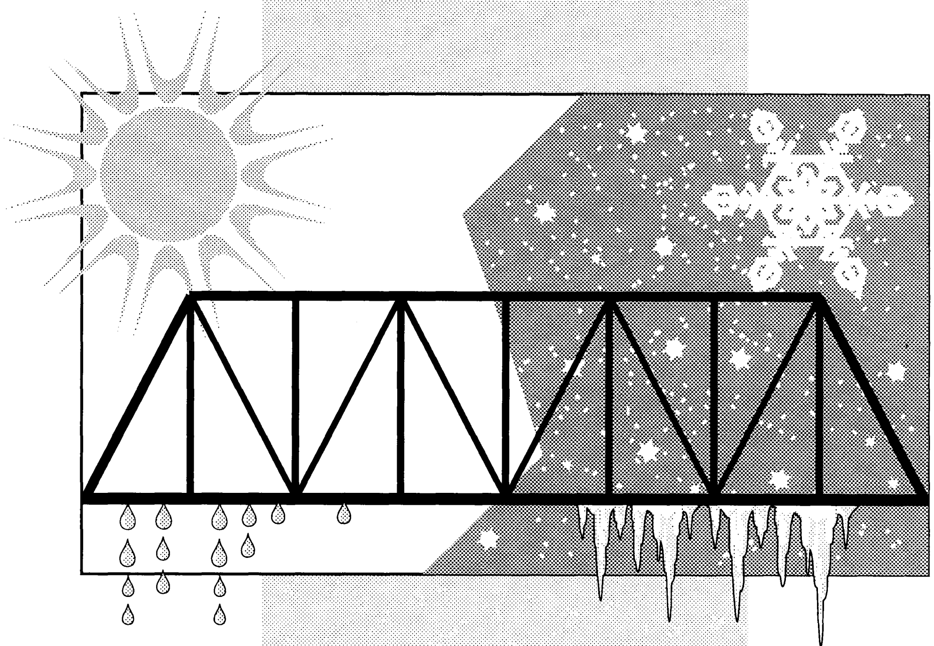
Final Report

FREEZE-THAW DURABILITY OF COMPOSITE MATERIALS



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Freeze-Thaw Durability of Composite Materials

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Abstract

Composite materials, produced from polymer resins and high strength fibers, have the potential to be widely used in construction because of their corrosion resistance and high strength-to-weight ratio, However, such environmental factors as extreme temperature fluctuation and water absorption adversely affect the material properties of composite materials produced from polymers. Cycles of freezing and thawing temperatures magnify the effects of water absorption. For use in highway structures, composite materials must be as durable as steel and concrete. Therefore, the behavior of composite materials subjected to cycles of freezing and thawing needs to be characterized. Two commercially available composite systems, both reinforced with fiberglass and produced by the pultrusion process, were studied. One system was produced with isophthalic polyester, the other with vinyl ester. Coupons were cut from plate stock and placed in a solution of water and 2% sodium chloride and subjected to cycles of freezing and thawing. Periodically, coupons were removed and tested in flexure to failure. Flexural strength values at various numbers of freeze-thaw cycles were compared to the strengths of virgin coupons. Prior to destructive testing, coupons were tested to determine the dynamic modulus of elasticity. Dynamic modulus values at various numbers of freeze-thaw cycles were compared to virgin values. Results indicate a significant loss of flexural strength (20% - 30%), rigidity, and toughness after 300 cycles. Data from dynamic modulus measurements when compared to modulus of elasticity calculations taken from load-deflection data, may not be an appropriate measure of durability for composites.

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ABSTRACT

Composite materials, produced from polymer resins and high strength fibers, have the potential to be widely used in construction because of their corrosion resistance and high strength-to-weight ratio. However, such environmental factors as extreme temperature fluctuation and water absorption adversely affect the material properties of composite materials produced from polymers. Cycles of freezing and thawing temperatures magnify the effects of water absorption. For use in highway structures, composite materials must be as durable as steel and concrete. Therefore, the behavior of composite materials subjected to cycles of freezing and thawing needs to be characterized.

