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IMPACT OF PRESERVATIVE TREATMENTS AND FUNGAL EXPOSURE ON PHENOLIC FIBER REINFORCED POLYMER (FRP) COMPOSITE MATERIAL UTILIZED IN WOOD REINFORCEMENT

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By Cihat Tascioglu

Thesis Advisor: Dr. Barry Goodell

An Abstract of the Thesis Presented
in Partial Fulfillment of the Requirements for the
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When wood products are exposed to environmental conditions conducive to biodeterioration, wood preservation becomes a necessity, especially when long-term utilization is desired. Although considerable literature exists on the treatment of laminated timbers and wood composites with wood preservatives, almost no information is available on the exposure of Fiber Reinforced Polymer (FRP) composites to wood preservative chemicals. In this work, FRP material was treated with common preservative chemicals and the effect of wood preservative treatments on mechanical properties of FRP material were investigated. Although the longitudinal elastic modulus was unaffected, some longitudinal strength losses were recorded for CCA and CDDC (water borne) treated FRP coupons. These results were supported by Scanning Electron (SEM) and light microscopy analyses of single glass fibers taken from preservative treated FRP coupons.

A further study evaluated the susceptibility of E-glass fiber reinforced polymer (FRP) /phenolic pultruded composite material to fungal degradation. Since the phenolic FRP material was designed for use as reinforcement with wood, two common wood decay fungi, a brown rot and a white rot, were chosen for exposure of the FRP material. Light, fluorescent and Scanning Electron Microscopy (SEM) indicated that both wood decay fungi actively grew and penetrated into the FRP material, especially in high-void content areas. The experimental results indicate that, the mechanical property evaluation technique (ILSS) is promising and sensitive enough to detect the effects of fungal degradation in phenolic FRP materials.

The durability of adhesive bonds on wood/FRP interfaces poses a continuing problem for the wood products industry. Wood preservative chemicals are known to interfere with adhesion mechanisms between wood laminates as well as wood/FRP interfaces. The purpose of the third part of this study was to determine the effects of various wood preservative treatments and manufacturing processes (pre- and post-treatment) on wood/FRP bond durability, shear strength and surface energy characteristics of wood and phenolic FRP material. While pre-treatment of individual laminates with oil borne (copper naphthenate, creosote and pentachlorophenol) and water borne (CCA and CDDC) preservatives increased the delamination between the wood and FRP, the post treatments had limited effects on delamination.

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EFFECTS OF WOOD PRESERVATIVE TREATMENTS ON MECHANICAL PROPERTIES OF E-GLASS / PHENOLIC PULTRUDED COMPOSITE REINFORCEMENT FOR WOOD

1.1. Introduction

Most structural wood used in exposed outdoor environments should be treated with appropriate wood preservatives to prevent deterioration from decay and insect attack. Although considerable literature exists on the treatment of laminated timbers and wood composites with wood preservatives, almost no information is available on the exposure of Fiber Reinforced Polymer (FRP) composites to wood preservative chemicals (Baileys et al. 1994, Blankenhorn et al. 1999, Hojo et al. 1998, Kilmer et al. 1998, Kshirsagar et al. 2000, Lopez-Anido and Wood 2001, Rodriguez 1987, Selbo 1957, Selbo and Gronvold 1958, Shaffer et al. 1991). Because more laminated composite products are being bonded to FRP materials and these products are being targeted to exterior exposures, determining the effect that wood preservatives may have on FRP materials was studied to provide appropriate background information to engineers and wood scientists working in the field. The production of preservative treated composite reinforced laminated timbers represents the latest stage of investigation and development and is of considerable interest to both the wood preserving and composite reinforced wood hybrid industry for civil infrastructure.

In this work, phenolic FRP material used for reinforcing laminated beams were treated with common preservative chemicals and the effect of wood preservative treatments (1- Oil-borne, 2-organo-and organometallic, 3- acid and amine based water-born) on mechanical properties of FRP material were investigated. ASTM D-3039 (longitudinal and transverse tensile) and D-2344 (short beam interlaminar shear) tests were used for mechanical characterization of preservative treated E-glass/phenolic pultruded material (ASTM 1984, ASTM 1995). Although the longitudinal elastic modulus was unaffected, some longitudinal strength losses were recorded for water-borne treated FRP coupons. A simple model was used to compute the average fiber strength within preservative treated FRP coupons. These results were supported by Scanning Electron (SEM) and light microscopy analyses of single glass fibers taken from treated FRP coupons.

The work also includes a discussion of property loses that occur in the presence of threshold preservative retention levels, and how these losses affect material capacity reduction factors (knock-down factors) used in design criteria. Recommendations for use of FRP composites for wood reinforcement in exterior environments are also provided for civil engineers and the FRP-wood reinforcement industry.

1.2. Literature Review

Modern production of laminated structural members for exterior use dates back to the development of resorcinol and phenol-resorcinol adhesives about 60 years ago (Selbo, 1957). Although biological deterioration of wooden laminated members occurred, it was not until the late 1970's that the American Institute of Timber Construction (AITC) developed recommendations requiring that all exterior use laminated members be treated with preservatives (AITC 1998). Like all wood used in exposed outdoor environments, wood laminations with or without FRP composites must be treated with appropriate wood preservatives to prevent deterioration from decay fungi, insect attack, and other environmental agents (Kshirsagar et al. 2000).

Recent studies have demonstrated that FRP reinforcement in the order of 1.1% can increase the allowable bending strength of glulam beams by greater than 60% (Dagher et al. 1996). These wood hybrids, with proven mechanical properties, hold the promise of improving structures to support longer spans and heavier loads not previously possible with wood-only composites. However, to achieve long lasting service life and prevent deterioration that will occur in exterior timbers, preservative treatments must be applied to these composites. When a "post treatment" (preservative application following composite fabrication) method is used to produce reinforced wood composites, the wood hybrid material is subjected to a vacuum-pressure treatment process and wood preservative chemicals, in addition to post treatment conditioning (AITC 1998, AWPA 1999a and 1999b).

Most of the wood preservation literature focuses only on wood and wood products (Baileys et al. 1994, Blankenhorn et al. 1999, Kilmer et al. 1998, Kimmel et al. 1994, Kuenzel et al. 1953, Manbeck et al. 1995, Truax et al. 1953). Almost no information is available on the treatment of FRP materials, or these materials combined with wood. The production of preservative treated composite reinforced laminated timbers represents the latest stage of investigation and development in the structural wood products industry and there is considerable interest by both the wood preserving and composite reinforced wood hybrid industry in the development of wood preservative compatible FRP systems.

Because little is known about the effects of preservative treatment on mechanical properties, study of the long-term durability of phenolic FRP materials was undertaken. In this paper, the effects of widely used wood preservative chemical treatments (Oil-borne; organo-and organometallic; and, acid and amine based waterbornes) on the mechanical properties of phenolic FRP material were investigated via mechanical tests supported by microscopy observations.

The objectives of this study were as follows:

1) Characterize the effects of wood preservative treatments on the mechanical properties of phenolic FRP material used in wood reinforcement.
2) Determine residual property retention after exposure to preservative chemicals and treatment, as a basis to develop material capacity reduction factors and threshold concentrations for common preservatives.
3) Develop preservative treatment recommendations and identify compatible preservatives with composite systems (matrix and fibers) for the preservative/pressure treated FRP-wood glued laminated industry.

1.3. Materials and Methods

The experimental plan was designed to determine tensile properties and apparent interlaminar shear properties of preservative treated FRP reinforcing material. Five wood preservative systems (acidic and basic waterborne and oil-borne [organometallic]) (Table 1.1) were tested over a range of concentrations to determine the effect on tensile and interlaminar shear properties of FRP reinforcing materials. Basic modeling was then performed to calculate the average fiber strength of preservative treated FRP material.

Table 1.1. Type and percent concentrations (weight/weight) of preservatives used. The treatment schedules and preservative solution concentrations used were developed for the treatment of southern yellow pine (SYP) sapwood to AWPA ground-contact and marine retentions (AWPA-C14 and C28-99). FRP materials do not take up the same amounts of chemicals as wood with treatment, and the SYP schedules allowed us to simulate chemical exposure of the FRP equivalent to typical wood treatments.

Preservative	**CCA-C[1]**	**CDDC[2]**	**Cu-N[3]**	**PCP[4]**	**Creosote[5]**
Ground contact retentions	2.5%	2.5%	0.5%	5%	100%
Marine retentions	10%	5%	2.5% & 8%	10%	100%

[1] Distilled water carrier. **CCA-C** = Chromated copper arsenic type C; Arsenic acid 17.0%, chromic acid 23.75% and copper oxide 9.25%

[2] Distilled water carrier. **CDDC** (Kodiak®) is a dual treatment process (ISK Biosciences, Memphis, TN.) The process consists of a monoethanolamine treatment followed by sodium dimethyldithiocarbamate treatment.

[3] Mineral spirits carrier. **Cu-N** = Copper naphthenate ; naphthenic acid, copper salt 60 - 80%, mineral spirits 15-25%

[4] Diesel fuel carrier. **PCP** = Pentachlorophenol ; pentachlorophenol 90-94%, 2,3,4,6-Tetrachlorophenol 0-1.5%, hydroxypolychlorodibenzo ethers 4-7%.

[5] Original solution. **Creosote** = complex mixture of hydrocarbons 100%

1.3.1. FRP Composite Material

Only one type of FRP composite material was used in this experiment: E-Glass / phenolic pultruded composite. This FRP material, identified as K-1, was developed by the Advanced Engineered Wood Composites Center at the University of Maine (Dagher et al. 1998) and manufactured by Strongwell Corporation, MN. The FRP material consisted of reinforced unidirectional (0°) E-glass continuous fiber rovings, and E-glass chopped strand mat (CSM) (0.75 oz / sq. ft.) made of randomly oriented short fibers. The short-fiber CSM was initially bonded with melamine resin binder to form a mat suitable for the pultrusion process. In the pultrusion process, the continuous fiber rovings were oriented in the core and integrated with exterior CSM layers using a phenolic resin matrix. . A resol based phenolic resin was used in the production of the FRP composite material (Kajander 2002). A variation of the pultrusion process was applied in which the continuous rovings were impregnated in phenolic resin, while the CSM mats were pulled dry into the die. As a result of this processing scheme, a resin-starved surface layer that improves bonding to wood was produced. The corresponding average volume contents for the fabricated FRP plate were; $V_f = 54\%$, $V_m = 21\%$, and $V_v = 25\%$ where V_f = fiber volume fraction, V_m = matrix volume fraction, V_v = void volume fraction. The resulting high void content leads to an open structure that favors movement and diffusion of moisture within the FRP composite material, and potentially could enhance the penetration of preservatives with the attendant capacity for increased chemical attack on the FRP material.

1.3.2. Determination of Void Content with Ignition Loss Test

Ignition testing was performed in accordance with ASTM D2584 and D2734 for Ignition Loss of Cured Reinforced Resins and Standard Test Methods for Void Content of Reinforced Plastics (ASTM 1994a, ASTM 1994b, ASTM 1991). The standards are based on the ignition of FRP material in a high-temperature muffle furnace at 565 °C (1050 °F) for combustion of all organic matrix material leaving only glass fiber residue. The ignition mass loss can therefore be considered equivalent to the resin content of the sample (the small amount of volatiles, e.g. water, residual solvents or sizing agents are ignored in this test). A reflected light microscope with a calibrated digital image analysis system was used to measure thicknesses of CSM and the continuous fiber roving core layers. Thickness measurements were made on the surface CSM layer and the continuous fiber roving core, which were removed for measurement using a razor blade. An average of 15 measurements were taken on each sample. Based on measured values, the following equation was used;

$$V_f^{CSM} = V_f \,.\, t - (V_f^{roving} \text{ x } t_{roving}) / (t - t_{roving}) \qquad [1]$$

where V_f^{CSM} = fiber volume fracture of CSM, V_f = fiber volume fraction of composite, V_f^{roving} = fiber volume fraction of the unidirectional roving, t_{roving} = thickness of the unidirectional roving and t = thickness of the composite (Figure 1.1). The same formula was also used to compute V_m^{CSM} (matrix volume fraction of chopped strand mat).

$$V_f^{roving} = V_{roving} / t_{roving} \,.\, A^*$$

$$V_f = V_{roving} + V_{CSM} / t \,.\, A^*$$

$$A^* = \text{width x depth}$$

$$V_{roving} = V_f^{roving}\, t_{roving}\, A^*$$

$$V_{CSM} = V_f\ t\ \ A^* - V_{roving} = V_f\ t\ A^* - V_f^{roving}\, t_{roving}\, A^*$$

$$t_{CSM} = t - t_{roving}$$

$$V_f^{CSM} = V_f \,.\, t - (V_f^{roving} \,.\, t_{roving}) / (t - t_{roving})$$

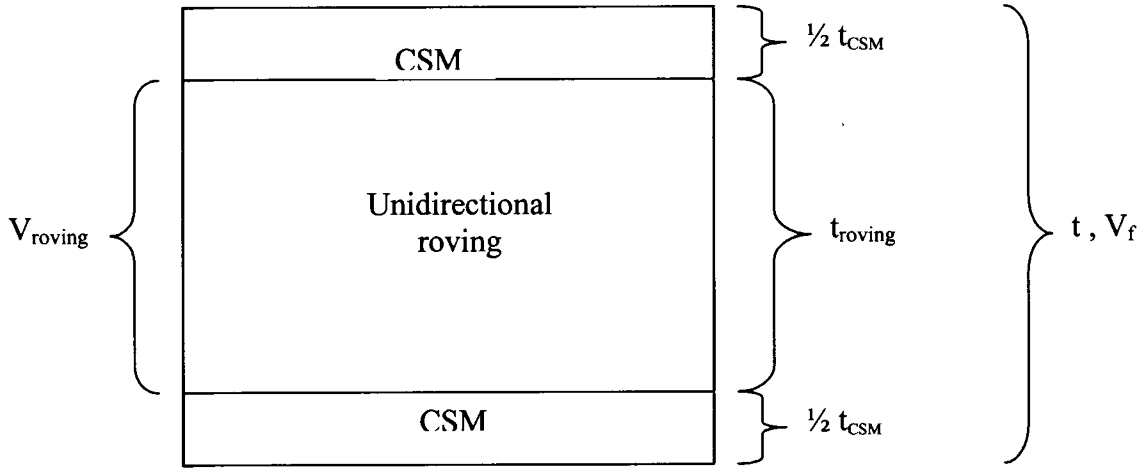

Figure 1.1. Schematic representation of cross section of K-1 pultruded composite

After ignition, the remaining fiber in the crucible was found to consist of the unidirectional continuous fiber roving core and the surface CSM layer. Both constituents were loose and had little to no cohesiveness indicating that all the resin had been burned off.

