
***NIST Workshop on Standards Development
for the Use of Fiber Reinforced Polymers for the
Rehabilitation of Concrete and Masonry Structures,
January 7-8, 1998, Tucson, Arizona.
Proceedings***

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United States Department of Commerce
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ENVIRONMENTAL DURABILITY OF COMPOSITES FOR SEISMIC RETROFIT OF BRIDGE COLUMNS

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Several composite overwrap systems have been proposed to the California Department of Transportation as alternative column casings for seismic retrofit. Environmental durability of the proposed composite casing materials is being determined as part of a qualification program. Environmental exposures include 100 % humidity, salt water, an alkali solution, diesel fuel, ultraviolet light, elevated temperature (60 °C or 140 °F), and a cyclic freeze/thaw test. Most carbon-fiber-reinforced-epoxy systems are showing excellent durability after 10 000 h exposures. However, one carbon/epoxy system had up to a 50 % reduction in short beam shear strength and a significant reduction in glass transition temperature associated with moisture absorption. The reduced glass transition temperature caused an unacceptable reduction in tensile strength at 50 °C (122 °F). E-glass-reinforced-polymer systems were susceptible to strength reductions after exposure to moist environments. For most systems and environments, this reduction was less than 20 % after 10 000 h exposures. However, one E-glass system had a 35 % reduction in tensile strength after 10 000 h in 100 % humidity at 38 °C (100 °F). None of the carbon/epoxy or E-glass/polymer systems had a significant reduction in Young's modulus from the environmental exposures.

KEY WORDS: Carbon, Composites, Durability, Environment, Fiberglass, Freezing, Moisture, Retrofit, Seismic, Thawing, Ultraviolet.

INTRODUCTION

In December 1995, the California Department of Transportation (Caltrans) formally initiated a program for the evaluation and qualification of advanced composite materials for seismic retrofit and rehabilitation of structures [1-3]. This program has been described with updates on its progress by Sultan et al. (1995, 1997, 1997). The Caltrans program is a model public-private partnership with funding from the California Department of Transportation (Caltrans), the Federal Highway Administration (FHWA), and private industry. A significant portion of the program is administered by the Society for the Advancement of Materials and Process Engineering (SAMPE) in order to facilitate the cooperative process with industry. The Aerospace Corporation is supporting Caltrans in the qualification program and was selected as an independent material testing facility. Structural testing is principally conducted at the University of California at Irvine (UCI).

The principal initial application of composites by Caltrans is a casing or overwrap on bridge columns for enhancing seismic resistance. Several composite manufacturers have developed composite casing systems that have potential for being cost effective relative to current steel casing designs. In April 1996, Caltrans issued pre-qualification requirements for alternative column casings for seismic retrofit and later amended these requirements in January 1997 [Chapman et al. (1997)]. These requirements include durability testing to demonstrate the ability of the proposed composite material systems to withstand a variety of climatic and unnatural exposure conditions. Environmental exposures include 100 % humidity

at 38 °C (100 °F), immersion in salt water, immersion in an alkali solution, ultraviolet light, dry heat at 60 °C (140 °F), a freeze/thaw test, and immersion in diesel fuel. The effects of the environmental exposures are being quantified by measurements of the composite panel mass, tensile modulus, strength, failure strain, interlaminar shear strength, and glass transition temperature. Property measurements are being made after exposure intervals of 1 000 h, 3 000 h, and 10 000 h to allow estimates of degradation over the projected service life

In this paper, the candidate composite overwrap systems are described and the preliminary results of the environmental durability testing are presented. The objective of the durability program is to determine whether the initial, baseline properties are maintained after the environmental exposures. Complete descriptions of the environmental exposure conditions and property test methods are given.

EXPERIMENTAL PROCEDURES

Composite Overwrap Systems

Through January 1998, 13 composite overwrap systems were undergoing environmental durability qualification testing for seismic retrofit of bridge columns. The overwrap system manufacturers are identified in Table 1 along with generic

Table 1--Composite systems undergoing environmental durability qualification testing

SUPPLIER	COMPOSITE SYSTEMS
Fyfe Company	2 E-Glass/Epoxy & 1 Carbon/Epoxy
XXsys Technologies, Inc	3 Carbon/Epoxy Systems
Hardcore DuPont Composites L.L.C.	E-Glass/Vinyl Ester
CMI, Incorporated	E-Glass/Polyester
TONEN Corporation	2 Carbon/Epoxy Systems
Mitsubishi Chemical Corp.	Carbon/Epoxy
Mitsubishi Chemical Obayashi Corp.	Carbon/Epoxy
Mitsubishi Chemical Toray Industries, Inc.	Carbon/Epoxy

descriptions of the composite types. The list of systems includes nine carbon/epoxy systems, two E-glass/epoxy systems, one E-glass/vinyl ester system, and one E-glass/polyester composite.

The Hardcore DuPont and CMI systems are prefabricated shells that are manufactured in a factory and bonded to the column. The XXsys and Mitsubishi/Obayashi systems are applied to the column using filament winding techniques. XXsys uses preimpregnated fiber tows and an elevated-temperature-curing resin system while Mitsubishi/Obayashi uses wet winding and an ambient-temperature-curing resin system. The Fyfe Co., Tonen, Mitsubishi, and Mitsubishi/Toray overwraps are all hand lay-up systems utilizing ambient-temperature-curing epoxy matrices. Fyfe Co. employs a portable saturation machine to preimpregnate the resin into the glass or carbon fabric immediately before applying the fabric to the column. The other hand lay-up systems all involve separate application of the resin and fiber onto the column and subsequent impregnation using special rollers or squeegees.