Two commercially available composite systems, both reinforced with fiberglass and produced by the pultrusion process, were studied. One system was produced with isophthalic polyester, the other with vinyl ester. Coupons 304.8 mm (12 in) long and 25.4 mm (1 in) wide were cut from plate stock 9.525 mm (0.375 in) in thickness, and then placed in a solution of water and 2% sodium chloride and subjected to cycles of freezing and thawing, with the temperature profile ranging between -17.8°C (0°F) and 4.4°C (40°F). Periodically, coupons were removed and tested in flexure to failure. Flexural strength values at various numbers of freeze-thaw cycles were compared to the strengths of virgin coupons.

Prior to destructive testing, coupons were tested to determine the dynamic modulus of elasticity. This involved placing the coupons in a simply-supported configuration and subjecting them to an impulse load. An accelerometer attached to the coupon measured its response to the impulse load. The signal from the accelerometer was recorded and conditioned to determine the natural frequency of the coupon. The dynamic modulus of elasticity was then back-calculated from the natural frequency. Dynamic modulus values at various numbers of freeze-thaw cycles were compared to virgin values.

Results indicate a significant loss of flexural strength (20% - 30%), rigidity, and toughness after 300 cycles. Data from dynamic modulus measurements when compared to modulus of elasticity calculations taken from load-deflection data, may not be an appropriate measure of durability for composites.

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INTRODUCTION

Many of America's bridges are in a serious state of decay.[1] The current state of the bridge inventory is due in part to the vulnerability of current construction materials, steel and concrete, to hostile environments. Because of their corrosion resistance, composite materials (polymer resin-high strength fiber systems) are emerging as an alternative to conventional materials. Composite materials also offer other advantages, including high strength and rigidity to weight ratios. However, environmental factors such as extreme temperature fluctuation and water absorption adversely affect composite materials produced from polymers.

Water absorption reduces the strength and stiffness of polymeric composites by as much as 30%, compared to dry material. Absorbed water results in swelling and warping, delaminating the individual composite plies and reducing the load bearing capacity of the composite system. Water absorption also breaks down the interface between the reinforcing fiber and the resin matrix, leading to loss of strength and rigidity, key design parameters.[2]

Cycles of freezing and thawing temperatures will probably magnify the effects of water absorption. The expansion of the freezing water causes further delamination and interfacial failure. Composite materials show great promise in rehabilitating and retrofitting existing transportation structures. Their relatively high initial costs could be justified if user costs from construction delays and detours are included in the overall cost of repair and rehabilitation. However, for use in highway structures, composite materials must be as durable as steel and concrete. The behavior of composite materials subjected to cycles of freezing and thawing needs to be characterized.

Little research has been conducted on the freeze/thaw durability of composite materials. Most of the research in this area has been devoted to advanced composite systems used in the aerospace industry.[3] These advanced systems, typically made up of ceramic reinforcing in a metallic matrix material, and designed for temperature ranges from cryogenic to several hundred degrees Celsius, are far too costly to be used for highway structures.

Chajes et al.[4] investigated the durability of several composite systems externally attached to concrete beams. A number of beams were exposed to cycles of freezing and thawing.

Another set of beams was exposed to cycles of wetting and drying. The results of the study indicated that flexural strength was lost due to a degradation of the bond between the concrete and the external composite reinforcing. Degradation of the composite materials was not reported.

Sen et al.[5] investigated the durability of S-2 glass/epoxy pretensioned beams subjected to cycles of wetting and drying. The exposure to wet/dry cycles was chosen to simulate tidal waves. The pretensioned beams were designed and prepared to model piles driven in a tidal environment. Several specimens were initially cracked, to simulate pile-driving damage. Identical specimens were fabricated with steel pretensioning tendons for comparison. The results indicated extensive damage in the fiberglass pretensioned beams, leading to an unacceptable level of strength loss.