1.3.3. Mechanical Test Methods

Two ASTM tests were used in this experiment (Table 1.2);

Table 1.2. Test methods for mechanical characterization of preservative treated E-glass/ phenolic pultruded material (unidirectional lamina).

Tested Property (ASTM Standard)	**Elastic Properties**	**Strength parameters**	**Related property**
Longitudinal Tension D3039	E_1, ν_{12}	F_{1t}	fiber
Transverse Tension D3039	E_2, ν_{21}	F_{2t}	matrix
Interlaminar Shear (short beam) D2344		ILSS, (approximate F_5)	matrix or fiber-matrix interface

The ASTM D 3039 Standard Test Method for Tensile Properties of Polymer Matrix Composite Materials was modified for sample preparation and the inclusion of a post-treatment procedure. The longitudinal tensile modulus, E_1, and the longitudinal tensile strength, F_{1t} are two fiber-dominated composite properties. Conversely, the transverse tensile modulus, E_2, is typically a matrix-dominated property. These composite properties can be measured based on tensile testing according to ASTM D3039 using material coupons cut in the longitudinal and transverse directions. E_1 and F_{1t} are extensively used in structural design and have been used as performance indicators to characterize environmental effects on composite materials (Lopez-Anido and Wood

2001). Contribution of the CSM layer to the longitudinal and transversal tensile strength was ignored in the mechanical test series used.

The interlaminar shear strength (ILSS) of a fiber-reinforced composite is controlled by its matrix properties and the fiber-matrix interface properties. The apparent ILSS can be measured based on the short-beam test method according to ASTM D2344. In this method, a composite specimen with small span-to-depth (l/d) ratio is tested in three-point bending to induce the interlaminar shear mode of failure. The apparent shear strength is computed assuming a continuous parabolic shear stress distribution in the cross-section, as predicted by elementary beam theory for homogeneous materials. However, it has been shown that the shear stress distribution is dominated by stress concentrations in the regions close to the loading nose and the supports (Muszynski et al. 2000). For this reason, the apparent shear strength from the short-beam test cannot be used for design data. In spite of these limitations, the short-beam test has become one of the most popular methods for determination of the interlaminar bond quality of composites due to the ease of specimen preparation and the simplicity of the experimental procedure. The ILSS of a composite laminate has been widely used as a performance indicator to assess the compatibility of fiber-matrix systems (fiber surface treatments), the effect of processing defects in the matrix (void content and micro cracks), and also environmental effects on composite materials (Lopez-Anido and Wood 2001).

Mechanical testing was conducted using an Instron 8801, 22 kip (100kN) servo-hydraulic testing machine for the tensile tests, and an Instron 8001 2 kip (9kN) electro-mechanical testing machine for the interlaminar shear tests. The test condition temperature ranged from 21-25 °C (70-77 °F) with 35-55% RH. A crosshead speed of

0.05 inch/min (1.3 mm/min) was used for both tests. The tensile test specimens were 10" x 0.5" x 0.125" (254 mm x 12.7 mm x 3.18 mm) and the interlaminar shear sample size was 1" x 0.22" x 0.125" (25.4 mm x 5.6 mm x 3.18 mm). No tabbing was applied to the tensile test specimens, since hydraulic grips supplied sufficient frictional force without sample damage in preliminary tests.

For the samples treated with copper naphthanate preservative, a 5-minute high strength epoxy adhesive was applied as a coating on both ends (1.5" from each end) covering the gripping area to prevent surface CSM layer softening. This softening was observed in preliminary tests and was presumed to be due to a reaction of naphthenic acid with resin components of the FRP.

The total number of specimens was 272. For the tensile test, 7 specimens were used for each preservative treatment group including the untreated and carrier-treated (water, mineral spirits, diesel fuel) control and reference groups (128 samples total). For the interlaminar shear test 144 specimens were used, with 9 specimens in each treatment group including untreated, carrier control and reference groups. The samples were cut using a fluid cooled (Glasgrind® oil-free synthetic grinding fluid) diamond tip saw.

1.3.4. Pressure Treatment Schedule

All pressure treatments were performed in a 118" x 20" diameter (3m x 0.5m diameter) pressure treatment vessel. The pressure treatment schedule was the same for all preservative groups and included an initial vacuum of -84.7 kPa (25" Hg) for 10 minutes followed by a pressure of 1.034 MPa (150 psi.) for 15 minutes in a "full-cell" treatment (AWPA 1999a). The total contact time of the FRP samples with the solutions was approximately 60 minutes. Water- and solvent-borne preservative treatments (CCA-C, CDDC, Cu-N) and their controls were treated at ambient temperature. Oil-borne preservative treatments (Creosote, PCP) and their controls were performed at 149-154°F (65-68°C).

1.3.5. Post-treatment Conditioning

Fixation period: A three-day wet storage/fixation period of the samples was followed by air drying and conditioning at 65°F (18°C) and 50 % RH until the specimens reached equilibrium weight (2 - 4 weeks).

1.3.6. Computation of Longitudinal Tensile Strength (F_{1t}) and Interlaminar Shear Strength (ILSS)

The longitudinal tensile strength of a unidirectional lamina is calculated as:

$$F_{1t} = P_{max} / A \qquad [2]$$

where

P_{max} = ultimate tensile load prior to failure (lb.)

A = average cross sectional area (in^2)

The interlaminar shear strength was calculated based on beam theory, as follows:

$$S_H = 0.75\ P_B / b * d \qquad [3]$$

where

S_H = shear strength (psi)

P_B = ultimate applied transverse load prior to failure (lb.)

b = width of specimen (in)

d = thickness of specimen (in)

1.3.7. Modeling of σ_{fa} for FRP Treated with Wood Preservatives

The average fiber strength (σ_{fa}) was back-computed from the longitudinal strength of the FRP material according to the Rule of Mixtures (ROM), as suggested in Barbero (1999).

The ROM for computing the longitudinal elastic modulus is

$$E_1 = E_f V_f + E_m V_m \qquad [4]$$

The property values and assumptions used in these computations are as follows;

E_f = 72.345 GPa for E glass fiber (Barbero 1999)

E_m = 5.52 GPa for phenolic matrix (Bauccio 1994)

For the fiber roving core V_f = 0.701 and V_m = 0.124 was obtained from the ignition loss test (Table 1.3, Figure 1.2). Considering only the continuous roving core fibers (fibers oriented at 0°) results in: E_1 = 72.345 (0.701) + 5.52 (0.124) = 51.4 GPa. This longitudinal elastic modulus is larger than the experimental value for the pultruded plate because the effect of the surface CSM layers is not considered.

Similarly, longitudinal tensile strength (F_{1t}) values for a unidirectional lamina can be calculated based on the following ROM equation.

$$F_{1t} = \sigma_{fa} V_f + \sigma_m (V_m) \qquad [5]$$

Where $\sigma_m = \sigma_{fa} E_m / E_f$

It is worth noting that for these pultruded FRP composite material results, $(1\text{-}V_f) > V_m$ due to the relatively high void content. Deriving σ_{fa} from the F_{1t} using the ROM equation, the following formula can be obtained.

$$\sigma_{fa} = F_{1t} / [V_f + (E_m / E_f) V_m] \qquad [6]$$

Although the theoretical ultimate tensile strength value for unprocessed glass fibers is 3.45 GPa, the actual σ_{fa} value is expected to be reduced by 50% or more during the production process (Barbero 1999).

The FRP composite putruded sheet was modeled as an unidirectional continuous laminate without considering the contribution of the CSM surface layers. Since the continuous roving fibers contribute almost exclusively to the longitudinal tensile strength and elastic modulus of the pultruded sheet, this assumption yields satisfactory results for the analysis presented in this work.

1.3.8. Light and Scanning Electron Microscopy (SEM) Analysis

Following preservative treatments, either single glass fibers or 5 mm (0.196") long sections cut from specimens were examined under the light or scanning electron microscope. Because of the transparent nature of the glass fibers a combination of transmitted bright field and oil immersion techniques were successfully used for light microscopy studies. The SEM samples taken from preservative exposed FRPs were coated with gold using a Polaron E5000 sputter device and observed using a Cambridge S150 scanning electron microscope operated at 5, 10 and 20 kV.

1.3.9. Statistical Analysis

In addition to average, standard deviation, and coefficient of variation values, SYSTAT Analysis of Variance (ANOVA) was also performed for longitudinal tensile strength (E_{1t}), transverse tensile strength (F_{2t}), ILSS and longitudinal elastic modulus (E_1) values. A pairwise probability test was also used for comparison of the treatments.

1.4. Results and Discussion

1.4.1. Void Content

The unidirectional continuous fiber roving core contained approximately 70.1% fiber volume fraction (Table 1.3, Figure 1.2). This ratio is very close to $V_{fmax} = 78.5\%$, the theoretical maximum fiber volume fraction value, when fibers are arranged in a rectangular array (Barbero 1999).

Table 1.3. Fiber architecture of E-glass/phenolic FRP based on the ignition loss test (ASTM D-2584).

Sample ID	Thickness (mm)	Ignition loss (%)	Fiber weight fraction (%)	Matrix weight fraction (%)	Fiber volume fraction (%)	Matrix volume fraction (%)	Void volume fraction (%)
Plate (roving core + surface CSM)	3.34 0.81[3]	14.19 0.48* 3.40**	85.81 0.48* 0.56**	14.19 0.48* 3.40**	**54.2** 0.71* 1.31**	**21.0** 0.61* 2.89**	**24.7** 0.46* 1.87**
Roving core layer only	2.19 1.88[3]	6.98 0.38* 5.39**	93.02 0.38* 0.40**	6.98 0.38* 5.39**	**70.1** 0.34* 0.48**	**12.4** 0.66* 5.31**	**17.6** 0.32* 1.82**
Surface CSM layer only	0.59 1.69[3]	-	-	-	**24.0**	**37.7**	**38.3**

(*) standard deviation of 6 specimens.

(**) Coefficient of variation (COV %) of 6 specimens.

([3]) Coefficient of variation (COV %) of 15 measurements.

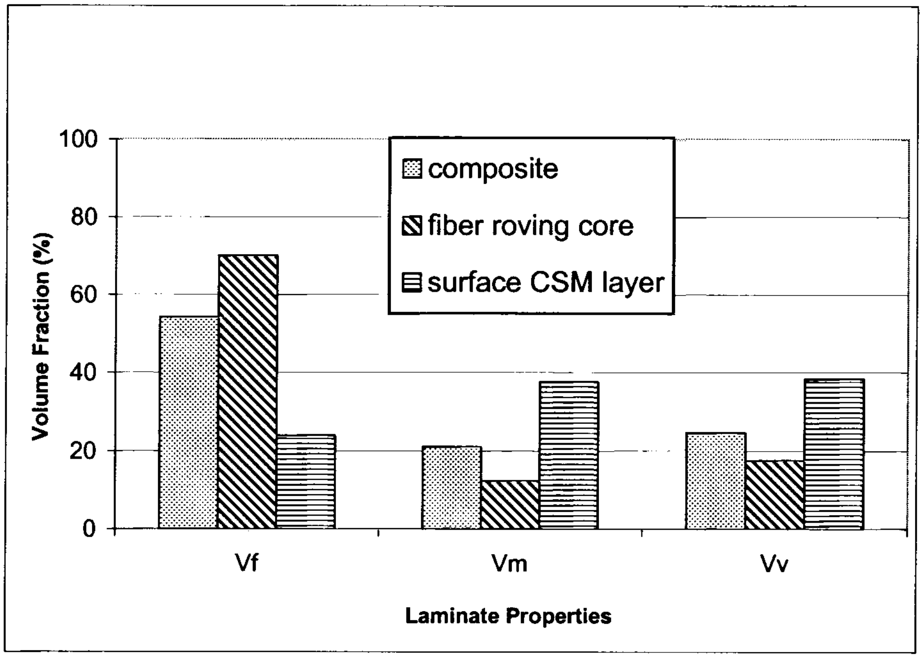

Figure 1.2. A comparison of laminate fiber architecture of the composite, unidirectional core and surface layer only, of FRP material (V_f = fiber volume fraction, V_m = Matrix volume fraction, V_v = Void volume fraction).

1.4.2. Preservative Retentions

Under the same treatment conditions, all specimens showed similar solution retentions. Small differences may be accounted for by the different densities of the preservative solutions used. As expected, the CDDC treatment resulted in the highest retention values because it is a dual treatment process. Because of differences in solution concentrations, the average active chemical retentions varied among the treatment groups. The highest active retention recorded was 16.21 pcf (259.74 kg/m^3) for creosote when used as an undiluted solution (Table 1.4).

Table 1.4. Average solution and active ingredient retention values of pressure treated FRP specimens.