All 13 overwrap systems are essentially passive systems in which the overwrap is not under any significant stress until an earthquake occurs. Their effectiveness in enhancing seismic resistance of bridge columns depends upon confinement of the column concrete. Thus, high strength and stiffness are required in the hoop direction of the column overwrap and maximum fiber loading is in this direction. High strength and stiffness must be maintained in the hoop direction throughout the design life of the overwrap. Thus, the environmental durability qualification test program places a strong emphasis on determining any environmental effects on Young's modulus, tensile strength, and failure strain in the hoop direction of the composite overwrap systems.

The seismic retrofit of bridge columns application is unique in that the composite fully encases the column so that a strong adhesive bond between the composite and the concrete is probably not required. Also, as noted above, the

composite is not under any significant stress under normal conditions. Thus, the effects of environmental exposures on fatigue and creep properties of the composites and composite-to-concrete bond strength are not addressed in this program. However, these are important issues for other composite retrofit applications, such as beam strengthening, and must be studied in other programs.

Environmental Exposures

The test matrix of environmental durability exposure conditions required by Caltrans is given in Table 2. Flat laminates of each candidate composite system are being subjected to these environmental exposures for the times or numbers of cycles indicated. Each panel is subjected to one exposure condition. Thus, the individual effects of each exposure condition are being evaluated. Synergism between the different exposures is not being evaluated except as indicated in the ultraviolet/condensation and freeze/thaw exposures. Natural or climatic exposures include: water resistance, salt water resistance, ultraviolet resistance, and a cyclic freeze/thaw test. Additional exposures include 4 h in diesel fuel to evaluate the effects of a fuel spill following a vehicular accident and an alkali solution

Table 2--Environmental durability test matrix

ENVIRONMENTAL DURABILITY TEST	TEST CONDITIONS	TEST DURATION h
Water Resistance	100 % Humidity At 38 °C	1 000, 3 000, & 10 000
Salt Water Resistance	Immersion At 23 °C	1 000, 3 000, & 10 000
Alkali Resistance	Immersion In CaCO ₃ pH = 9.5 & 23 °C	1 000, 3 000, & 10 000
Dry Heat Resistance	Furnace At 60 °C	1 000 & 3 000
Fuel Resistance	Immersion At 23 °C	4
Ultraviolet Light Resistance	Cycle Between UV At 60 °C & Condensate At 40 °C	4 per Condition, 100 Cycles
Freeze/Thaw Resistance	Cycle Between 100 % Humidity At 38 °C & Freezer At -18 °C	24 per Cycle, 20 Cycles

exposure to evaluate long-term compatibility between the concrete column and composite overwrap.

For water resistance, 100 % humidity at 38 °C (100 °F) was selected as an accelerated test. This exposure is considered more severe than an immersion test at ambient temperature because the elevated temperature increases water absorption and chemical reaction rates and the high humidity exposure allows for atmospheric reactions that would not occur in an immersion test. The humidity exposure was performed following the procedures of ASTM D 2247 (1995). The composite panels were mounted on racks in the humidity chamber and held in a vertical position. The humidity chamber was set up to provide condensation on the panel surfaces.

An immersion test was selected for salt water resistance to test the effects of prolonged immersion in ocean water. Substitute ocean water prepared following ASTM D 1141 (1995) was used for the salt water resistance exposure. The composite panels were immersed in 10 L of substitute ocean water which was maintained in a 36 L, closed polypropylene container having the approximate inside dimensions of 50 cm x 35 cm x 15 cm. All test panels for a given composite system were exposed in a single container, but separate containers were used for different systems. The test panels rested on the bottom of the containers in a horizontal position with adequate gaps between panels to maintain chemical equilibrium throughout the liquid bath.

The 60 °C (140 °F) exposure was selected as the maximum exposure temperature anticipated in service. At the elevated temperature, it was anticipated that any degradation would occur rapidly. Therefore, the maximum exposure time was limited to 3 000 h. The exposure was carried out following ASTM D 3045 (1995) with the panels resting on horizontal racks in a forced-draft circulating air furnace. All composite systems were exposed in the same furnace with a separate rack for each system.

A standard ultraviolet (UV) resistance test [ASTM G 53 (1995)] is being used to determine

the effects of alternating ultraviolet light and condensating humidity exposures. One side of the composite panels is exposed to cyclic exposures of fluorescent ultraviolet light at 60 °C (140 °F) for 4 h followed by water condensation at 40 °C (104 °F) for 4 h. Total exposure will be for 100 cycles. The ultraviolet resistance test was initiated during January 1998 and was not completed until after preparation of this paper. Therefore, no UV results are included.

The freeze/thaw test was developed to determine the effects on the composite systems of freezing following significant water absorption. The panels were maintained in the humidity chamber at 100 % humidity and 38 °C (100 °F) for a minimum of two weeks prior to the initial exposure to the freezer at -18 °C (0 °F). Typically, the panels were placed in the freezer at the beginning of the work day and returned to the humidity chamber at the end of the day. Thus, each 24 h cycle included approximately 9 h in the freezer and 15 h in the humidity chamber. It was anticipated that any effects of the freeze-thaw exposure would become apparent after a few cycles and the test was performed for only 20 cycles. However, it was recognized that the effects could become more pronounced with additional cycling. Therefore, allowance was made to perform additional freeze/thaw cycles on any composite systems showing susceptibility to this exposure.