EXPERIMENTAL PROGRAM

The purpose of the experimental investigation was to characterize the behavior of two candidate composite materials for use in bridges and other structures in a harsh, moist environment with cycles of freezing and thawing. All testing was done in the laboratory using representative samples of composite materials.

The coupons were subjected to cycles of freezing and thawing while submerged in a solution of 2% sodium chloride and water. Periodically, coupons of each Fiber Reinforced Plastic (FRP) system were removed and allowed to return to room temperature. The room temperature coupons were then tested to determine dynamic modulus and flexural strength. Flexural testing indicates the quality of the bond between the individual fibers and the surrounding matrix. This bond may be susceptible to water damage, which will be accentuated by the freeze/thaw action.

Samples of both composite systems were placed in a solution of 2% sodium chloride and water but not subjected to cycles of freezing and thawing. Coupons were removed at times corresponding to the intervals of the freeze/thaw cycles. They were then tested identically to the freeze/thaw specimens. This was done as a control to determine the magnitude of damage due to freezing and thawing alone.

Dynamic modulus of elasticity determination is a well-established indicator of concrete degradation due to freezing and thawing.[6] It is a noninvasive means to measure degradation and should indicate freeze/thaw-induced degradation for composite materials. However, no such testing could be found in the literature. Therefore, coupons were tested for dynamic modulus determination before testing in flexure.

Materials

Two composite systems were studied. Both systems were reinforced with fiberglass fibers with one using vinyl ester and the other, isophthalic polyester as binding, or matrix materials. Flat sheets were produced by the pultrusion process. Two types of glass reinforcement were used: continuous strand mat for multidimensional strength properties and continuous strand rovings for strength in the pultruded direction. Coupons, rectangular in cross-section, and measuring 9.525 mm (0.375 in) thick, 304.8 mm (12 in) long, and 25.4 mm (1 in) wide were cut from these sheets. The cut edges were coated with an epoxy sealant to restrict moisture infiltration prior to testing. A later series of coupons was cut but not coated with epoxy prior to testing.

Test Methods

The composite material coupons were subjected to cycles of freezing and thawing using the guidelines set forth in ASTM C-666, Standard Test Method for Resistance of Concrete to Rapid Freezing and Thawing. The rationale for following this test was that the composite materials used to externally reinforce concrete structures must meet the same durability requirements as the concrete. This standard specifies a temperature range of -17.8°C (0°F) to 4.4°C (40°F), which is the accepted temperature limit for infrastructural materials. The coupons were placed in a 2% solution of NaCl and water. They were then subjected to cycles of freezing and thawing. A complete cycle consisted of a ramp down from 4.4°C (40°F) to -17.8°C (0°F), followed by a hold at -17.8°C (0°F), a ramp up to 4.4°C (40°F), and another hold at this temperature. One complete cycle took about three hours to complete. At 50-cycle intervals groups of three coupons were removed from the chamber for testing. Coupons placed in a solution of NaCl and water but not subjected to cycles of freezing and thawing were removed at times equivalent to the 50-cycle interval and tested.

The coupons were tested to determine the dynamic modulus. Procedures outlined in ASTM C-215, Standard Test Method for Fundamental Transverse, Longitudinal, and Torsional Frequencies of Concrete Specimens, were used to determine dynamic modulus. There is no ASTM standard for the determination of the dynamic modulus of composite materials. However, the methodology in ASTM C-215 should yield reasonable results when applied to composite materials. In this procedure, specimens are placed on elastic supports. A small accelerometer is then placed on the specimen. This accelerometer is attached to a Fast-Fourier Transform analyzer, which transforms the response of the accelerometer from the time domain to the frequency domain. The specimen is then impacted with a small force. The results yield the fundamental frequency for the material. The dynamic modulus is then back-calculated from an equation derived from classical vibration analysis for the fundamental frequency of a simply supported beam. No attempt was made to relate dynamic modulus to modulus of elasticity for these composite systems.

The coupons were then tested to failure in flexure following the procedure outlined in ASTM D-790, Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials. The coupons were placed in a flexural test fixture in a simply supported configuration and loaded at midspan. Load and midspan deflection data were recorded continuously during the testing.