Treatment	Average Solution Uptake (g/plate)	Average Solution Retention (kg / m^3) [pcf]	Average Active Ingredient Retention (kg / m^3) [pcf]	Average Weight (w/w) Change (%)	Initial Solution pH
Untreated	-	-	0 [0]	0	-
Distilled water	22.55	228.22 [14.25]	0 [0]	14	-
CCA-C 10%	24.60	249.83 [15.60]	24.99 [1.56]	15	2
CCA-C 2.5%	23.60	237.89 [14.85]	5.95 [0.37]	15	2.5
CDDC 2.5%	28.30	283.30 [17.68]	7.08 [0.44]	18	11
CDDC 5%	26.70	269.20 [16.80]	13.46 [0.84]	17	11
Cu-N 8%	21.30	213.09 [13.30]	17.05 [1.06]	13	N/A
Cu-N 2.5%	19.90	199.21 [12.44]	4.98 [0.31]	12	N/A
Cu-N 0.5%	21.40	214.27 [13.38]	1.07 [0.07]	13	N/A
Creosote 100%	26.15	259.74 [16.21]	259.74 [16.21]	17	N/A
PCP 5%	27.10	271.23 [16.93]	13.56 [0.85]	17	N/A
PCP 10%	25.00	252.06 [15.73]	25.21 [1.57]	16	N/A
Mineral spirits	19.30	194.51 [12.14]	0 [0]	12	N/A
Diesel fuel	21.20	213.75 [13.34]	0 [0]	13	N/A

For all treatments, the average solution uptake of 15.3% indicates that preservative treatments filled 85% of the void volume in FRP material highlighting the importance of void volume content and its role in preservative uptake and retention.

1.4.3. Longitudinal, Transverse Tensile and Interlaminar Shear Strength

In general, the experimental results and related statistical analysis clearly show that the longitudinal elastic modulus, E_l, values of preservative treated FRP coupons in the tensile test were not affected by the preservative chemical treatments (Table 1.5, Figure 1.3).

Table 1.5. Summary of statistically significant strength reductions in longitudinal, transverse elastic modules of preservative treated E-glass/phenolic pultruded FRP.

Modulus Reduction	**Water-borne preservatives**				**Oil-borne preservatives**					
	CCA 2.5%	CCA 10%	CD* 2.5%	CD* 5%	Cu-N 0.5%	Cu-N 2.5%	Cu-N 8 %	PCP 5 %	PCP 10 %	Creosote
Longitudinal MOE	C	C	C	C	C	C	C	C	C	C
Transversal MOE	-	C	-	C	-	C	-	C	-	C

A = Statistically significant reduction at 95 % confidence level (p-value is between 0.000-0.050)
B = Statistically insignificant reduction at 90 % confidence level (p-value is between 0.000-0.100)
C = Statistically no reduction
* = CDDC (Kodiak ®)

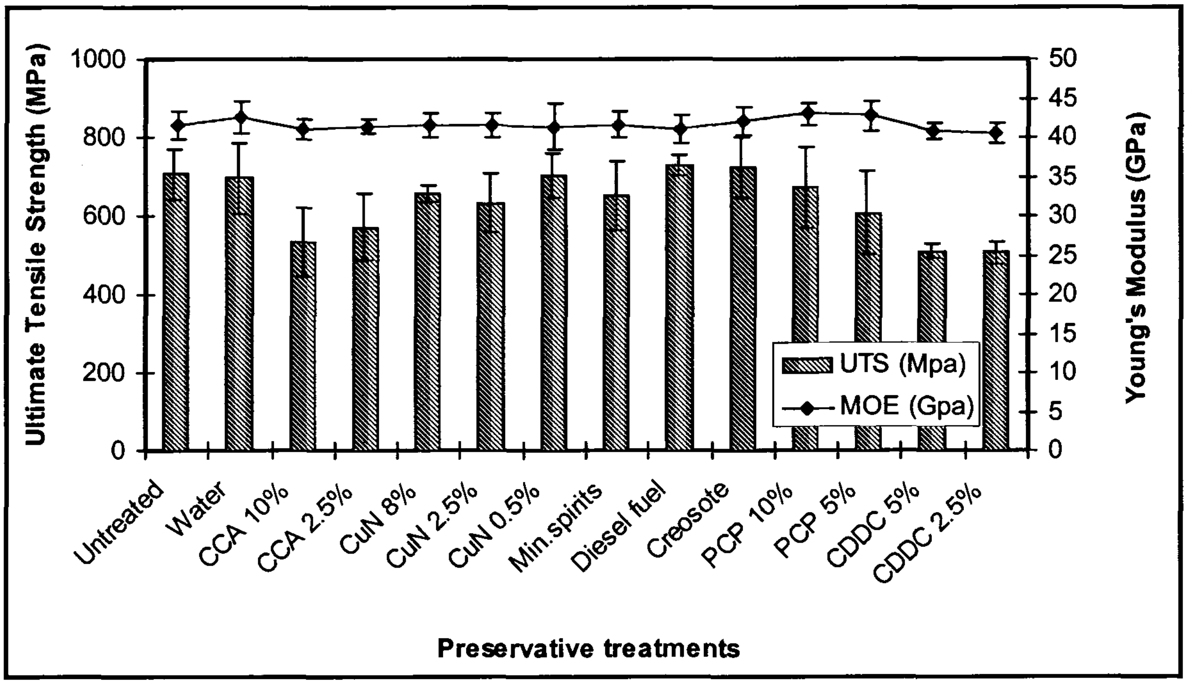

Figure 1.3. Effects of different wood preservative and control treatments on longitudinal tensile strength and tensile modulus of FRP material.

These observations are in general agreement with findings from durability studies where E-glass epoxy FRP reinforcements for concrete were exposed to water and salt-water (Kshirsagar et al. 2000). However, the longitudinal tensile strength, F_{lt}, data show statistically significant reductions in strength values of FRP treated with CDDC (27% reduction) and the high concentration of CCA (25% reduction) when compared to other treatments and the untreated controls (Tables 1.6 and 1.7).

Table 1.6. Summary of statistically significant strength reductions in longitudinal, transverse tensile and interlaminar shear tests of preservative treated E-glass/phenolic pultruded FRP composite.

Strength Reduction	**Water-borne preservatives**				**Oil-borne preservatives**					
	CCA 2.5%	CCA 10%	CD 2.5%	CD 5%	Cu-N 0.5%	Cu-N 2.5%	Cu-N 8 %	PCP 5 %	PCP 10 %	Creosote
Long. Tensile test (ASTM D 3039)	B	A	A	A	C	C	C	C	C	C
Trans.Tensile test (ASTM D 3039)	-	C	-	C	-	C	-	C	-	C
Interlaminar shear (ASTM D 2344)	C	C	A	A	C	C	C	C	C	A

A = Statistically significant reduction at 95 % confidence level (p-value is between 0.0-0.05)
B = Statistically insignificant reduction at 90 % confidence level (p-value is between 0.0-0.10)
C = Statistically no reduction

Table 1.7. Average longitudinal tensile, interlaminar shear strength (ILSS), longitudinal tensile modulus values of FRP composite plate and σ_{fa} "average fiber strength" of E-glass fibers.

Treatments	**Composite long. tensile strength (MPa)**	**E-glass fiber strength σ_{fa} (MPa)**	**Composite ILSS (MPa)**	**Composite long. elastic modulus (GPa)**
Untreated	705.4	1264	27.06	41.53
Water	695.4	1246	26.38	42.54
CCA 10%	530.9	951	26.36	41.05
CCA 2.5%	571.5	1024	26.24	41.31
CuN 8%	658.5	1180	26.76	41.51
CuN 2.5%	632.9	1134	25.91	41.53
CuN 0.5%	705.1	1263	26.64	41.37
Min.spirits	651.4	1167	26.33	41.60
Diesel fuel	728.9	1306	25.55	41.01
Creosote	722.8	1295	24.71	42.08
PCP 10%	672.0	1204	26.75	43.01
PCP 5%	605.9	1086	26.73	42.71
CDDC 5%	509.8	913	23.40	40.72
CDDC 2.5%	506.7	908	22.98	40.52

This can be explained by the extreme pH values of these preservative solutions (pH 1.5-2 for CCA and pH 11-12 for CDDC) and the likelihood of chemical attack on E-glass fibers in FRP composites by alkali and acid chemicals. The chemicals in CCA or CDDC solutions (CrO_3, CuO, As_2O_5, monoethanolamine, alkylamine and sodium dimethyldithiocarbamate) may oxidize or erode the glass fibers causing reduction of tensile properties of treated material. Light and Scanning Electron Microscopy (SEM) analysis revealed spiral cracks and longitudinal fissures on some individual glass fibers taken from CCA- and CDDC-treated FRP coupons while untreated fibers had undamaged surfaces (Figures 1.4, 1.5, 1.6).

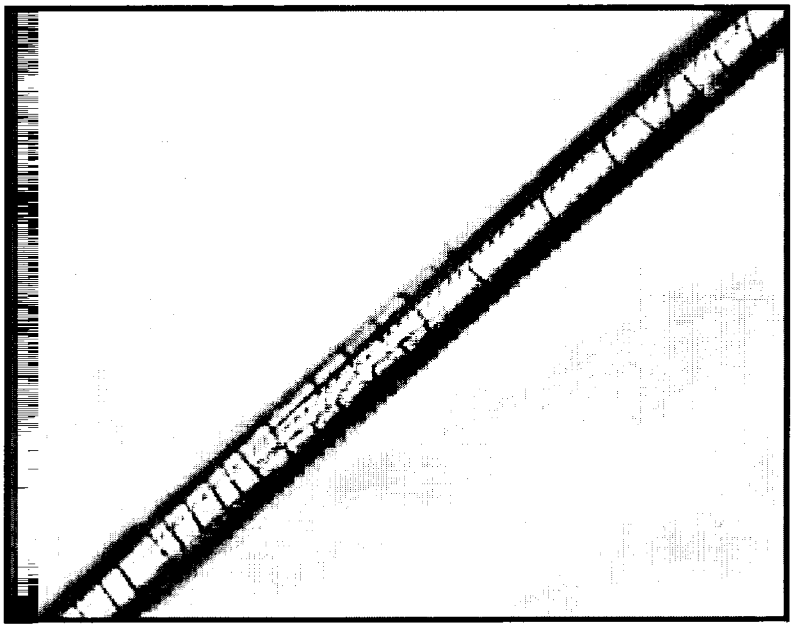

Figure 1.4. Spiral cracks and longitudinal fissures on single glass fibers taken from CCA treated FRP coupons (transmitted bright field oil immersion technique, 600x).

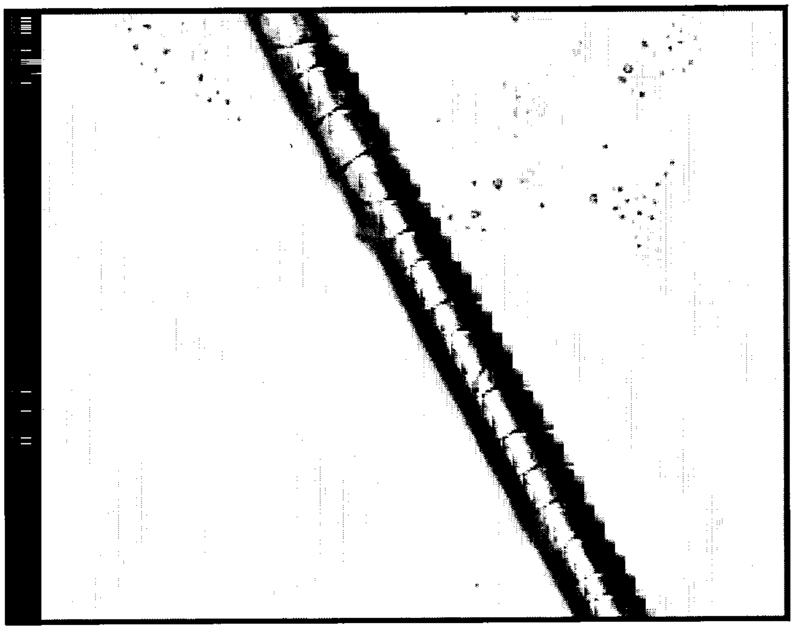

Figure 1.5. Spiral cracks on single glass fibers taken from CCA treated FRP coupons (transmitted bright field oil immersion technique, 600x).

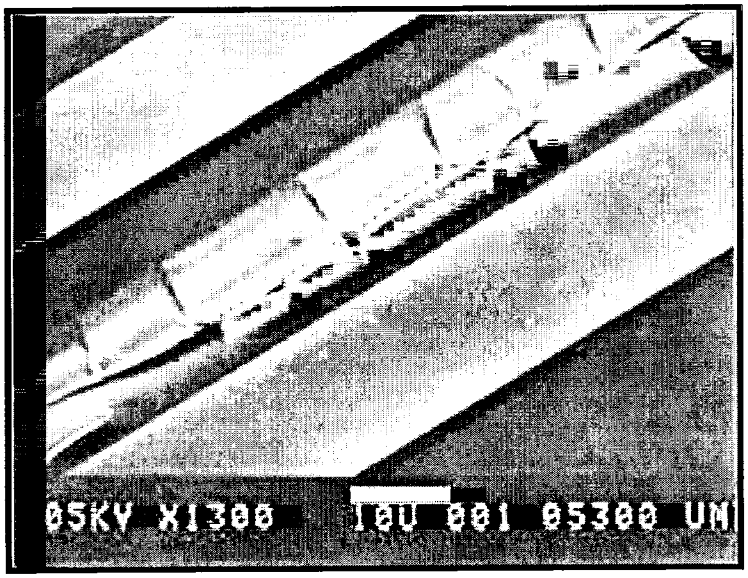

Figure 1.6. SEM micrograph showing spiral cracks and longitudinal fissures on a glass fiber partially embedded in a CCA treated FRP coupon.