The alkali resistance test was performed to determine any effects on composite overwraps from the high alkalinity of concrete columns. This is an important test because it is well known, as demonstrated by Litherland et. al. (1991) and Yilmaz (1991), that unprotected glass fibers are severely degraded in alkaline solutions. Seymour (1988) has reported that many organic resins are also susceptible to chemical attack in strong alkali solutions. A saturated solution of calcium carbonate, CaCO₃, in water having a pH of 9.5 was selected for this exposure. Tremper (1966) reported that fresh concrete, or the interior of aged concrete, has a much higher alkalinity (pH ≥ 14). However, for the seismic retrofit of bridge

columns application, all columns requiring retrofit are at least 20 years old. Concrete reacts with the atmosphere to form CaCO₃ and it was anticipated that this would be the appropriate alkaline solution exposure for this program. Field tests were performed on aged columns under Interstate 10 in Los Angeles and indicated that even after light surface grinding, representative of typical column wrapping surface preparation, concrete pH did not exceed 9.0 [Steckel (1998)]. Therefore, a saturated solution of CaCO₃ having a pH of 9.5 was verified to be an appropriate alkalinity exposure for the seismic retrofit of bridge columns application. The alkaline and diesel fuel exposures were performed in the same type of container and followed the same immersion procedures as described above for the salt water resistance exposure.

The exposure panels were approximately 30 cm x 30 cm (12 in x 12 in) and had thicknesses which were not allowed to exceed the minimum thickness of a column overwrap. For most systems, the panels had thicknesses much less than a column overwrap, thus adding to the conservative approach of the qualification program. Exposure panels were required to have the same lay-up and, to the greatest possible extent, follow the same processing procedures as a column overwrap. For example, exposure panels for filament wound systems had to be wound using the same filament winding equipment used for column wrapping. Composite column overwraps have minimal exposure of edges to the environment. Therefore, edge protection was allowed along all four edges of the exposure panels. The edge sealant, typically epoxy, was selected by each manufacturer and approved by The Aerospace Corporation and Caltrans. Although most systems are painted following application to bridge columns, no painting of environmental durability panels was allowed. A single panel was exposed to each environmental condition for each required duration. Thus, for each system, a total of 14 panels were required for the environmental durability test matrix. An

additional four panels were required for establishing baseline material properties.

Material Property Measurements

The effects of the environmental exposures were determined from measurements of tensile properties (Young's modulus, ultimate tensile strength, and strain to failure), short beam shear strength, and Shore D hardness of the composite and glass transition temperature of the resin matrix. Measurements on exposed panels were compared to baseline values determined for four unexposed panels for each composite system. Multiple panels were used for characterizing baseline properties in order to quantify panel-to-panel variations. Otherwise, misinterpretation of the effects of the environmental exposures on material properties could result. It is important to note that the environmental durability of each system is being evaluated based upon a comparison with the baseline properties for that system. No comparisons of absolute values of material properties for different systems are being made since each system has a unique overwrap design and, therefore, unique material requirements.

Mass measurements were made on each panel before and after the environmental exposures and periodically throughout the 10 000 h exposures. The primary purpose of these measurements was to monitor moisture absorption during the humidity, salt water, alkali solution, freeze/thaw, and ultraviolet/condensation exposures and moisture dry-out from the oven exposure. These measurements are very important for determining the time to reach equilibrium in each environment, for establishing any relationship between moisture content and property changes, and for predicting long-term effects.

For those systems in which prefabricated composite shells are installed onto the columns with adhesive bonding between the composite and column and/or between successive layers of the prefabricated composite, environmental durability testing is also required for the adhesive. Separate test panels were required for each exposure

condition given in Table 2 for adhesive durability testing. Lap shear strength measurements were made on samples having composite-to-composite bonds to determine adhesive degradation. At the present time, the Hardcore DuPont and CMI overwraps are the only systems requiring adhesive qualification. Adhesive qualification results are not included in this paper.

A schematic drawing of an exposure panel in Figure 1 shows the typical sectioning of the panels following exposure for property measurements. This drawing was followed for sectioning panels unless visible defects, unrelated to the environmental exposure, which could affect property measurements were observed. Whenever possible, the sectioning plan was changed to avoid such defects. Although the edges of the panels were sealed, a 25 mm border around the outside of each exposure panel was discarded. A 25.4 cm x 15.2 cm area was cut out for the preparation of 5 tensile samples. Strips 6.5 mm and 13 mm wide were cut out for 6 short beam shear samples and 1 glass transition temperature sample, respectively. All tensile, short beam shear, and glass transition temperature samples were cut out with the sample length parallel to the primary fiber-reinforced direction of the composite panels. All panel sectioning was performed using a water-cooled diamond cut-off wheel.

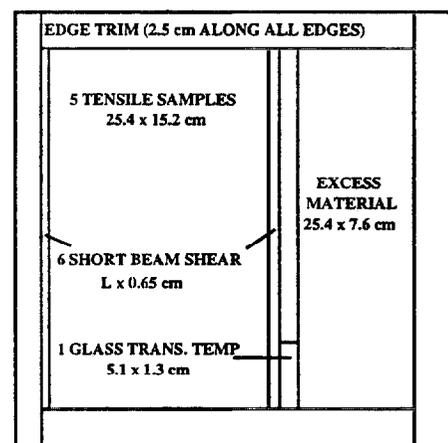


Fig. 1-- Lay-out for cutting samples from a 30 cm x 30 cm composite durability panel

All property tests were performed within 7 d after the panels were removed from the exposure environments. Maintaining this schedule was particularly important for panels exposed to the various moisture absorption environments in order to minimize moisture dry-out prior to testing. In order to minimize moisture dry-out rates or other atmosphere/panel interactions, all panels were maintained in sealed plastic bags following exposure.