Plots of flexural strength and dynamic modulus were constructed. The values were normalized with respect to virgin values and plotted versus the number of freeze/thaw cycles. Additionally, Young's modulus, calculated from the load-deflection data, and the modulus of toughness, defined as the area under the load-deflection curve, were determined at each cycle for each coupon tested. The toughness of a material is related to its ductility as well as its ultimate strength. The modulus of toughness value, which is a quantifiable term used to describe ductility, normalized to virgin values, was used for comparison to further evaluate any degradation due to freeze/thaw cycles.

RESULTS

Figure 1 shows a plot of load versus deflection for both FRP systems for a virgin coupon as well as a coupon subjected to 300 cycles of freezing and thawing. Figure 2 is an identical plot for coupons that were not sealed with epoxy. These coupons were cut normal to the direction of pultrusion and hence the lower strengths. It is clear from these figures that there is damage from cycles of freezing and thawing. The damage is magnified if the cut edges are not sealed with epoxy. Loss in flexural strength and toughness are apparent in both sets of data.

Further, flexural rigidity is lost, as evidenced by the changes in slope of the load-deflection curves. This loss in rigidity can be attributed to loss in Young's modulus since there was no measurable change in cross sectional dimensions and thus no change in moment of inertia. Back calculating the Young's modulus value from the expression for maximum deflection of a simply supported beam loaded at midspan yields an average loss of 24% (±15%) for the sealed isophthalic polyester composite and 22% (± 14%) for the sealed vinyl ester composite. The average loss in modulus of elasticity for the unsealed vinyl ester composite was 35% (±3%) whereas the unsealed isophthalic polyester lost 18% (±11%). It should be noted that the 18% loss in Young's modulus does not follow the trend set forth by the other values. A more reasonable value at 300 cycles would be obtained by extrapolating the first six data points.