Treatment residues were present on the surface of fibers in some instances, but these did not appear to affect the integrity of the fibers. If spiral cracks occur on the surface of the glass with CCA or CDDC treatment, the resulting flaw will reduce fiber tensile strength as predicted by the well-known Griffith's formula. The surface failures would then promote weakening of the FRP. The corrosion of glass fibers in aqueous environments (acidic or basic) has been extensively documented in the literature (Ehrenstein et al. 1990, Fujii et al. 1993, Hojo et al. 1998, Kshirsagar et al. 2000, Ranney and Parker 1995, Ramachandran et al. 1980). Chemical attack mechanisms on glass surfaces have been identified as leaching and/or etching processes. Leaching can be described as selective removal of soluble contents via ion exchange and it is more common in acidic media. Etching, on the other hand, is known as a first order reaction that involves hydration followed by total dissolution of the glass. Etching is more common in alkaline media (Rodriguez 1987). Water, particularly at an elevated temperature, can weaken glass fibers (Kshirsagar et al. 2000) by etching them and by leaching out some of the glass constituents. This results in fissures or crevices, as observed in the SEM, which may lead to stress concentrations around the flaws reducing the average fiber strength. The reactions that occur between glass and solutions also depend on the chemical composition of the glass (Rodriguez 1987). Different types of glass fiber (S-glass or C-glass), or other fibers produced from different materials (carbon, aramid, boron etc.) would be expected be more or less resistance to degradation by the preservative solution components. However, the use of more resistant glass products may be cost-prohibitive, and E-glass is currently the predominant material used in FRP pultruded materials by industry.

The average fiber strength, σ_{fa}, of E glass in the FRP pultruded material also followed the same pattern observed in general for E-glass fibers. From equation [4] we can observe how the reduction in σ_{fa} following exposure to preservative treatments is correlated with a reduction in the longitudinal tensile strength of the composite, F_{1t}. Equation [5] was applied to back-compute approximate σ_{fa} values for treated and control groups by neglecting the effect of the surface CSM layers.

Examining the ILSS data, CCA did not cause any reduction in the interlaminar shear strength of the FRP, indicating that no drastic effects on the phenolic matrix or fiber-matrix interface occurred (Figures 1.7 and 1.8).

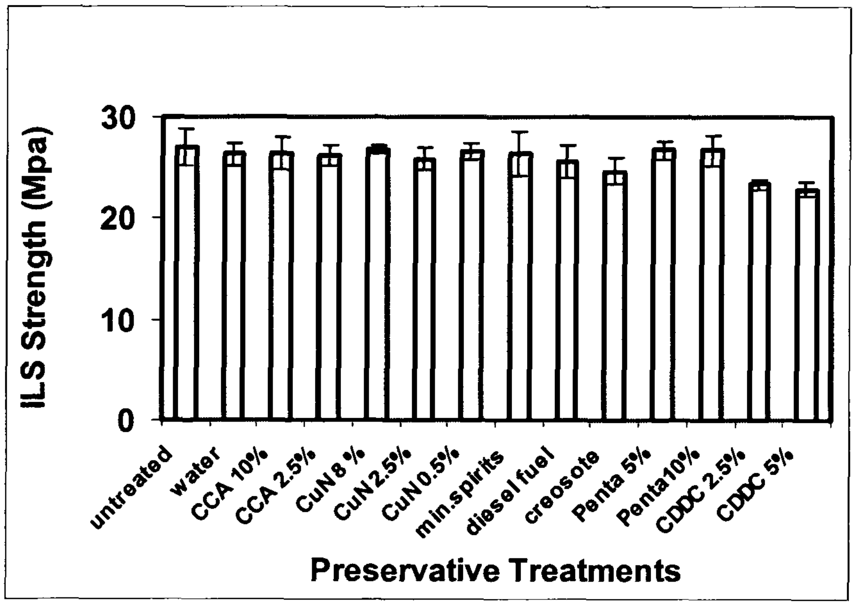

Figure 1.7. Effects of preservative and control treatments on apparent interlaminar shear strength (ILSS) of FRP material.

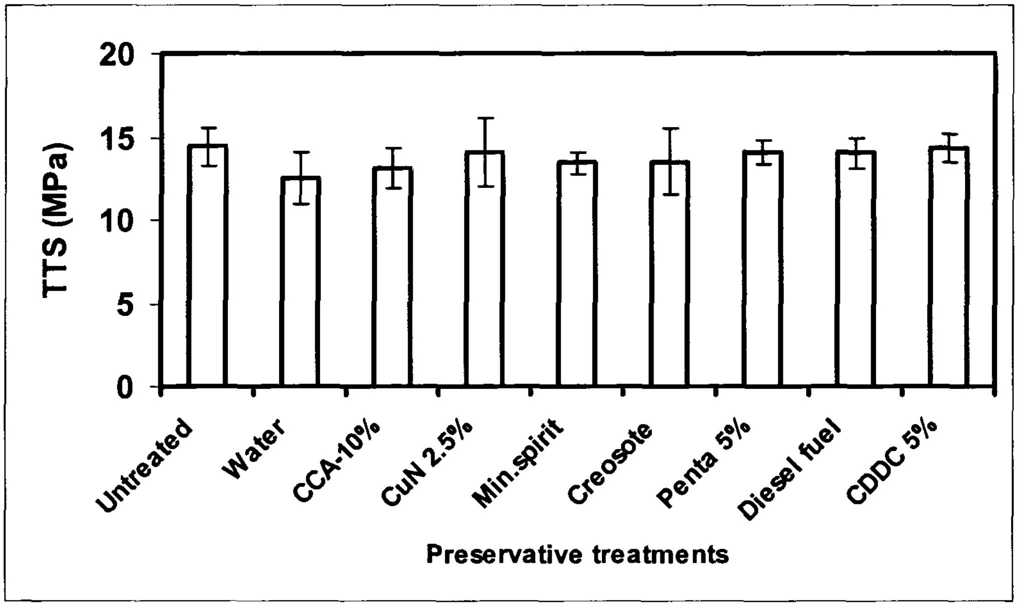

Figure 1.8. Effects of preservative and control treatments on transversal tensile strength (TTS) of FRP material.

However, the CDDC and creosote treated ILSS data showed a statistical reduction in ILSS suggesting that the alkaline nature of CDDC and the aromatic nature of creosote may affect the matrix and/or fiber-matrix interface. Since the high sensitivity of phenolic resins to strong bases has been reported in the literature (Bauccio 1994 and Schweitzer 2000), the high pH of CDDC may affect the matrix causing ILSS reduction. The pH sensitivity might be different if a novolak based phenolic resin were used in the FRP production. It is possible that the fiber-matrix interface was weakened by removing or neutralizing the chemical coupling agent used to coat the E-glass fiber surface that promotes adhesion between the fibers and the matrix. Creosote accumulations on glass fiber surfaces (Figure 1.9) suggest that creosote may penetrate the fiber/matrix interface and promote ILSS reduction. Since aromatic phenolic matrixes have previously been reported to be chemically inert to hydrocarbons in 25° C and 93° C environments (Bauccio 1994, Nagae et al. 1996) and attack of the fiber was not observable by SEM, the likely alternative explanation is degradation of the fiber-matrix interface. Exposure of samples to the higher concentrations of CCA or CDDC did not cause any significant reduction of tensile strength at the 95% ($p = 0.05$) significance level; however at the 90% ($p = 0.10$) level a 19% reduction in the strength of the CCA treated samples was observed.

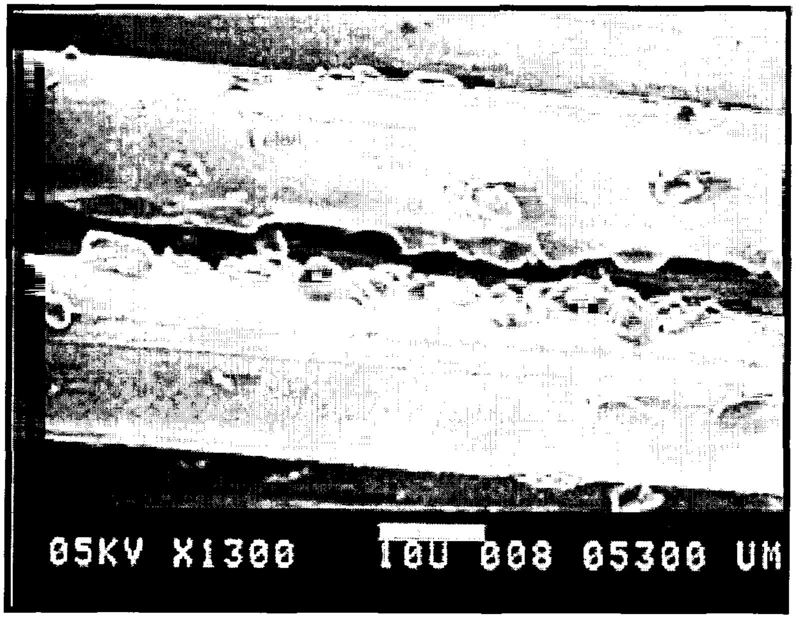

Figure 1.9. Creosote accumulation on fiber/matrix interfaces. Fibers were taken from creosote treated FRP coupons after testing.

1.4.4. Failure Modes

Failure modes of tension coupons were determined visually and recorded for all specimens after the specimens failed according to ASTM D-3039. In general, the dominant feature of specimen failure was categorized as massive debonding and rupture of the glass fibers at the center of specimens, with fractured glass fibers protruding from the narrow (thickness) edge of the specimens (Table 1.8). In the untreated samples, the oil-borne preservative treated samples, and oil-borne controls, explosive failures (ASTM 1995, ASTM 1987) were observed in almost all cases. The CCA and CDDC treated FRP coupons failed with longitudinal splitting and less explosive type of fractures. These later coupons had very brittle properties associated with the presence of flaws in the glass fiber reinforcement.

Table 1.8. Failure modes of the longitudinal tensile coupons according to ASTM D-3039.

ASTM Failure Mode	Overall percentage (%)
"XGM"	85
"SGM"	11
"GAT"	4

"XGM" = explosive, gage, middle
"SGM" = long. splitting, gage, middle
"GAT" = grip/tab, at grip/tab, middle

1.5. Conclusions

1.5.1. General Conclusions

The effect of preservative treatment on FRP composite mechanical properties (e.g., longitudinal tensile strength, longitudinal modulus, and interlaminar shear strength) is quantified by computing residual property factors. Residual property factors are computed as the ratio of the property value of the degraded material (exposed to preservative treatments) and the property value of the baseline control material (untreated). In this way the effect of preservative treatments can be incorporated in engineering design calculations. Furthermore, threshold limits for residual property factors can be defined as part of a performance-based acceptance criteria for FRP composite reinforcement of glulam members.

Several types of wood preservatives were used in this study to represent different chemical exposures (acidic and basic water-borne, mineral spirit carrier and oil-borne [organo- and organometallic]), including some of the most commonly used wood preservatives in North America. These preservatives are recommended by AWPA and are in common use for structural timber treatment, highway bridge applications and waterfront piers (AWPA 1999a). The retention levels utilized in this work simulated different exposure levels of phenolic FRP material to preservative chemicals that would be used in industry for a range of treated wood applications. Our results indicate that a reduction in tensile strength and ILSS occurred in water-borne preservative treated phenolic FRP composites when either ground contact or marine retention levels (19 – 28% reduction, respectively) were used. These reductions should be taken into account in design calculations. The ground contact retention of CCA caused a non-significant 19% tensile reduction (p value 0.081, Table 1.9).

Table 1.9. Statistically significant percent reductions (p=0.05) in longitudinal tensile strength and ILSS tests.

Treatments for long. Tensile strength	% reduction	p-value
CCA 2.5%	19	0.081
CCA 10%	25	0.004
CDDC 2.5%	28	0.001
CDDC 5%	28	0.000

Treatments for ILSS	% reduction	p-value
Creosote	9	0.000
CDDC 2.5%	14	0.000
CDDC 5%	15	0.000

Further study is needed, but these data indicate that CCA retentions, at least those at the marine exposure level will cause significant strength loss of the E-glass/phenolic pultruded FRP. For CDDC treatments, however, increased retention did not cause a change in tensile strength. No statistically significant reduction in longitudinal tensile strength was recorded in the oil-borne treated samples regardless of preservative type (PCP in diesel fuel, Cu-N in mineral spirits or creosote) or retention level. Therefore, oil-borne treatments used in this experiment could be considered compatible with E-glass phenolic pultruded material. Creosote treatment, however, resulted in a statistically significant (10%) reduction in ILSS while other oil-borne and CCA treatments had no effect on this mechanical property. These results indicate that the differing chemical composition of preservatives can affect different mechanical properties in phenolic FRPs, which should be taken into account in the design criteria for preservative treated phenolic FRP-wood hybrids. Structural engineers should be aware of the effects of wood preservatives to allow the selection of compatible fiber and matrix systems. Compatibility tests with potential wood preservatives and different fiber and matrix systems for wood reinforcement should be performed in advance. Use of "rating values" to estimate the effects of preservative treatment on FRP strength properties can be developed; however, these would need to be corrected based on the environment where the material would ultimately be exposed.

1.5.2. Recommendations for Civil Engineers and Wood Reinforcement Industry

Based on this work, the following issues have been identified that require further study:

1- Material capacity reduction factors for design specifications must be developed using broader retention levels for above-ground, ground-contact and marine exposure, taking into consideration the short and long-term strength loss effects of preservative treatments. Civil engineers and wood scientists should conduct screening tests (different preservatives at different retention levels for different FRP composites) as part of durability studies.

2- Threshold concentration limits, for effective treatment with minimal or no strength loss, must be incorporated into written recommendations for structural engineers and glulam beam manufacturers.

3- Guidelines should be prepared for pre and post preservative treatment schedules for the FRP reinforced glulam beam industry.

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Chapter 2

MONITORING FUNGAL DEGRADATION OF E-GLASS FIBER/PHENOLIC PULTRUDED (FRP) COMPOSITE USED IN WOOD REINFORCEMENT

2.1. Introduction

The susceptibility of E-glass fiber reinforced polymer (FRP)/phenolic pultruded composite plates to fungal degradation was examined. Interlaminar shear strength by short beam testing was applied to monitor fungal degradation of glass fiber reinforced polymer composites. Since the FRP material was designed for use as reinforcement with wood, two common wood decay fungi, a brown rot and a white rot, were chosen for exposure of the FRP material. Light and Scanning Electron Microscopy (SEM) indicated that both wood decay fungi actively grew and penetrated into the FRP material, especially in high-void content areas. There was no apparent reduction in interlaminar shear strength (ILSS) of the brown rot exposed FRP material. The experimental results indicate that, the ILSS mechanical property evaluation technique is promising and may be sensitive enough to detect the effects of fungal degradation in FRP materials.