Uniaxial tensile tests were performed using straight-sided, tabbed samples following sample preparation and test procedures specified in ASTM D 3039 (1995). G10 fiberglass/epoxy grip tabs 1.6 mm-thick and 51 mm-long with a 7° taper were bonded across both ends on each side of the panel section for tensile samples shown in Figure 1. The grip tabs were bonded using Hysol EA 9394 adhesive which was cured at ambient temperature. The adhesive was allowed to cure for a minimum of 2 d before five 1.9 cm-wide tensile samples were cut from the tabbed panel section using a water-cooled diamond cut-off wheel. The grip tabs were allowed to cure a minimum of 5 d prior to tensile testing. Tensile testing was performed using an Instron Universal Testing Machine having wedge grips. Strain was measured throughout the test using a 5.1 cm-gage length, clip-on extensometer. Samples were loaded to failure at a constant crosshead rate of 5.1 mm/min, giving an approximate strain rate of 0.0006 /sec. Load and strain were recorded with a strip chart recorder and a computer data acquisition system. Young's modulus was calculated by a least squares analysis of the stress-strain curve over the strain range from 0 to 0.0050.

Hardness measurements were made on each composite panel using a Shore D durometer. A total of 6 measurements were made on each panel, 3 on each side. The hardness measurements were made on the grip region of the tensile samples prior to the application of grip tabs.

Apparent interlaminar shear strength measurements were made by the short beam shear method following ASTM D 2344 (1995). ASTM D 2344 recommends support span/composite

thickness ratios of 5 for glass fiber-reinforced composites and 4 for carbon fiber-reinforced composites. Recommended diameters for support pins and the nose pin are 3.2 mm and 6.4 mm, respectively. The minimum span length was defined as the length for which the nose pin fits between the support pins, 9.6 mm for the recommended pin diameters. Therefore, the minimum sample thicknesses were approximately 2.4 mm for carbon fiber systems and 1.9 mm for glass fiber systems. For the glass fiber systems, the panel thicknesses selected for the test program exceeded the minimum thickness requirement for short beam shear strength (SBSS) testing. But for the carbon fiber systems, the selected panel thicknesses were typically around 1.3 mm, much too thin for SBSS testing. Therefore, separate panels having a minimum thickness of 2 mm, but typically greater than 2.5 mm were fabricated for the SBSS tests. These thicker panels were used only for short beam shear testing and relatively small panels (typically 9 cm x 9 cm) were exposed along with the larger panels. Sample thicknesses for the SBSS testing varied for the different composite systems from approximately 2 mm to 5 mm and the support span was varied to maintain the recommended span/thickness ratio. Sample lengths were also varied to maintain the recommended length/thickness ratios of 7 for glass fiber systems and 6 for carbon fiber systems. For any given composite overwrap system, constant sample and span lengths were maintained for all exposures.

The glass transition temperature of the composite matrix was determined using a Rheometrics Dynamic Mechanical Analyzer (DMA). The Rheometrics DMA subjects a 5.1 cm x 1.3 cm sample to cyclic torsional deformations and quantifies the material response by measuring the shear modulus, G' , the shear loss modulus, G'' , and the lag angle between the applied stress and resulting strain, $\tan \delta$, as functions of temperature. Plots of any of these three parameters versus temperature can be used to determine the glass transition temperature, T_g . In this program, the G'' curve was used because it

usually gives a sharp peak at the transition, making it easier to determine T_g than for the $\tan \delta$ or G' curves.

The mechanical and physical property measurements discussed in this section are the only measurements specifically required for assessing durability in the Caltrans prequalification requirements document [Chapman (1997)]. However, the document states that additional tests may be imposed to ensure the durability of any proposed composite casing system. For example, as will be discussed below, one system was susceptible to significant reductions in glass transition temperature due to moisture absorption. The T_g was reduced to the point that there were concerns that the tensile strength could be significantly reduced at the higher service temperatures. Therefore, additional tensile testing was performed at 50 °C (122 °F) which verified a potential strength problem at elevated temperatures.

One of the prefabricated systems having bonded shells uses an adhesive which also has a low glass transition temperature. For this system, additional lap shear strength tests were performed at temperatures up to 50 °C (122 °F). In addition, split-D tests were performed on 50 cm-diameter rings at temperatures up to 60 °C (140 °F) to ensure that this system maintained the required strength and stiffness at maximum service temperatures.

Thus, although limited testing is required, the test matrix was designed to provide both engineering data and fundamental material response data so that potential problems could be identified. When potential problems are revealed, additional tests are instituted to ensure that the composite casing system under evaluation meets Caltrans requirements.

RESULTS AND DISCUSSION

Through January 1998, material property testing following all exposures except the cyclic UV/condensation exposure was completed for three glass fiber/polymer resin systems and four carbon fiber/epoxy resin systems. Testing for two

additional carbon fiber/epoxy systems was completed following the 3 000 h exposures. The 10 000 h exposures and property testing for these two systems was scheduled for completion during March 1998. Two other carbon fiber systems and one glass fiber system had been tested following the 1 000 h exposures and were on schedule for completion of the 3 000 h exposures in March 1998 and the 10 000 h exposure in January 1999. The other carbon/epoxy system was still in the panel fabrication stage.

