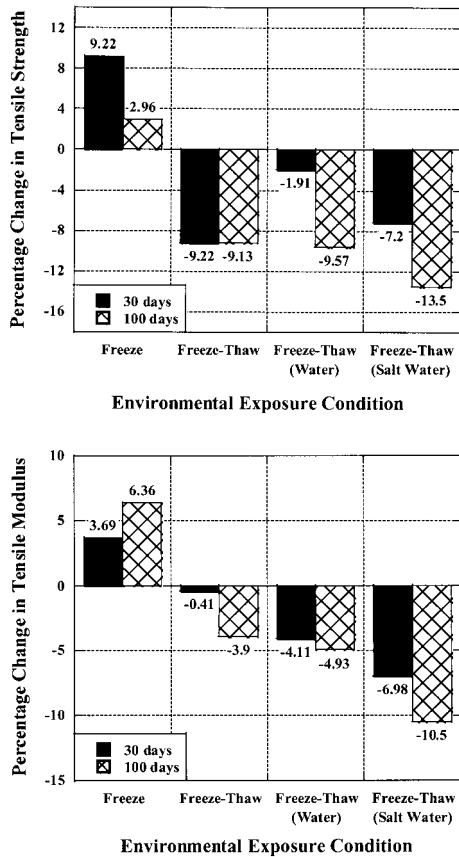


Figure 4 Effects of exposure conditions after 2400 h on tensile response. (a) Percentage change in longitudinal strength from unexposed. (b) Percentage change in longitudinal modulus from unexposed.

freeze-thaw cases wherein an initial peak was attained fairly rapidly, after which the level of moisture uptake holds constant for a short period of time and then shows anomalous decrease in weight gain due to degradation and loss of material.

Effect on tensile properties

The longitudinal tensile strength and modulus of the unexposed E-glass/vinylester coupons was 32.19 and 792.93 GPa, respectively, with variation of 2.53 and 3.57%, respectively, over the set of five specimens tested. The effect of exposure conditions on the tensile strength and modulus are shown in Figure 4(a) and (b), respectively. It is seen that exposure to the -10°C conditions results in an increase in strength and modulus, whereas both properties decrease as a result of the freeze-thaw exposure. Following Hartwig¹⁴ it can be shown that the matrix stiffens with decrease in temperature resulting in an increase in modulus as determined by

$$E_{m(T)} = E_{m(T_0)} + K(T_0 - T) \quad (2)$$

where $E_{m(T_0)}$ is the matrix modulus at temperature T_0 , $E_{m(T)}$ is the matrix modulus at temperature T , wherein $T_0 > T$ and is measured in $^{\circ}\text{C}$, and K is an empirical constant of the order of 20 MPa/ $^{\circ}\text{C}$. Using this in conjunction with the rule of mixtures it is seen that the experimentally determined range of 34.8 GPa at 720 h and 35.71 GPa at 2400 h exposure to -10°C compares reasonably with the predicted value of 35.19 GPa. Freeze-thaw exposures, especially in an aqueous environment cause fiber-matrix debonding and matrix microcracking resulting in a decrease in both tensile strength and modulus. Allread¹⁵ reported that the cycling of kevlar/epoxy laminates between -28 and 51.7°C caused a decrease in tensile strength of 23% after 360 cycles and 63% after 1170 cycles. The maximum degradation in the current study is seen to occur as a result of freeze-thaw in sea water. The diffusion and wicking of NaCl in solution is seen as the reason for this with the crystallization causing an increased level of interfacial debonding and crack opening during each freeze-thaw cycle.