2.2. Literature Review

Fiber reinforced polymer (FRP) composite materials are becoming increasingly accepted for use in the construction industry because they combine the advantages of both fibers (typically E-glass) and the resin matrix (Lopez-Anido and

Karbhari 2000). These performance advantages include increased strength-to-weight ratio, hardness, wear and corrosion resistance, stiffness and improved creep behavior (Wagner et al. 1996, Mallick 1993). As more applications are found for wood/FRP hybrids, (e.g., laminated lumber for bridge applications, waterfront piers) their use in exterior and high-decay-hazard environments is expected to grow. Unfortunately, little information is available on the exposure resistance of FRP composites against fungi or the behavior of organisms that decay wood in these composites. Since these reinforcements are used with wood, the mechanical strength and resistance to degradation of FRP material exposed to common wood decay fungi were evaluated in this experiment via qualitative (microscopic observation) and quantitative techniques (mechanical testing).

It was only recently recognized that fiber reinforced polymeric (FRP) composite materials were susceptible to biological attack (Gu et al., 1995a, 95b, 96, 97, 2000, Wagner et al. 1996, Thorp et al. 1994, Sampath et al. 1997, Sand 1994). Gu et al. reported that impurities and additives in FRP composites can promote fungal and bacterial growth and can serve as carbon and energy sources for these microorganisms (Gu et al., 1995a, 95b, 96, 97, 2000). Furthermore, they concluded that biological damage to FRP composite materials may significantly affect their physical integrity and fatigue performance. Specific surfaces or voids in FRP materials may concentrate nutrients providing a favorable micro-environment for microbial development. Fibers may serve as capillaries to improve the movement and distribution of moisture and chemical species within the material, and may enhance the spread of microorganisms along the fiber-matrix interface within the composite structure. Physical performance of composite material can be drastically affected by slight chemical changes in localized regions (Gu et al., 1995a, 95b, 96, 97, 2000, Wagner et al. 1996). Several mechanical and NDE (e.g. Acoustic Emission, EIS [Electrochemical Impedance Spectroscopy]) techniques were previously examined for potential in evaluating the residual strength of microbial-exposed FRP materials. However, most of these techniques were found not sensitive enough to determine mechanical changes in the samples evaluated (Gu et al. 1995a, 1995b, 1996, 1997, 2000, Wagner et al.1996).

Mechanical characterization tests can directly measure strength properties, and therefore have had greater acceptance compared to NDE (see Appendix A for ultrasonic NDE application and preliminary results) in material qualification for assessment of the action of degradative agents (UV exposure, weathering, chemical and thermal exposure, etc.) (Lopez-Anido and Wood 2001, Prian and Barkatt 1999). The standard test procedure "Interlaminar shear strength of FRP composites by Short-Beam Method" (ASTM 1984) is a widely accepted method for the determination of fiber/matrix interface characteristics (Mallick 1993, Muszynski et al. 2000). The apparent interlaminar shear strength can be measured based on the short-beam test method according to ASTM D2344. In this method, a composite specimen with small span to depth (l/d) ratio is tested in three point bending to induce the interlaminar shear mode of failure. The apparent shear strength is computed assuming a continuous parabolic shear stress distribution in the cross-section, as predicted by elementary beam theory for homogeneous materials. However, it has been shown that the shear stress distribution is dominated by stress concentrations in the regions close to the loading nose and the supports (Muszynski et al. 2000). In spite of these limitations, the short-beam test has become one of the most popular methods used by the industry to determine the interlaminar shear bond quality of composites due to the ease of specimen preparation and the simplicity of the experimental procedure. This method was used in our research as a performance indicator to assess the effects of fungal exposure on E-glass fiber / phenolic matrix composites.

2.3. Materials and Methods

2.3.1. FRP Material

One type of FRP was used in this experiment: E-Glass / phenolic pultruded composite. This FRP composite, identified as K-1, was developed by the Advanced Engineered Wood Composites Center at the University of Maine (Dagher et. al. 1998) and manufactured by Strongwell Corporation, MN. The K-1 FRP pultruded composite consists of unidirectional (0°) E-glass continuous fiber roving in the core with a melamine-coated glass chopped strand mat (CSM) (0.75 oz / sq. ft.) at the surfaces, all embedded in a phenolic matrix. In the fabrication process, the CSM mat was pulled dry in the pultrusion die to generate a resin-starved surface that improves bonding to wood. The corresponding average volume contents for the pultruded plate were obtained based on ignition loss tests according to ASTM D-2584 and ASTM D-2734 procedures (ASTM 1994b, 1994a), as follows:

$V_f = 54\%$, $V_m = 21\%$, and $V_v = 25\%$

Where V_f = fiber volume fraction (both fiber roving and CSM), V_m = Matrix volume fraction, V_v = Void volume fraction.

The resulting high void content leads to an open structure that favors movement and distribution of moisture within the composite material, and may enhance the growth of microorganisms. The density of E-glass fiber was 2.54 g/cm^3 and the density of the phenolic matrix was 1.2 g/cm^3.

2.3.2. Sample Preparation and Decay Testing

A total of 16, 1"x 1"x 0.125" (25.4 x 25.4 x 3.175 mm) square coupons were wet cut, air dried, oven dried and autoclaved respectively, from the same FRP plate (Figure 2.1).

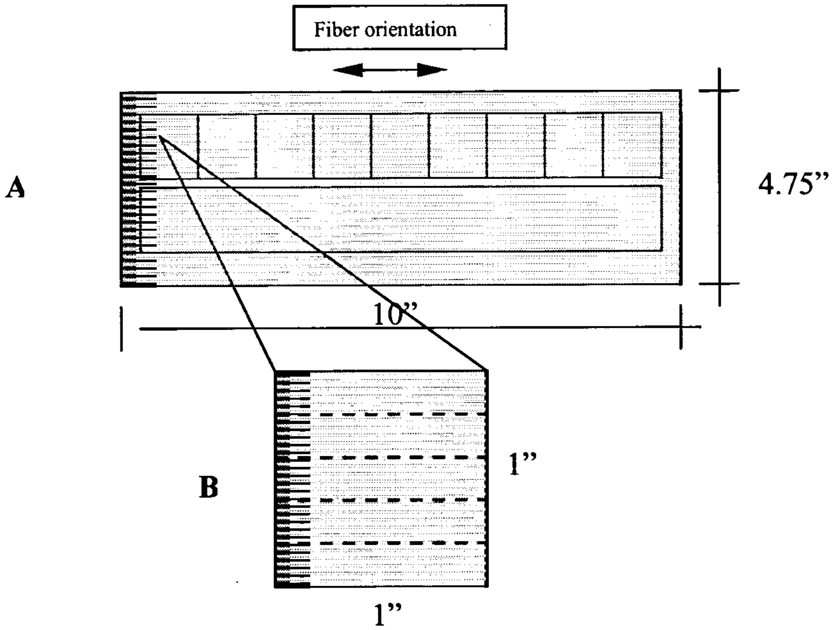

Figure 2.1. Cutting schematic (representative) of FRP specimens. **A:** 1" (25.4 mm) square coupons for soil block and ultrasonic NDE tests, thickness 0.125" (3.175 mm). **B:** Short beams were cut oriented with the unidirectional core fiber direction for interlaminar shear testing. Specimen size was 1"x 0.235" x 0.125" (25.4 x 6 x 3.175 mm) and the span/thickness ratio was 5.

Oven-dry specimen weights were determined prior to inoculation. Autoclaving was performed at 121.1°C (250° F) for 20 minutes to sterilize the coupons before incubation. Four coupons were exposed to the brown rot wood decay fungus, *Gloeophyllum trabeum* (Persoon:Fries) (ATCC # 11539) and four were exposed to the white rot wood decay fungus, *Trametes versicolor* (Linnaeus:Fries) (ATCC 12679) utilizing a modified AWPA soil block test (AWPA E-10 1999c). In this test, four uninoculated FRP control samples were maintained under the same soil block conditions but without exposure to the fungi, and 4 samples were keep in the conditioning room as true controls. An equal number of 1"x 1" x 0.5" (25.4 x 25.4 x 12.7 mm) southern yellow pine sapwood blocks were also cut, air dried, oven dried, autoclaved respectively then incubated with same fungal species as the FRP samples. All test samples were sandwiched between birch feeder strips (Figure 2.2) to simulate exposure conditions of an in-service FRP composite used to reinforce wood laminates in exterior environments. The test was modified to extend the exposure period to 24 weeks to allow a longer time for fungal attack of the FRP composite. The samples were then removed from the chambers, mycelium was brushed from their surfaces, and the samples were oven dried at 103 °C (217.4° F) before weighing. Weight loss was expressed as a function of initial oven dry (OD) weight.

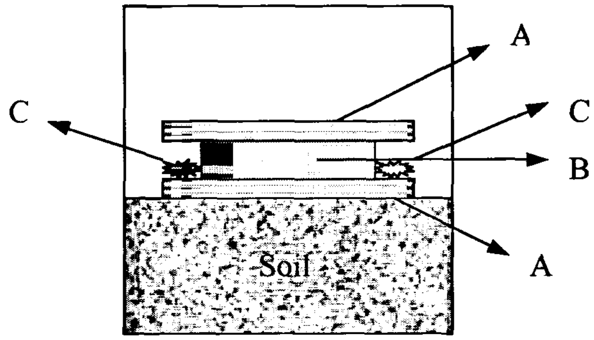

Figure 2.2. Decay exposure details of FRP coupons in soil jars; (A) Birch feeder strips, (B) Square FRP coupons, (C) Fungal culture (transferred from petri dishes).

2.3.3. Interlaminar Shear Testing

Following fungal exposure, all decay-exposed and uninoculated composites were sized with a diamond tipped wet saw blade to strips of an approximate dimension of 1"x 0.235" x 0.125" (25.4 x 6 x 3.175 mm). Three to four ILSS strips were cut from all one-inch square coupons except those that had become inadvertently contaminated in the decay tests. A total of 47 specimens were tested for all exposures representing unexposed, soil-exposed, and the two groups of decay-exposed samples. The specific distribution of multiple replicates from the tested exposures were; 13 miniature strips from four unexposed square coupons, 14 miniature strips from four soil exposed square coupons, 9 miniature strips from three *G. trabeum* exposed square coupons and, 11 miniature strips from three *T. versicolor* exposed square coupons. Specimens were tested in three-point flexure with a span-to-thickness ratio of 5:1 to promote interlaminar shear failure parallel to the plane of core lamination (ASTM 1984) (Figure 2.3 and 2.4). Since the experimental design was originally based on exposures and failed to account for jar to jar variability, the data were artificially regrouped after cutting according to their ILSS strength for statistical analysis to provide a 'worst case' significance evaluation (see Results and Discussion section).

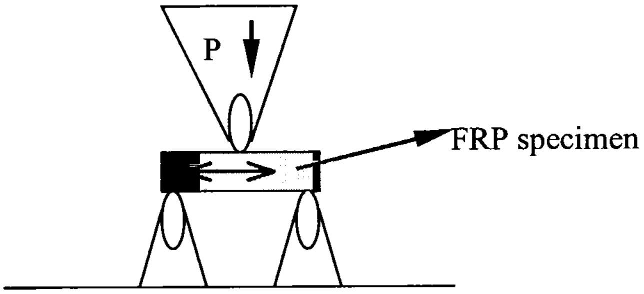

Figure 2.3. Application detail of ILSS test on a short beam specimen.

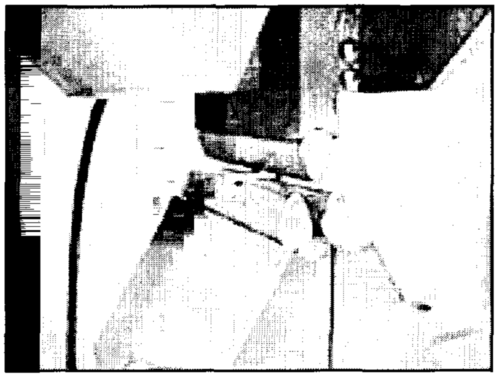

Figure 2.4. Close-up of ILSS test of a FRP short beam specimen.

Interlaminar shear strength (ILSS) depends primarily on the fiber/matrix interfacial shear strength and/or matrix properties rather than the fiber properties. This test has been used in material qualification programs (Lopez-Anido and Wood 2001) as a mechanical property indicator to assess retained "apparent" interlaminar shear strength after environmental exposures. ILSS is also considered a valuable screening tool to evaluate new fiber-resin systems, and compatibility of new fiber coupling agents (sizing) with matrix resins. In this research we applied this technique to evaluate the effects of biodegradation/biodeterioration on FRP composites. Failure modes were noted and interlaminar shear properties were confirmed using SEM and light microscope analysis. The apparent interlaminar shear strength (psi) at the mid-surface is computed according to beam theory (ASTM 1984), as follows:

$$S_H = 0.75\ P_B / b * d \qquad [1]$$

where P_B = ultimate applied transverse load prior to failure (lb.)
b = width of specimen (in)
d = thickness of specimen (in)

2.3.4. SEM and Fluorescent Microscopy Sample Preparation

Selected samples of decay-exposed FRP composite material were prepared for SEM. The SEM samples were treated with 3% glutaraldehyde, buffered and washed with 0.2M sodium cacodylate in DI water and fixed with 1% osmium tetraoxide. Treated samples were mounted on aluminum stubs and coated with gold using a Polaron E5000 sputter device, and observed using a Cambridge S150 scanning electron microscope operated at 5, 10 and 20 kV. Fungal colonization, distribution, and localized deterioration/disruption were examined on the fungal-exposed samples.