In this paper, highlights are being presented of the experimental results for the seven systems for which the test matrix has been completed. In presenting the data, the manufacturers are not identified. The carbon fiber systems are identified as C1, C2, C3, and C4 and the glass fiber systems are identified as G1, G2, and G3. In addition, the absolute values of mechanical properties are not reported. All mechanical property data for each exposure condition for any given material system are normalized by dividing by the average property value for the control samples for that system. Therefore, the exposure results are shown as fractions of the average control values, so any degradation due to the exposures is easily identified. For tensile properties, the exposure data were determined from the average of 5 samples and the control data were for the average of 20 samples. For the SBSS, the exposure data were for the average of 6 samples and the control data were for the average of 24 samples. Graphs showing plots of normalized, averaged properties as functions of exposure time will be presented. These graphs will also show the coefficient of variation (CV) for the control samples. This information is useful for judging the significance of any property changes resulting from the various exposures relative to scatter bands for control data.

Before presenting the results for the individual E-glass/polymer and carbon/epoxy systems, certain general observations that applied to all systems will be discussed. One of the most important findings was that no significant reduction in Young's modulus was measured for

any system following any of the environmental exposures. No reductions in Young's modulus exceeding 5 % were measured. This is an important result since the design of composite casings for seismic retrofit is stiffness critical.

Another important implication of the fact that Young's modulus was not affected by the various exposures is that any changes in failure strain arising from an exposure condition were essentially equal to changes in tensile strength. This is due to the fact that all of the systems under evaluation are either unidirectionally reinforced or are reinforced with highly unbalanced, essentially unidirectional woven fabrics. As a result, the stress-strain curves for all seven systems were nearly linear to fracture. Thus, it follows that if the modulus did not change, any changes in strength and failure strain were approximately equivalent. In the discussion that follows, reductions in tensile strength due to some of the environmental exposures will be presented. The reader should be aware that although data for failure strain will not be presented, any reduction in normalized tensile strength was accompanied by a similar reduction in normalized failure strain.

A second general observation was that the exposure to 60 °C (140 °F) had no degrading effects on the mechanical and physical properties for any system. Room temperature tensile properties were unaffected by this exposure. All systems experienced a small decrease in mass (0.1 % to 1.0 %) due to moisture dry-out at the elevated temperature. Furthermore, the ambient-temperature-cured systems generally had an increase in glass transition temperature. T_g ranged from 60 °C to 68 °C (140 °F to 154 °F) for the control panels for the different ambient-temperature-cured systems and ranged from 66 °C to 95 °C (151 °F to 203 °F) for these systems after the 3 000 h exposure to 60 °C (140 °F). Thus, the only effects of the elevated temperature exposure were to drive off absorbed moisture for all composites and to advance the cure of the ambient-temperature-cured systems. As a result of these two effects, all systems had a small increase in short beam shear strength following

the 60 °C (140 °F) exposure. After 3 000 h, the increase in SBSS was between 5 % and 10 % for the elevated-temperature-cured systems and between 10 % and 15 % for the ambient-temperature-cured systems.

It was anticipated that the only potential effects of the 4 h exposure in diesel fuel might be some surface reaction or dissolution of the polymer matrix. These effects might be detected by a reduction in hardness, T_g , or SBSS. None of these properties were affected by the diesel fuel exposure. One E-glass/polymer system, G1, and one carbon/epoxy system, C2, did have small reductions in tensile strength and failure strain. The apparent reductions were around 10 % and were probably due to panel-to-panel variations for these two systems. Nevertheless, the 4 h diesel fuel exposure and subsequent property measurements will be repeated for systems G1 and C2 to resolve this issue. No other systems showed any effects from the diesel fuel exposure.

It will be shown in the discussion that follows that the polymer matrix for some systems was significantly softened due to moisture absorption. This plasticization of some polymer matrices was detected by reduced T_g 's and lower SBSS. Despite this softening of the composite matrix for some systems, Shore D hardness measured with a durometer was not affected by any exposure for any system. Durometer hardness measurements for composites are dominated by the reinforcement unless the sample has a thick layer of resin on the surface. None of the systems studied had a thick resin layer on the panel surfaces. Therefore, since the hardness of carbon or E-glass fibers is probably not affected by the exposure conditions studied in this program, it is not surprising that no changes in Shore D hardness were measured.

E-Glass/Polymer Systems G1, G2, and G3

All three E-glass/polymer systems demonstrated some degree of susceptibility to tensile strength degradation from long-term moisture exposure. This degradation is demonstrated in Figure 2 which shows plots of normalized tensile strength

as a function of exposure time in 100 % humidity at 38 °C (100 °F) or in the pH 9.5 alkali solution. In these plots, exposure time is expressed in days. Thus, exposure times are 41.7 d, 125 d, and 417 d for the 1 000 h, 3 000 h, and 10 000 h exposures, respectively. Note that the plots for 100 % humidity include the freeze/thaw panels which were exposed to 36 d in the humidity chamber. The graphs in Figure 2 also show the coefficients of variation for the control samples. The coefficients of variation were around 12 % for systems G1 and G3, but only 6 % for system G2.