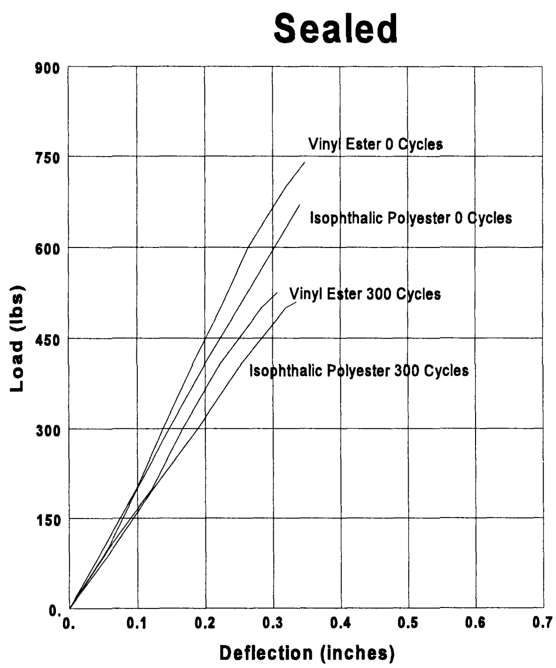

Figure 1. Load vs. Deflection, Sealed Edges

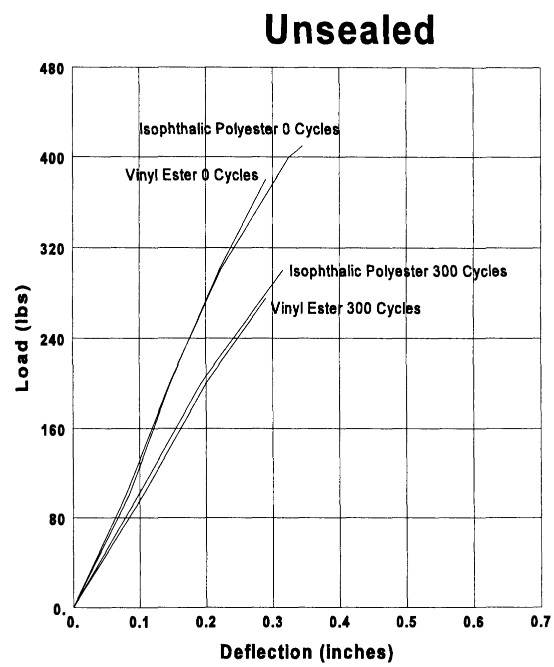

Figure 2. Load vs. Deflection, Unsealed Edges

Figures 3 and 4 are plots of percent loss in flexural strength, modulus of toughness, Young's modulus, and dynamic modulus, versus number of freeze/thaw cycles for each FRP system, both sealed and unsealed. The data points represent the average value for 9 coupons for the coated FRP systems and the average of 5 coupons for the unsealed edges.

The unsealed vinyl ester coupons lost 32% (±5%) of their initial flexural strength at the termination of cycling, while the sealed coupons lost 22% (±13%). Both sealed and unsealed coupons lost an average of 3% (±2%) of their initial dynamic modulus values. Both also lost between 22% and 32% (±13%) of their initial modulus of toughness values, again indicating a loss in ductility. As previously noted, the data trend is lower than these values The moisture contents at the termination of cycling were determined to be 0.14% for the unsealed coupons and 0.07% for the sealed.

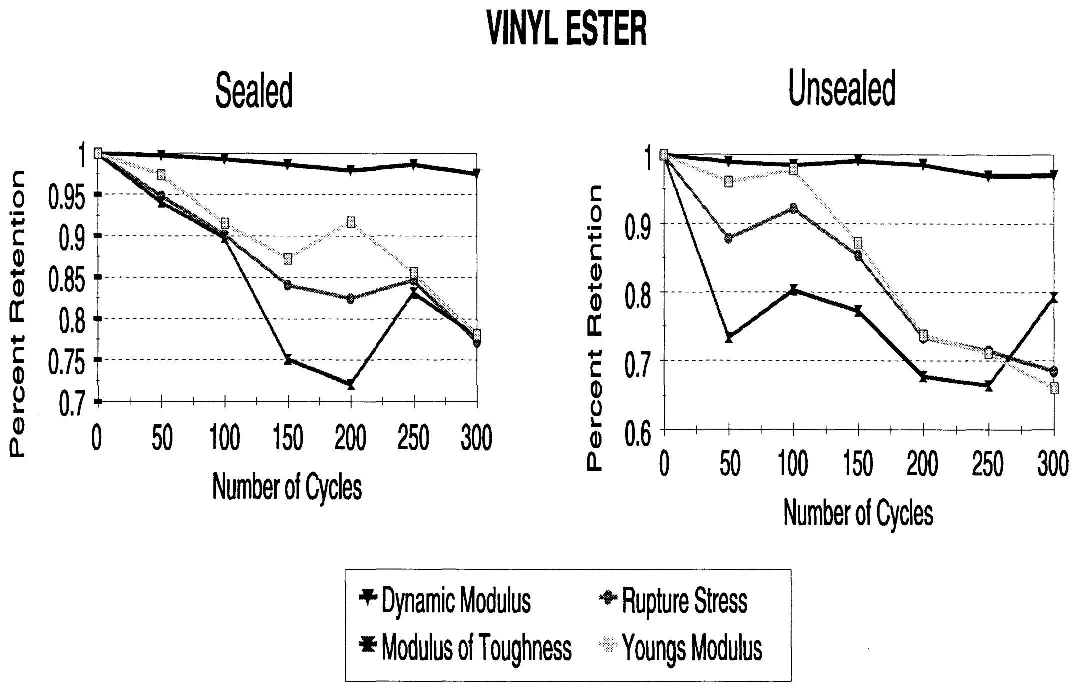

Figure 3. Vinyl Ester freeze/thaw degradation.