The excitation wavelength for the fungi was determined using pure cultures under the fluorescent microscope. The wavelength and filters were adjusted until the self-fluorescent image was digitally captured by a CCD camera. The same wavelength and filters were used to illuminate hyphae in decay exposed FRP specimens .

2.3.5. Determination of Surface pH

The surface pH of *Gloeophyllum trabeum,* and *Trametes versicolor* exposed FRP, as well as the surface pH of *Chaetomioum globusom* (a soft rot fungus) exposed FRP was tested. After removal of surface mycelium, surface pH measurements were performed according to TAPPI standard (T 529 om-88 1988). This particular method was preferred because its non-destructive nature provides a better representation of surface acidity, with high accuracy and repeatability. To conduct the test, a 10 μm droplet of reagent water was applied to the surface of the FRP with a micropipet and a flat combination electrode was then immersed into the droplet (Figure 2.5). The pH measurements were taken after equilibrium was reached. Eight drops were used for each type of exposed surface, including autoclaved reference- and soil-exposed FRP material. Eight drops were used for each type of exposed surface, including autoclaved reference-, soil-exposed, and the three fungus-exposed FRP materials. Three sets of samples were used as replicates totaling 120 samples.

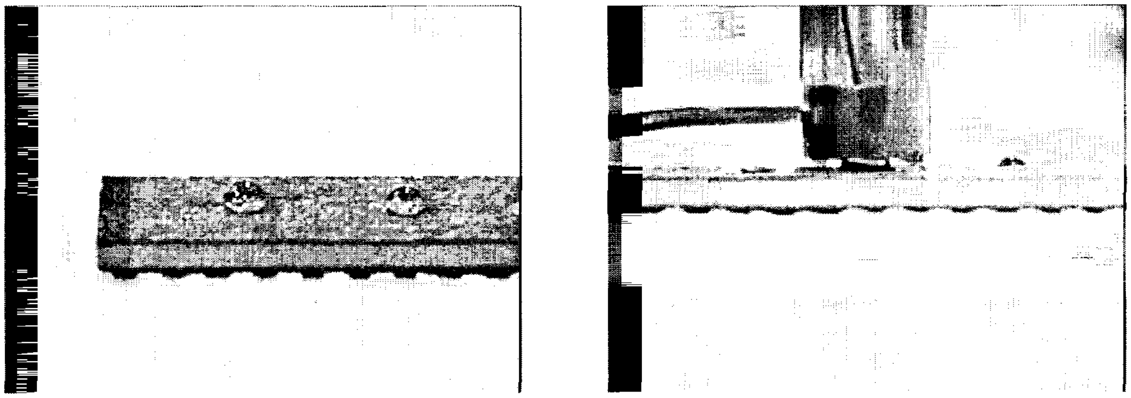

Figure 2.5. Surface pH measurement on decay exposed FRP surfaces.
Left: Transfer of reagent with the micropipette. **Right:** Immersion of the flat head combination pH electrode into the reagent water drop, which is already in contact with the exposed surface.

2.3.6. Determination of Moisture Content and Water Uptake

A water uptake study was also performed on FRP coupons of the same size and fiber orientation as outlined in section 2.3.5. Oven dried FRP coupons with unsealed edges were immersed in deionized water in plastic petri dishes. The dishes were covered to prevent evaporation losses. Every 24 hours, individual FRP coupons were taken from the petri dishes, pat dried for 10-15 seconds and weighed immediately. Weight changes were recorded over time for all specimens for 17 days (408 hours). The percent moisture content was calculated based on the original oven dry weights and averaged for all specimens.

2.4. Results and Discussion

2.4.1. Decay Evaluation and Microscopic Analysis

The post-decay moisture contents and average weight losses of both wood and FRP samples are listed in Table 2.1. Following incubation, all test specimens were fully covered with fungal mycelium in both brown-and white-rot test chambers indicating that any leachable chemicals in the K-1 type FRP material did not inhibit fungal growth. The FRP composite coupons all appeared in sound condition after the surface mycelium was removed (Figure 2.6 and 2.7); however, the FRP surface beneath the hyphae displayed a bleached appearance, which could be explained the etching effect of organic acids produced by the fungus (Chung et al. 1999, Goodell et al.1997, Green et al. 1991).

Table 2.1. Average post decay moisture contents and weight loss of FRP coupons after the soil block test (Standard deviation values are in parentheses).

Specimen Type	Average post decay moisture content (%) [based on post decay oven dry weight]			Average weight loss (%) [based on oven dry weight]		
	Soil Exposed Control	*G. trabeum*	*T. versicolor*	Soil Exposed Control	*G. trabeum*	*T. versicolor*
FRP	0.84 (0.10)	1.40 (0.09)	1.56 (0.55)	0.1 (0)	0 (0.1)	0 (0)
SYP reference	-	-	-	0.8 (0.4)	69.6 (0.4)	51.4 (5.1)

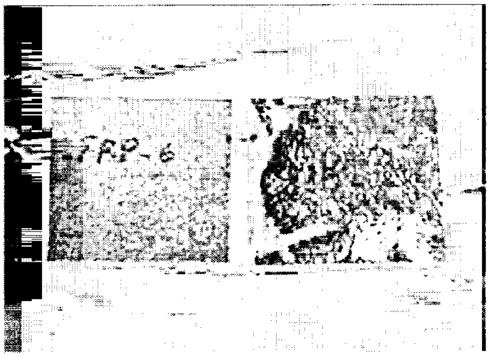

Figure 2.6. Fungal growth and white mycelia mat coverage on phenolic FRP surfaces and cross sections. Sterile soil-exposed FRP control, left; *T. versicolor* exposed FRP, right.

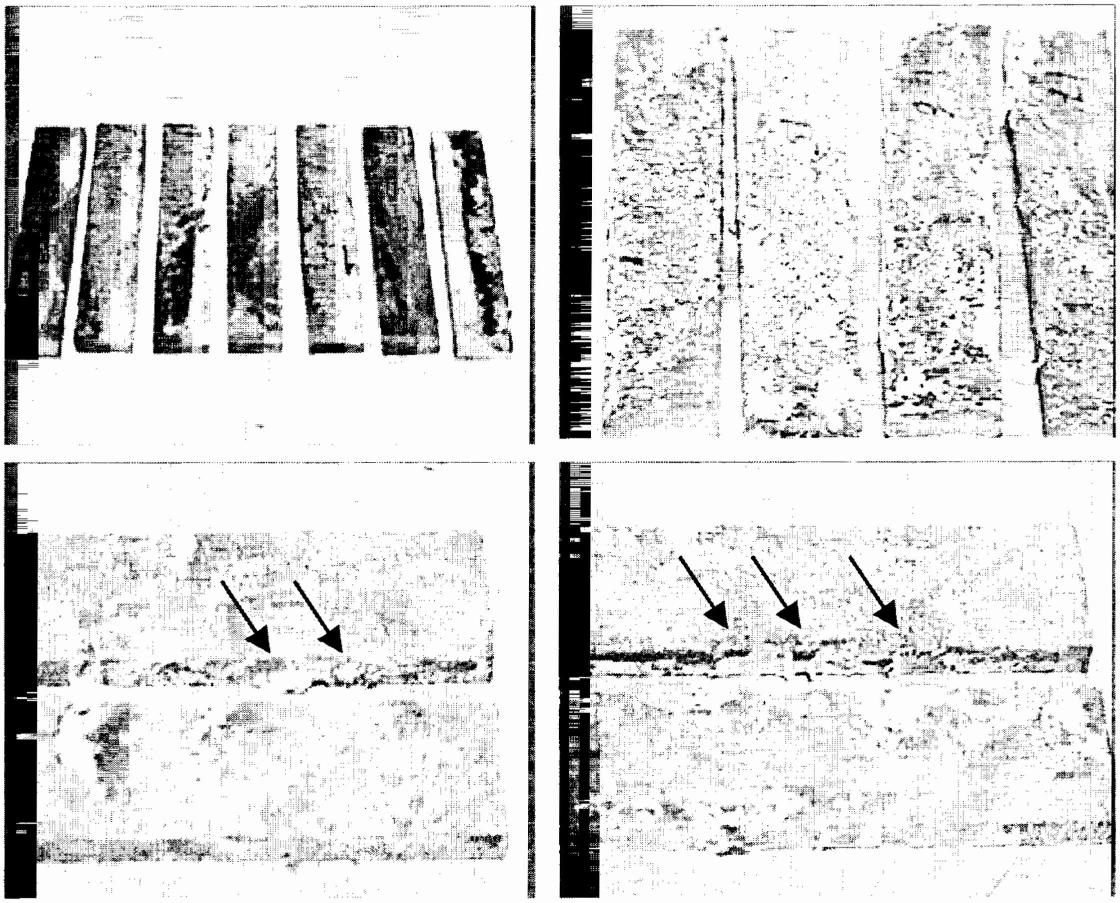

Figure 2.7. Fungal growth and mycelial mat coverage on K-1 FRP surfaces and cross sections (impact test specimens). *C. globosum* exposed, upper left; *T. versicolor* exposed, upper right; *G. trabeum* exposed; lower left and right, arrows show the extensive growth on cross sections.

The decay-exposed FRP coupons were weighed immediately after the surface mycelium was removed. Moisture uptake was calculated based on the post decay oven dry weight and post decay weights of FRP coupons. *T. versicolor* and *G. trabeum* exposed coupons gained 67% and 86% more moisture than sterile soil-exposed controls, respectively. The increased moisture uptake in the fungal exposed samples was associated with fungal activity in the FRP coupons perhaps affecting the fiber/matrix interface capillaries.

After drying, there was no detectable weight loss (based on oven dried weight) of the FRP coupons after 24 weeks of exposure. Southern yellow pine sapwood control blocks, however, sustained approximately 70% and 50% weight loss for *G. trabeum* and *T. versicolor* respectively, over the 24-week exposure period (Figure 2.8). This suggests that any degradation products produced in the soil block exposure of FRP were not metabolized by the fungi.

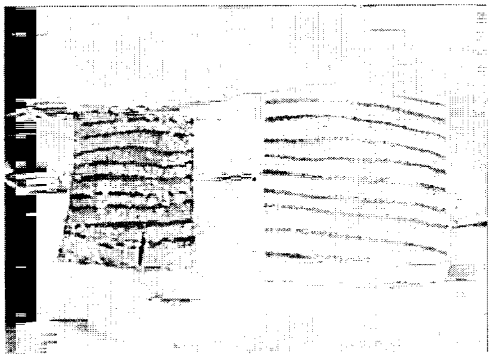

Figure 2.8. Volumetric shrinkage of SYP reference blocks. (*G. trabeum* exposed at right, undecayed at left).

2.4.2. Interlaminar Shear Strength Test

Table 2.2 summarizes the average interlaminar shear strength values of the unexposed, sterile soil-exposed and decay-exposed (*T. versicolor* and *G. trabeum*) specimens after 24 weeks of exposure. A non-significant ILSS reduction of 7.4 % was recorded for the *G. trabeum* exposed K-1 FRP material. The *T. versicolor* exposed FRP material showed a non-significant 3.9 % reduction (Figure 2.9). The coefficient of variation (COV) values for decay-exposed FRP (Table 2.2) materials were greater than the COV values for the control (unexposed, soil-exposed) specimens. This is an important observation since the FRP composite allowable values depend on both the mean and COV. The higher COV values drastically reduce the allowable design values.

Table 2.2. Summary table of ILSS values of differentially exposed K-1 FRP material for 24 weeks.

Exposure conditions	Average ILSS (MPa)	COV (%)	ILSS Change (%)
Unexposed	26.42	3.4	0.0
Soil-exposed	26.72	4.5	1.1
T. versicolor	25.39	7.2	-3.9
G. trabeum	24.45	7.9	-7.4

Unfortunately, the initial statistical analysis performed assumed that all strips in each treatment group had been independently treated. This would be an appropriate assumption if each strip represented a sub-sample taken from individual ASTM soil block chambers. However, because a variable number of strip samples were taken from the 3-4 exposed blocks versus 12 independent samples, it is possible that the probability values given in Appendix B, which show a significant decrease in ILSS strength for *G. trabeum*, do not adequately reflect true population variability.

A secondary attempt to analyze the data was performed using an artificial grouping technique (grouping the closest actual data points assuming they represented samples from the same exposure chambers) to test the effects of exposures and exposure chamber variability together. This technique allowed a 'worst case' statistical evaluation to be determined. The resulting p values varied upon the artificial grouping (p values 0.175-0.186) and indicated a weaker level of confidence than the original analysis where sources of variation were not partitioned adequately. Because of this, further work will be needed to verify that the ILSS reduction seen for *G. trabeum* is statistically significant at conventionally used confidence levels.