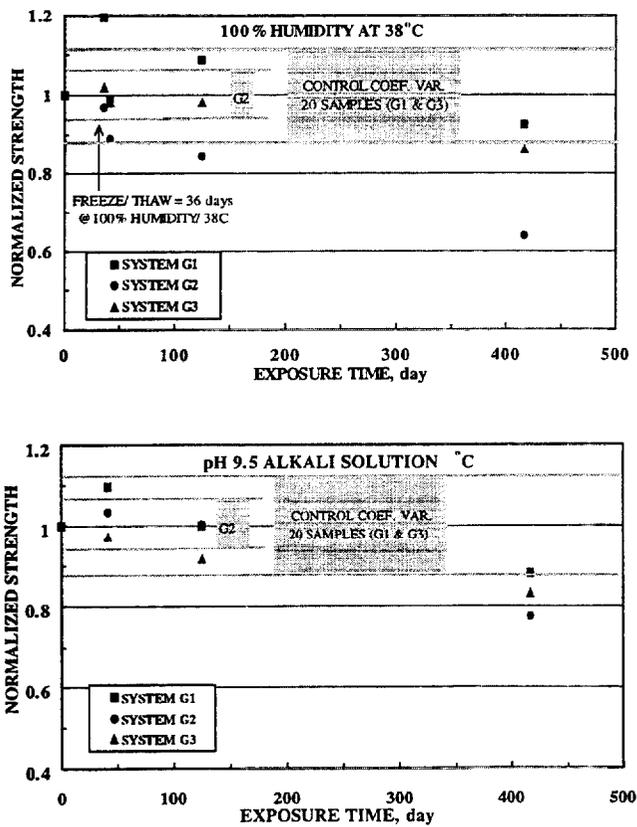


Fig. 2--Normalized tensile strength for systems G1, G2, and G3 as functions of exposure time in 100 % humidity at 38 °C (100 °F) or pH 9.5 alkali solution at 23 °C (73 °F).

The most severe degradation in tensile strength was experienced by system G2 when exposed to 100 % humidity at 38 °C (100 °F). The degradation in tensile strength progressively

increased from approximately 10 % after 1 000 h (41.7 d) to 35 % after 10 000 h (417 d). The most alarming observation was that there was no indication that the rate of degradation was diminishing with exposure time. Thus, additional degradation would be expected for longer exposure times. The 100 % humidity at 38 °C (100 °F) environment is clearly an accelerated test for system G2 relative to an ambient temperature immersion test. This is demonstrated by the much lower degradation rate for system G2 from the alkali solution immersion. Similar results were obtained for the salt water exposure. There was no apparent degradation in tensile strength of system G2 after 1 000 h or 3 000 h (41.7 d or 125 d) exposures in the alkali or salt water solutions. But a degradation of approximately 20 % was measured after 10 000 h (417 d) immersions. Interpretation of the tensile strength results for systems G1 and G3 was complicated by the relatively high scatter for the control samples. The high scatter was due to large panel-to-panel variations. For example, the spread in average tensile strength between the strongest and weakest control panels was 38 % for system G3 and 29 % for system G1. On the other hand, the coefficient of variation for the five tensile tests for any given panel did not exceed 7.5 %. Panel-to-panel variations were particularly undesirable since separate panels were used for each exposure and for control testing. Figure 2 shows that after 1 000 h and 3 000 h (41.7 d and 125 d) exposures in the humidity chamber or alkali solution, the tensile strength for systems G1 and G3 was within the scatter band established by the control samples. Similar results were obtained for the salt water exposure. After 10 000 h (417 d) exposures, the normalized tensile strength for system G3 was below the control sample scatter band for all three moisture exposure conditions. The apparent degradation varied from 13 % for the 100 % humidity at 38 °C (100 °F) exposure to 20 % for the salt water exposure. Thus, it was concluded that the tensile strength of system G3 was affected by the 10 000 h (417 d) exposures to moist environments.

For System G3, 61 cm by 61 cm panels were fabricated and subsequently sawed into four 30 cm by 30 cm subpanels for durability testing. One of these large panels was used for the humidity exposures, a second was used for salt water, and a third was used for alkali. In each case, one subpanel was used as a control panel and the other three were used for the three different exposure times. It was assumed, and later verified by the experimental results, that panel-to-panel variations would be smaller for the four subpanels sawed from a single large panel than for subpanels from different large panels. Therefore, it is more appropriate to normalize the data for each of these exposures relative to the average tensile strength for the control panel sawed from the same large panel, rather than relative to the average data for all four control panels (which were sawed from four different large panels). When this data reduction approach was followed, there was no degradation in tensile strength for system G1 from the 1 000 h or 3 000 h exposures in the humidity chamber, salt water, or alkali solution. Degradation after 10 000 h exposures was 15 % for 100 % humidity at 38 °C (100 °F), 12 % for salt water, and only 6 % for the pH 9.5 alkali solution. The coefficients of variation for the control samples were 2 % for humidity, 7.5 % for salt water, and 5 % for alkali. Thus, it was concluded that system G1 had tensile strength reductions similar to those for system G3 after 10 000 h (417 d) exposures to moist environments.

In most cases, the tensile strength of the E-glass/polymer systems was unaffected by 1 000 h or 3 000 h exposures to the humidity chamber, salt water, or alkali solution, but was significantly degraded by 10 000 h exposures. Therefore, the current results are not sufficient to predict the effects of longer term exposures. It must be concluded that additional data, either from longer term exposures, accelerated testing, or both, will be needed. Until additional data are available, conservative design values for tensile strength and failure strain must be used, particularly for system

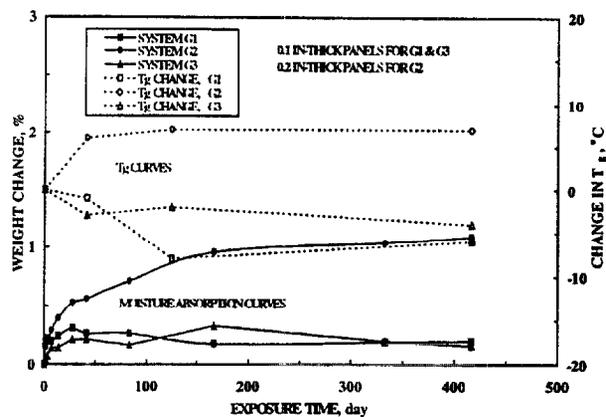


Fig. 3--Moisture absorption and change in glass transition temperature for systems G1, G2, and G3 as functions of exposure time in 100 % humidity at 38 °C (100 °F).