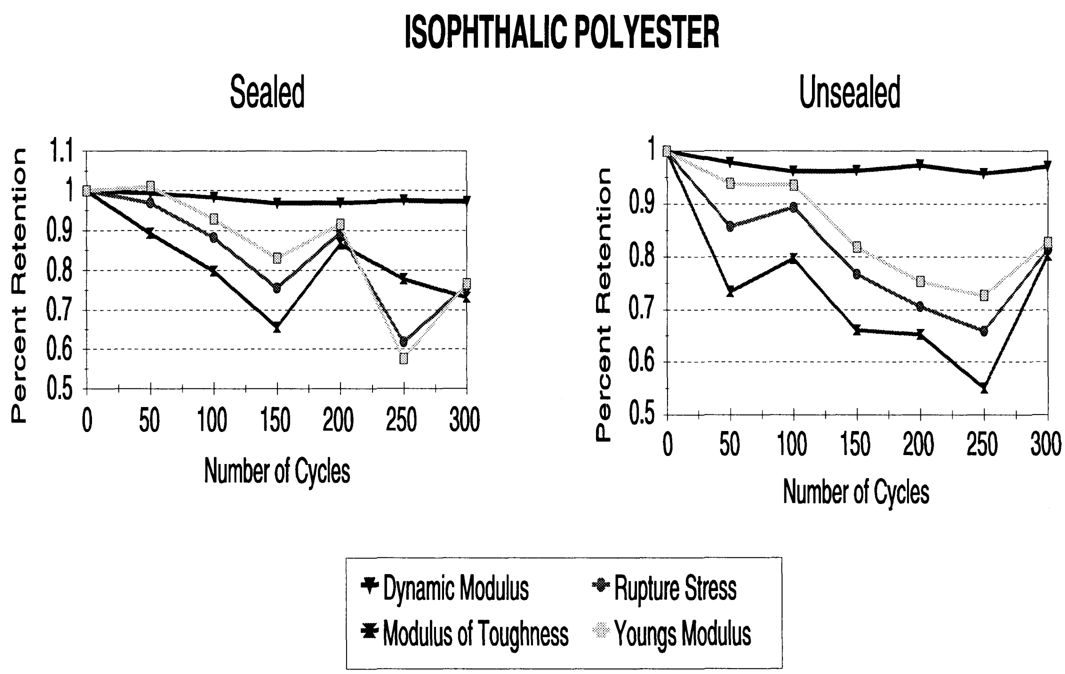

Figure 4. Isophthalic Polyester freeze/thaw degradation.

The unsealed isophthalic polyester coupons lost 19% (±8%)of their initial flexural strength at the termination of cycling, and the sealed specimens lost 24%, (±14%) as shown in Figure 4. The unsealed coupons lost 3% to 4% (±1%) of their initial dynamic modulus values whereas the sealed coupons lost between 2.5% and 3% (±3%). Losses in modulus of toughness were observed to be 20% (±22%) for the unsealed coupons and 27% (±15%) for the sealed coupons. As shown in figure 4, the 300 cycles values of the unsealed isophthalic polyester do not follow the trend set forth by the preceding values. These values are considered to be irregular and the actual loss in property is assumed to be greater than those values observed. The moisture contents at termination of cycling were determined to be 0.15% for the unsealed coupons and 0.14% for the sealed.

The results of the testing conducted on the coupons that were not subjected to freeze/thaw cycles can be seen in Table 1. This table lists the observed percent reduction of each individual property for each composite system, both sealed and unsealed, due to the effects of the salt water exposure alone at the time equivalent to 300 cycles of freezing and thawing

Table 1. Percent reduction due to salt water exposure effect at 300 cycles.

	Rupture Stress	Modulus of Toughness	Young's Modulus
Sealed Isophthalic Polyester	3%	7%	2%
Unsealed Isophthalic Polyester	5%	9%	5%
Sealed Vinyl Ester	6%	1%	3%
Unsealed Vinyl Ester	7%	15%	4%

Figures 5 and 6 show the results from the rupture stress and Young's modulus calculations in more detail (these are the more important parameters considered in design). These plots include the overall average of all the data points as well as the standard deviation of each property at the fifty cycle increments. These figures give the range of each property's performance at each given freeze/thaw cycle. It is obvious from Figures 5 and 6 that there is a distinct decline in the performance of each material for an increase in freeze/thaw cycles. The materials do tend to stabilize to a lower bound value after 200 cycles. This might be useful to designers, much like the endurance limit for steel subjected to cyclic mechanical strains.