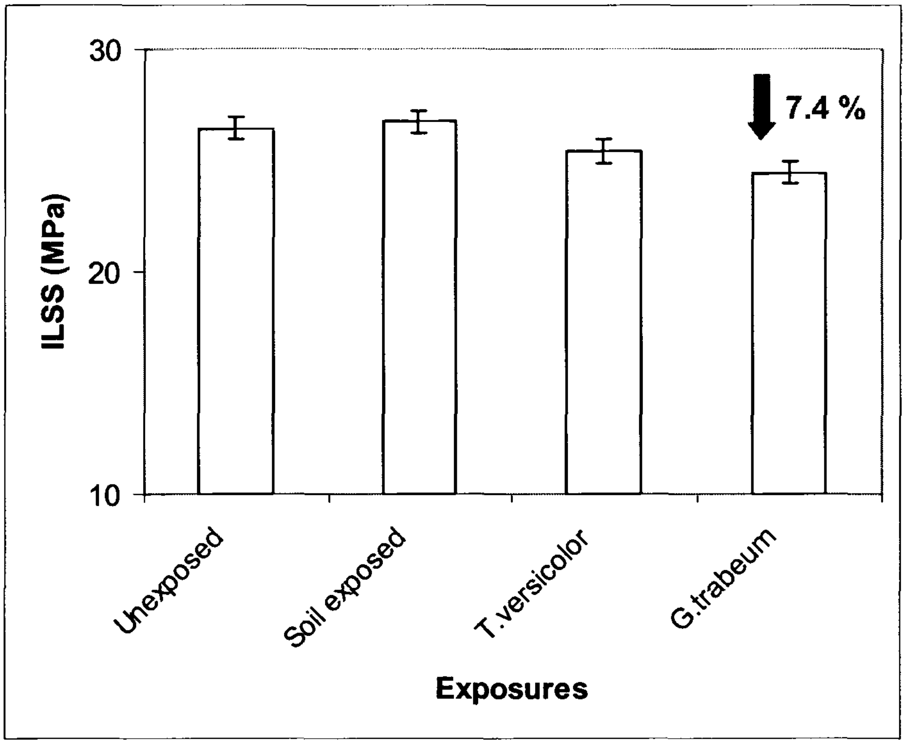

Figure 2.9. Comparison of average interlaminar shear strength values of control and decay-exposed FRP material after 24 weeks. (The y-axis error bars on the columns show standard errors).

2.4.3. Surface pH After Fungal Exposure

The following figure (Figure 2.10) summarizes the average surface pH of decay-exposed, soil-exposed and unexposed E-glass/phenolic pultruded FRP composite material.

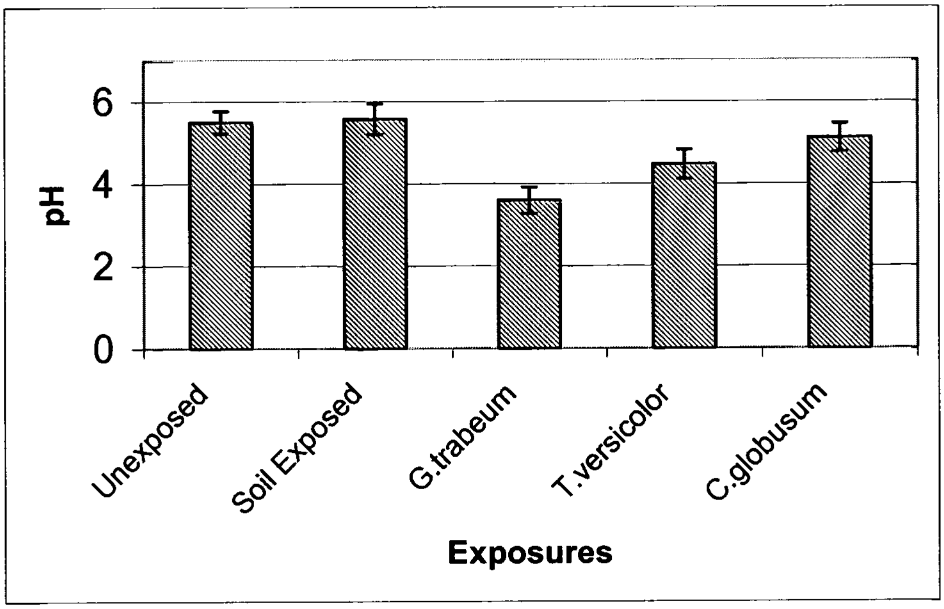

Figure 2.10. A comparison of the surface pH values with fungal exposure after 24 weeks. (The y-axis error bars on the columns show standard errors).

The *G. trabeum* exposed FRP demonstrated significantly lower surface pH values compared to the other samples. This high acidity can be attributed to brown rot activity in connection with oxalic acid production. Large quantities of oxalic acid ($pK_1 = 1.27$, $pK_2 = 4.26$) production by brown rot fungi are widely reported in the literature (Jellison et al. 1997, Humar et al. 2001) concurrent with a decrease in pH in early brown rot stages. Seven to 14 days after inoculation, the pH values of wood were reported to drop to 2.5-1.6 (Jellison et al. 1997). This suggests that the FRP coupons evaluated may have been exposed to pH 3.6 for almost 20-22 weeks (the remaining time in a 24 week exposure following the inoculum growth phase). Further analysis of exposed surfaces with SEM revealed that putative calcium oxalate crystal accumulation occurred especially on the resin rich areas of the *G. trabeum* exposed FRP material (Figure 2.11). Observations of oxalate crystals have commonly been reported in brown rot cultures, and degraded wood. Connolly et al. (1996) list three major types of calcium oxalate crystals association with decay fungal hyphae: encrusting crystals, adhering crystals, and free crystals. Our results indicate that *G. trabeum* produced mostly adhering type of calcium oxalate crystals on the phenolic resin surface of the FRP composite material.

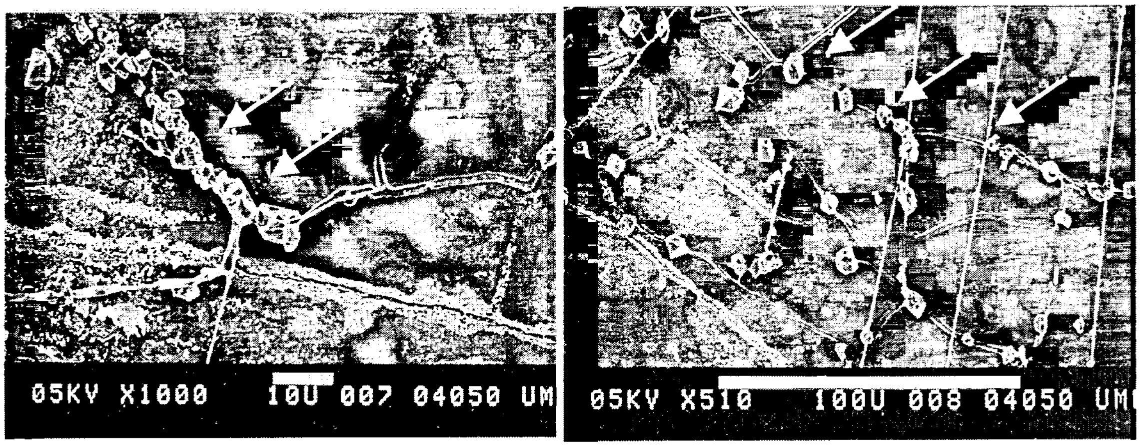

Figure 2.11. SEM micrographs showing "adhering" type crystals (putatively identified as calcium oxalate) associated with the fungal hyphae of *G. trabeum* on an FRP surface. Note the crystal accumulation aligned with the hyphal orientation on resin surface (white arrows).

2.4.4. Determination of Moisture Content and Water Uptake

Figure 2.12 summarizes the average post decay moisture contents of decay exposed and soil exposed FRP composite material. The *G. trabeum* exposed FRP material had a 4.5 % MC at the end of the fungal exposure test whereas the other samples attained only an average MC value of approximately 2.2%.

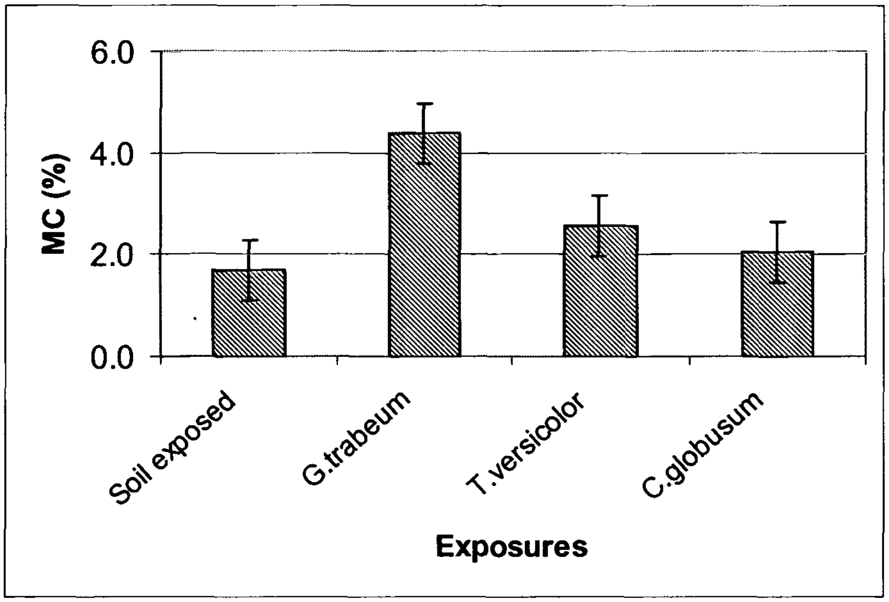

Figure 2.12. Average post decay moisture content (MC %) of decay exposed FRP coupons (The y-axis error bars on the columns show standard errors).

Figure 2.13 represents the MC (%) changes (water uptake) over time in E-glass/phenolic FRP material, which had unsealed edges, immersed in water. The time required to reach approximately 3.5-4 % MC was over 400 hours under water immersion conditions.

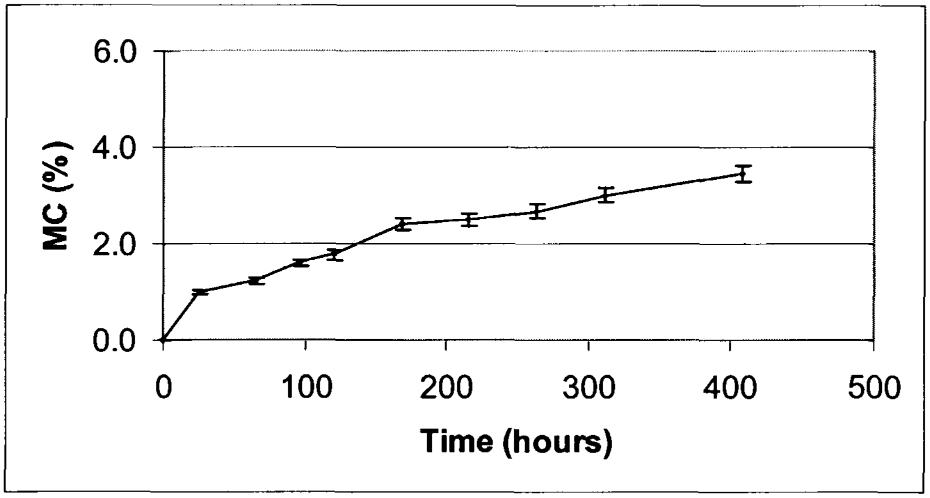

Figure 2.13. Moisture uptake of FRP material immersed in deionized water as a function of time.

2.4.5. Microscopic Evaluations

Visual, stereoscopic, and light microscopy (LM) inspections showed that, after fungal exposure, mycelial mats were firmly attached to the FRP surface veil, with hyphal penetration by both fungi into the high-void-content region (V_v = 38% for surface veil only). Further LM and SEM analysis on the cross section of FRP exposed coupons also verified hyphal penetration (Figure 2.14). The presence of large amounts of crystal development was also observed on the FRP surface for both fungi (Figure 2.11). Light, fluorescence and scanning electron (SEM) microscopy observations all indicated that the K-1 FRP material is susceptible to fungal penetration by hyphae, with fluorescence and SEM showing the presence of fungal hyphae within the fiber-matrix interface of the FRP unidirectional fiber core of failed

ILSS tests specimens. (Figures 2.15, 2.16, and 2.17) This may be particularly important in helping to explain the reductions of interlaminar shear strength in the FRP material. Although it is unlikely that substrate-specific enzymes secreted by the fungi were responsible for the degradative effects, the production of acids which can reduce the pH of fungal microenvironments down to 2 or even less (Jellison et al.1997) would likely have caused this type of degradation. The preferential distribution of bacteria and crystals along the fiber/matrix interface was also reported by Wagner et al. (1996) and Ray et al. (1997).

Figure 2.14. Cross-sectional views of decay-exposed FRP. **Left:** Micrograph showing fungal hyphae penetrating into the fiber/matrix interface. **Right:** Micrograph showing fungal hyphae wrapped around (top arrow) a glass fiber and penetrating into the fiber/matrix interface (lower arrow).

Figure 2.15. Fluorescence micrograph of 24-week, *T. versicolor* white rot exposed FRP sections. The images were taken digitally with an Olympus BX-60 microscope equipped with a multi wavelength filter cube (UC 83 103 and 83 360 UV band and triple UV/blue/green). The surface veil area is shown with hyphae randomly dispersed in the void space (a) and horizontal white streaks show the auto-fluorescing hyphae aligned with the unidirectional glass fibers in the core (b). The surface of this sample was covered with a mycelial mat (below the section marked b, not shown).

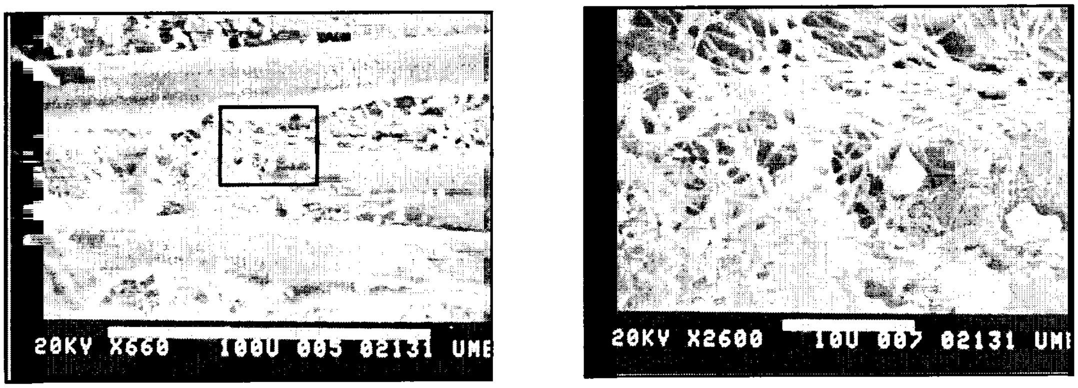

Figure 2.16. Fungal growth within the fiber/matrix interface approximately 1mm deep in decay exposed (*T. versicolor*) FRP. **Left:** fungal hyphae traverse several glass fibers. **Right:** a close up of the boxed region in the left image showing fungal hyphae in the debonded fiber/matrix interface.