Effect on split-D properties

The effect of environmental exposure on Split-D test determined hoop strength is shown in Figure 5. It is noted that in this test configuration small imperfections can have a profound effect on local instability. As can be seen from Figure 5, the “dry” freeze-thaw exposure has an imperceptible effect, whereas freeze-thaw cycling in deionized water has the greatest detrimental effect. Freeze-thaw exposure causes fiber-matrix debonding and matrix microcracking as described previously, resulting in nonuniform stress transfer between the hoop wound fibers, resulting in overall degradation in load capacity. It is noted that the fiber volume fraction in the split-D specimens is significantly lower than that achieved in the flat plate specimens causing environmental effects on the bulk

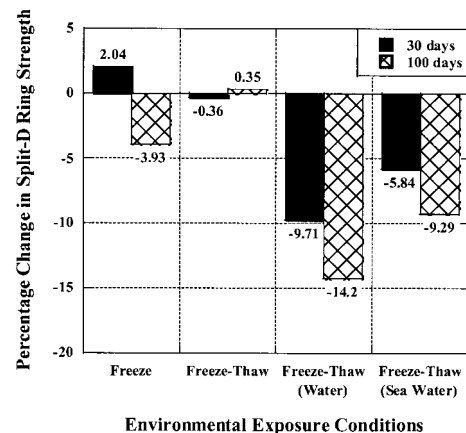


Figure 5 Effect of 2400 h/100 cycles of exposure on Split-D Ring strength.

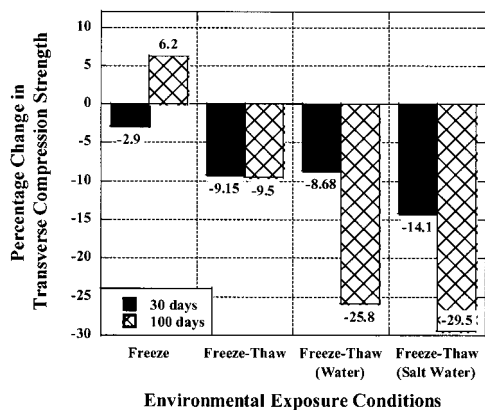


Figure 6 Percentage change in transverse compression strength after 2400 h/100 cycles of exposure.

resin to have a greater effect in these specimens. Based on results of moisture uptake studies it is seen (Table II) that there is a significantly higher amount of moisture-based weight gain in deionized water compared to sea water (0.38% compared to 0.25% at the peak level) and the results of split-D tests after exposure to freeze-thaw in the two aqueous solutions correspond to this with the greater amount of moisture uptake relating to a higher drop in split-D tensile hoop strength.

Effect on compressive strength

The compressive tests were conducted in the transverse direction to assess effects on the resin and the fiber-matrix interface. Although the tests inherently lack the preciseness of tensile tests due to potential effects of local defects on buckling, local kinking and crushing, the test provides a useful assessment of the sensitivity of the resin and the system to environmental exposure. The ambient compressive strength was measured as 33.37 MPa, with a maximum variation of 2.60%. As can be seen from Figure 6, exposure to -10°C initially causes a minor decrease, but at the end of 2400 h results in a 6.2% increase in strength due to matrix hardening, following the trends of earlier results reported by Dutta.¹⁶ Freeze-thaw cycling is seen to increase microcrack density and accentuate effect of defects and morphologic heterogeneities. The addition of aqueous immersion increases degradation significantly, with the salt water solution having a greater detrimental effect due to increased pressure on crack faces and voids/gaps along fiber-matrix disbonds. In this aspect the results of the tensile and compressive tests, both conducted on specimens from the flat plates, correlate well.

SUMMARY

It is seen that although exposure to low temperatures causes matrix stiffening and hence minor increases in

flat coupon tensile strength and stiffness of the E-Glass/vinylester composite, the exposure to freeze-thaw cycling causes accumulation of damage resulting in decrease in performance levels. The exposure to freeze-thaw in aqueous solutions causes a more pronounced effect due to moisture absorption and consequent hydrolysis of ester groups, as well as fiber-matrix debonding. The glass transition temperature is also depressed due to the level of moisture, and distinct changes are seen in viscoelastic transition response as a result of freeze-thaw exposure. In general, a decrease in both dynamic storage and loss moduli is noted. It is emphasized the effects are perhaps amplified due to the use of vinylester resins, which, under ambient temperature cure regimes can result in incomplete cure and morphologic inhomogeneities. This not only affects moisture uptake kinetics but also degradation mechanisms.

Further study is warranted in developing an understanding of moisture kinetics and damage evolution in these materials as related to freeze-thaw exposure, for application not only in civil infrastructure renewal but also for use in construction and maintenance of offshore structures.

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