G2, to account for potential long-term moisture exposure effects.

Figure 3 shows plots of weight change and changes in the glass transition temperature for systems G1, G2, and G3 as functions of exposure time in the humidity chamber. The weight change is assumed to be due to moisture absorption. Although the moisture absorption for system G2 was not unusually high at around 1 %, it was 4 to 5 times higher than that for either system G1 or system G3. Also note that although most of the moisture absorption for system G2 occurred during the first 3 000 h (125 d) in the humidity chamber, the moisture content was still increasing after 10 000 h (417 d). Moisture absorption rates in the salt water and pH 9.5 alkali solutions were similar to those in the humidity chamber for each of the three E-glass/polymer systems. It is well documented that E-glass fibers are susceptible to tensile strength degradation when exposed to moisture. It is assumed that the tensile strength reductions measured for systems G1, G2, and G3 from the 100 % humidity at 38 °C (100 °F), alkali, and salt water exposures are due to this effect. System G2 absorbed significantly more moisture and therefore had larger strength reductions. Since elevated temperatures accelerate the degradation rate [Litherland et. al (1991) and Bank et. al. (1998)], the degradation for system G2 was much higher in the humidity chamber than for the

room temperature immersions in salt water or CaCO_3 , even though the moisture absorption rates were similar.

Figure 3 shows that T_g for system G2 increased from the humidity chamber exposure, while T_g for systems G1 and G3 decreased. The T_g of system G2 increased because the 38 °C (100 °F) exposure advanced the cure state of the matrix. This offset any decrease in T_g due to moisture absorption. Systems G1 and G3 had fully cured matrices and therefore had a small decrease in T_g due to moisture absorption. The T_g for all three systems stabilized after 1 000 h to 3 000 h (42 d to 125 d) exposures. System G2 did show a small reduction in T_g due to the room temperature moisture absorption in the salt water and alkali solutions. However, the decrease did not exceed 5 °C. The biggest effect on T_g was for system G1 which had a 30 °C reduction in T_g after 3 000 h in the alkali solution. However, this was not a concern because no further reduction was observed after the 10 000 h exposure, the T_g was still over 40 °C higher than the maximum service temperature, and no effects on the hardness or SBSS were measured.

System G2 was the only E-glass/polymer system that had any significant reduction in short beam shear strength. It had reductions in SBSS of 10 % to 20 % after the 10 000 h humidity, salt water, and alkali solution exposures. System G2 also had a 12 % reduction in SBSS following 20 freeze/thaw cycles. The reductions in SBSS are consistent with the increased moisture absorption for system G2 as compared to systems G1 and G3.

Carbon/Epoxy Systems C1, C2, C3, and C4

The excellent environmental durability of carbon fibers was reconfirmed in this investigation. No significant reduction in Young's modulus, tensile strength, or failure strain was measured for any of the four carbon/epoxy systems after any exposure condition. The only notable change in tensile properties was a reduction in tensile strength and failure strain of approximately 15 % for system C2 following the 10 000 h exposure to 100 %

humidity at 38 °C (100 °F). However, this system had a layer of epoxy applied to the panels after the panels were cured. Due to improper surface preparation, the bond strength of this layer of epoxy decreased during the 10 000 h humidity exposure. The epoxy layer debonded under the grip tabs during tensile testing and caused premature failures under the grip tabs.

Figure 4 demonstrates the most dramatic effect of the environmental exposures. The short beam shear strength of carbon/epoxy system C1 following the 100 % humidity, salt water, alkali, and freeze/thaw exposures was reduced by up to 50 % (for humidity exposure). System C4 was also affected by these exposures, but as Figure 4 demonstrates, to a much lesser extent. Mass measurements (Figure 5) indicated that system C1 absorbed at least three times as much moisture for any exposure time as any other carbon or glass system under evaluation. The large reduction in SBSS for system C1 was undoubtedly due to the high moisture absorption.

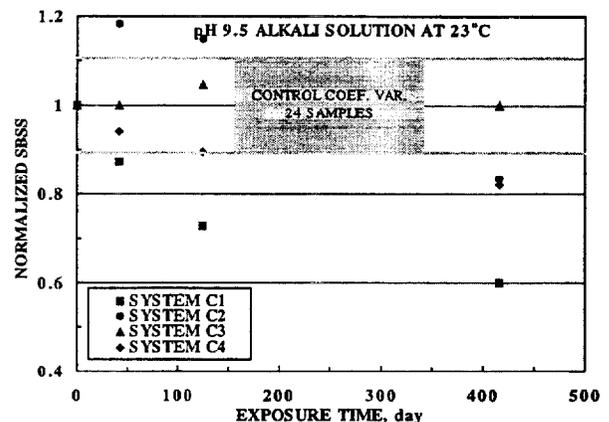


Fig. 4--Normalized short beam shear strength for systems C1, C2, C3, and C4 as functions of exposure time in pH 9.5 alkali solution at 23 °C (73 °F).

Although the SBSS data are a good indicator of changes in matrix properties, a reduction in SBSS is not expected to affect the performance of a column overwrap so long as there are no accompanying reductions in tensile properties. Thus, the primary concern of the high moisture

absorption of system C1 was the decrease in T_g . T_g for this system is normally around 65 °C (150 °F). However, as Figure 5 shows, T_g was reduced by moisture absorption to values as low as 44 °C (110 °F) following 20 freeze/thaw cycles or 50 °C (122 °F) after 3 000 h (125 d) in the alkali solution. Therefore, on a hot day the temperature of the column overwrap could exceed the matrix T_g . Under these conditions, the matrix may no longer provide adequate load transfer between fibers and the tensile strength could be degraded. Therefore, additional tensile tests were performed at 50 °C (122 °F) on control and exposed samples for system C1 to address this concern.