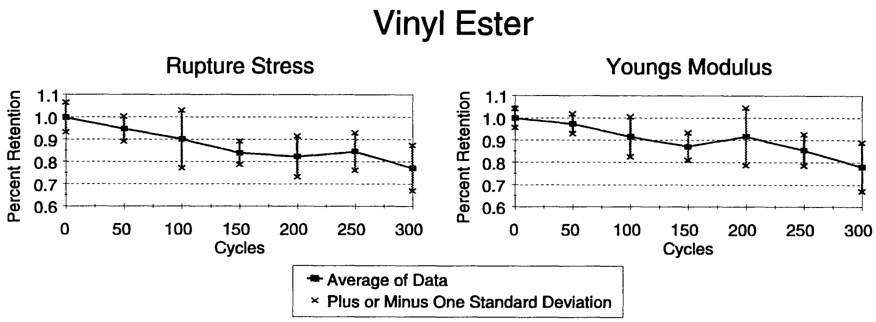

Figure 5. Rupture stress and Young's modulus calculations for Vinyl Ester.

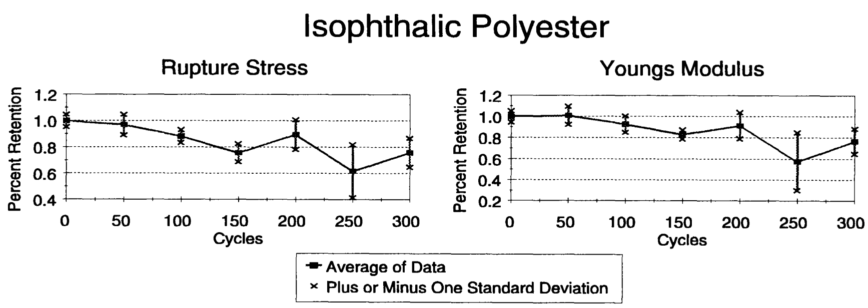

Figure 6. Rupture stress and Young's modulus calculations for Isophthalic Polyester.

CONCLUSIONS

The objective of this study was to characterize the behavior of two composite materials exposed to cycles of freezing and thawing. Results indicate significant losses in flexural strength and toughness after 300 cycles. Very little moisture was absorbed during the freeze/thaw cycles, yet loss in flexural strength compares to results reported due to much higher moisture contents.[7] When comparing values from Table 1 to the values observed from the freeze/thaw cycling, it can be seen that the freeze/thaw cycling does have a significant effect on the durability of the composite systems. It is hypothesized that damage was due to expansion of moisture during the freezing cycle, resulting in loss in strength, rigidity, and toughness. Damage to the fibers as well as to the bond between the fibers and matrix may have occurred. Microscopic evaluation of the fracture surfaces could perhaps distinguish the damage mechanisms causing material property degradation, but was beyond the scope of this study.

The dynamic modulus measurements, although showing degradation, may not be an appropriate measure of durability for composite materials. The results are far less indicative of damage when compared to the Young's modulus values.

Significant scatter in the data is noted. However, the scatter observed in the freeze/thaw coupons was relatively consistent with the scatter observed in the data from the virgin coupons. Statistical scatter in behavior of composite materials is well documented. The observed degradation in the material properties is concluded to be a direct result of freeze/thaw cycling.

The epoxy coating applied to the cut edges appeared to break down when subjected to freeze/thaw cycles. It did appear to function properly early on in freeze/thaw cycling. Perhaps a more durable coating would offer longer term protection.

The results are obviously only valid for the two FRPs evaluated in this study. There are a number of polymer matrix materials that offer greater protection in harsh environments, and other fibers, such as carbon. Further research in this area is necessary to assess the applicability of composite materials as viable alternatives to steel and concrete in the infrastructure.

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