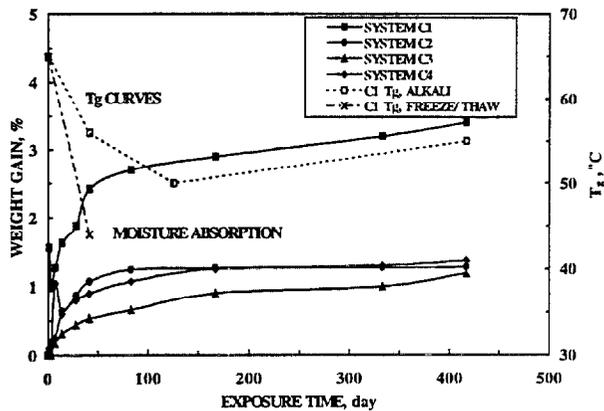


Fig. 5--Moisture absorption and glass transition temperature for systems C1, C2, C3, and C4 as functions of exposure time in pH 9.5 alkali solution at 23 °C (73 °F).

The elevated temperature tests showed that control samples having a T_g of at least 60 °C (140 °F) maintained at least 80 % of their room temperature [<27 °C (80 °F)] tensile strength when tested at 50 °C (122 °F). Samples exposed to 100 % humidity, 20 freeze/thaw cycles, or the pH 9.5 alkali solution and having a $T_g \leq 50$ °C (122 °F) had tensile strengths at 50 °C (122 °F) that were typically less than 60 % of the room temperature values. These large reductions in tensile strength at realistic service temperatures were unacceptable and system C1 was rejected by Caltrans due to its susceptibility to high moisture absorption.

The manufacturer for system C1 subsequently made modifications to the epoxy resin and resubmitted a new set of composite panels for durability testing. The 1 000 h exposures and property testing have been completed. As Figure 6 demonstrates, moisture absorption rates from the 100 % humidity at 38 °C (140 °F), salt water, and pH 9.5 alkali solution exposures were greatly reduced with the modified epoxy matrix. In addition, the glass transition temperature was much more stable with the modified epoxy matrix and was greater than or equal to 58 °C (136 °F) following all of the 1 000 h exposures. After 20 freeze/thaw cycles, the T_g with the modified epoxy resin was 67 °C (153 °F) as compared to 44 °C (110 °F) for the original resin. Finally, the effects of the moisture exposure environments on short beam shear strength were greatly diminished with the modified resin. Reductions in SBSS ranged from 13 % to 33 % after 1 000 h exposures with the original resin, but never exceeded 8 % with the modified resin. Thus, although 3 000 h and 10 000 h testing must be completed, 1 000 h data provide compelling evidence that the epoxy resin modification solved the moisture absorption problem.

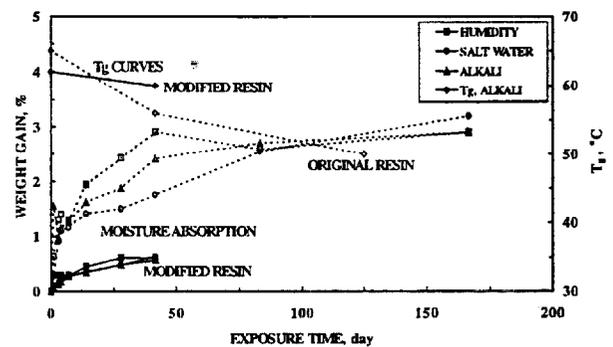


Fig. 6--Moisture absorption and glass transition temperature for system C1 with original and modified epoxy resins as functions of exposure time in moist environments.

SUMMARY AND CONCLUSIONS

Environmental durability testing is being performed on 13 composite systems that have been proposed to Caltrans for seismic retrofit of

bridge columns. 10 000 h exposures were completed for 7 systems (3 E-glass fiber/polymers and 4 carbon fiber/epoxies).

Most carbon/epoxy systems show excellent durability after 10 000 h exposures. However, one carbon/epoxy system had up to a 50 % reduction in short beam shear strength and a significant reduction in glass transition temperature associated with moisture absorption. The reduced glass transition temperature caused an unacceptable reduction in tensile strength at 50 °C.

As a result of these test results, the manufacturer modified the epoxy matrix for this system which resulted in greatly reduced moisture absorption and improved stability in the glass transition temperature and mechanical properties.

E-glass/polymer systems were susceptible to tensile strength and failure strain reductions after exposure to moist environments. For most systems and environments this reduction was less than 20 % after 10 000 h exposures. However, one E-glass system had a 35 % reduction in tensile strength and failure strain after 10 000 h in 100 % humidity at 38 °C. This system also had a 20 % reduction in short beam shear strength after 10 000 h exposures to moist environments. These effects were attributed to higher moisture absorption for this system than for the other E-glass/polymer composites. None of the other E-glass/polymer system had a significant reduction in short beam shear strength in any environment.

Although the tensile strength and failure strain for all three E-glass/polymer systems were degraded to some extent after 10 000 h exposures in salt water or the pH 9.5 alkali solution, these effects were attributed to moisture exposure. No degrading chemical effects were attributed to exposure to salts or a pH of 9.5 for any system.

None of the carbon/epoxy or E-glass/polymer systems had a significant reduction in Young's modulus from the environmental exposures.

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