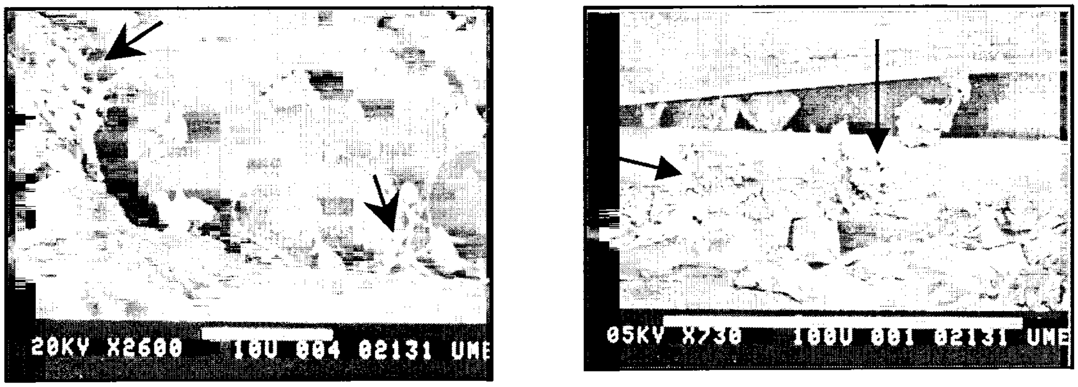

Figure 2.17. “Valley area” between the fiber and matrix of *G. trabeum* exposed FRP composite material. **Left:** Fungal hyphae attached to a glass fiber surface (bottom), traversing the fiber and ramifying into resin coated glass regions (arrows) at approximately 1mm depth from the FRP surface. **Right:** Accumulated fungal residue (arrows) on a debonded fiber/matrix interface.

Our microscopic investigation supports a theory involving the fiber/matrix interface weakening as a result of fungal attack. Since some sizing chemicals, including starch derivatives and acetylated celluloses are biodegradable (Gu et al.1997, Wagner et al. 1996, Sampath et al. 1997), enzymatic degradation of these compounds by wood decay fungi may be possible. Because of the proprietary nature of fiber sizing, the manufacturer has not disclosed the type of sizing used in our material. However, silanes are often used with phenolic/glass FRP pultruded materials, and the powerful organic acids (oxalic acid) produced by wood degrading fungi would be more likely to cause degradation of a non-organic sizing such as this. The chopped strand matt of our FRP material also contained a melamine resin binder and the high nitrogen content of this resin may have promoted degradation in this region. Other additives used with phenolic resins may also have affects on fungal growth. Some examples of the common additives used with phenolic resins include: antistatic agents (mainly amines, amides and their derivatives which contain nitrogen), colorants (quinacridone, anthraquinone, carbon black, zinc sulfide, metallic oxide browns), flame retardants (phosphate esters, alkyl diaryl phosphate, halogenated hydrocarbons, chlorinated paraffin, alumina trihydrate, antimony oxide, magnesium hydroxide, dibromophenol), lubricants (alcohol esters, glycerol esters, calcium stearate, PTFE waxes, synthetic wax soaps) (Chanda 1993, Guide to Plastics 1991). There are other chemical additives, used in commercial fiberglass sizing, that can be grouped as: film formers (unsaturated bisphenolic glycol-maleic polyester, polyvinyl acetate), antistatic agents (cationic organic quaternary ammonium salt), lubricants (cationic fatty acid amides, tetraethylene pentamine, polyethyleneimine polyamide), pH control agents (acetic acid), emulsifying agents (condensate of polypropylene oxide with propylene glycol) (Gardner 2002). Due to the proprietary nature of these additives, the exact composition of the chemicals used in our E-glass FRP sizing and phenolic pultrusion resin was unknown, limiting our ability to test some of these chemicals for support or repression of fungal growth. The consumption or decomposition of fiber sizing or binders by fungi or their organic acids can introduce localized weakening on the matrix/fiber interface, which indirectly reduces the interlaminar shear strength of decay-exposed FRP material. Addition of a fungicide to FRP components during manufacture might help to inhibit fungal degradation of these materials when they are exposed to moist environments that might promote fungal and other microbial activity. However, changes in surface energy and adhesion characteristics need to be taken into account and fabrication concerns may need to be addressed. Some quaternary ammonium-functional silanes were previously found to be effective against biocidal activity while serving as glass fiber coupling agents (Plueddemann 1991).

The addition of biocides to FRP materials introduces other important issues though. Tascioglu et al. (2001) reported that some waterborne biocides (e.g. CCA) chemically attack glass fibers and induce spiral cracks and fissures on the glass surface reducing their tensile strength. These factors must also be considered if biodegradation is to be controlled using chemical preservatives (Tascioglu et al. 2001).

2.5. Conclusions

The following conclusions can been drawn from this research:

1- E-glass fiber/phenolic resin matrix pultruded composite materials designed for wood reinforcement (with high void content) are susceptible to fungal penetration by common wood decay fungi.

2- Although no detectable weight loss of FRP material was recorded, there was a significant increase in the moisture content of both white and brown rot exposed samples as well as a weak relationship (maximal p values 0.175-0.186) between the reduction in interlaminar shear strength and exposure of the FRP material to *G. trabeum*. Additional studies with improved design procedures will have to be performed to determine if a more robust relationship exists between decay exposure and FRP ILSS values.

3- The application of the mechanical (interlaminar shear strength) technique shows promise for the monitoring of fungal activity in FRP composites. With further detailed work, this technique might be useful in time exposure vs. interlaminar shear strength loss modeling.

4- The fiber/matrix interface seems to be the key area for capillary distribution of fungal metabolites that may play an important role in interlaminar shear strength reduction.

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Chapter 3

BOND DURABILITY AND SURFACE ENERGY CHARACTERIZATION OF PRESERVATIVE TREATED WOOD / FRP INTERFACES

3.1. Introduction

Recent studies have demonstrated that Fiber-reinforced Polymer (FRP) composite reinforcement in the order of 1.1% can increase the allowable bending strength of glulam beams by greater than 60% (Dagher et al. 1996); however, the durability of adhesive bonds for preservative treated wood poses a continuing problem in the wood /FRP hybrid composites industry (Qiao et al. 1998). Like all wood used in exposed outdoor environments, wood laminations with or without FRP composites must be treated with appropriate wood preservatives to prevent deterioration from decay fungi, insect attack, and other environmental agents (AWPA 1999a). Pressure treatment with wood preservatives has been known to interfere with the bond integrity of solid wood glued specimens. Preservative type, preservative retention, and interaction with the surface were reported as highly significant factors affecting shear strength of glue bonds in solid wood samples (Vick 1996 and 1994, Vick et al. 1990, 1993).

Vick et al. (1990 and 1994) and Vick and Kuster (1992) reported that the lumen surfaces of Chromated copper arsenate (CCA, a water-borne wood preservative) treated southern yellow pine were completely covered by hemispherically shaped deposits ranging in diameter from around 1.0 μm to essentially invisible at a magnification of 5000x. Theoretically, these deposits reduce the molecular level contact between the adhesive and lignocellulosic wood material. They also proposed that in CCA treated wood, the insoluble metal oxides tie up aromatic hydrocarbon functional groups, reducing hydrogen bonding and/or perhaps covalent bonding opportunities between adhesive and lignocellulosic wood content.

Similarly, Kilmer et al. (1998) discussed the lack of bondability of four hardwood species after being treated with creosote (pre-treatment). No adhesive system tested was suitable for bonding creosote treated hardwood. The poor bonding was attributed to a combination of improper wetting of the wood surfaces as well as inhibition of moisture absorption from the adhesive film by the creosote thus delaying and/or preventing proper cure.

According to Raknes (1963), the presence of preservatives in the wood can modify moisture content, alter adhesive pH, inhibit condensation reactions and prevent the adhesive wetting of surfaces, influencing the adhesion phenomena.

Most literature provides durability data on untreated wood/FRP interfaces. Lopez-Anido et al. (2000) found that durable bonds between untreated eastern hemlock glulam panels and E-glass/vinyl ester FRP composites can be produced when an HMR coupling agent is used.

The lack of information available in the literature directly related to bond durability in wood and FRP composites prompted the initiation of this study. In this research, five wood preservatives (acidic and basic water-borne as well as oil-borne preservatives) at different retention levels with one wood species and one FRP composite type were evaluated. Specifically, the effects on FRP - FRP, and FRP - wood adhesive bonds were investigated. Preservatives and retention levels with the greatest compatibility for FRP-wood bonding were identified. ASTM D2559 cyclic delamination and several AWPA standards were followed for all pre and post-treated reinforced laminated beam sections.

The objectives of this study were as follows:

1) Characterize the effects of common wood preservative treatments on the durability of wood/FRP and wood/wood interfaces through an accelerated aging method.
2) Determine the surface energy characteristics of preservative treated wood and FRP surfaces and measure how these may change in relation to preservative retention.
3) Establish a relationship between surface energy and long-term bond durability of wood/FRP interfaces.
4) Develop preservative treatment recommendations and identify compatible preservative systems for use with FRP composites in pre- and post-treatment applications appropriate for the preservative/pressure treatment FRP-wood glued-lamination industry.

3.2. Literature Review

3.2.1. Laminating Preservative Treated Wood

Interest in gluing treated wood began soon after modern, synthetic thermoset adhesive systems were developed in the 1930s. Researchers have reported on the performance of softwood and hardwood glulam specimens.

There are essentially two methods for producing preservative treated laminated members.

1) Post-treatment: treating already glued and machined laminates.

2) Pre-treatment: treating individual laminate members and after treatment and post-conditioning gluing members of the required size and shape (Selbo 1952).

Both methods have their advantages and disadvantages.

A) Post-treatment:

Advantages:

a) Treatment of the finished laminated product permits application of the preservative after all cutting, boring, and other framing are completed and assures a protective coating on all exposed surfaces.

b) Handling of material at the treating plant is simplified when the finished members rather than the individual laminates are treated. Post treatment production of larger laminated beams, for example, eliminates the handling of individually treated boards.

c) Treatment of glued laminated members makes surface planing operations unnecessary and results in savings of heavily treated surface material and time.

Disadvantages:

a) Treatment can cause severe warpage, splits and checks, particularly when waterborne treatments are used.

b) The limited size of treatment cylinders precludes treatment of larger or unusually shaped laminated beams.

c) Penetration of preservatives has been reported to be blocked by glue lines to some extent, resulting in an envelope protection in a beam. If weathering checks develop deeper than treated envelope zone in service this may allow fungal decay to start (Selbo 1952 and 1959) (Figure 3.1).

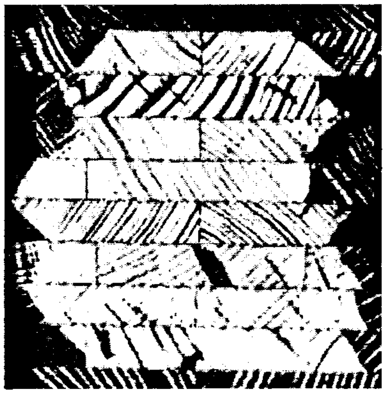

Figure 3.1. Cross-section of a 4-foot-long, end sealed, laminated southern pine beam pressure treated with zinc chloride solution. Note the blocking effect of the glue line (from Truax et al. 1953)

d) In treating curved laminated beams with water-borne preservatives some spring back or deviation in size and shape of the beam can be anticipated as the result of unequal swelling during the moisture changes which occur throughout the pressure treatment and post-conditioning periods (Truax et al. 1953, Selbo 1952, Selbo 1967)

B) Pre-treatment:

Advantages:

a) This method can be used to produce laminated beams of practically any size and shape that are well treated because relatively thin individual laminates can be completely penetrated with preservative chemicals. Complete preservative penetration is not possible with large cross sections.

b) Glued members consisting of fully penetrated laminates, can be shaped and bored with less danger of exposing untreated material.

c) This method allows the production of very large and uniquely shaped laminated beams that can not be treated with conventional treatment cylinders.

Disadvantages:

a) Each lamination must be surfaced. This removes the most heavily treated part of the treated lumber resulting in a waste of treated wood and time.

b) Machining this treated wood can result in increased hazards in the workplace due to the production of increased preservative treated wood dust.

c) Preservative chemicals on the surface of treated laminates can interfere differently with consistent adhesion and glue line performance.

3.2.2. Effects of Wood Preservative Treatment on Glueline Performance

Recent work by Kilmer et al. (1998) discussed the bonding of four hardwood species after treatment with creosote (pre-treatment). They utilized four hardwood species (chestnut oak, red oak, red maple, yellow-poplar) and southern pine, five adhesive systems, and two exposure levels (ambient and vacuum/pressure/soak). They recommended only an elevated temperature cure phenol resorcinol formaldehyde (PRF) resin system for creosote treated hardwoods since this adhesive produced the highest and most consistent glueline shear strength and percent wood failure values when compared to other PRF, RF, and isocyanate (EPI) resin systems. The EPI system produced some of the lowest average percent wood failure performance values under the vacuum/pressure/soak exposure. According to Kilmer et al. (1998), poor bonding of creosote treated wood was attributed to a combination of improper wetting of the wood surfaces as well as inhibition of moisture absorption from the glue film by the creosote thus delaying, or preventing proper cure. They used a two step surface process for creosote treated billets preparation:

1) Steam cleaning: Expose the samples to 115° C saturated steam at atmospheric pressure for one hour followed by a 50.7 kPa Hg vacuum for 30 min.
2) Surface planing: 1.6 mm surface planing immediately prior to layup. (Kilmer et al. 1998)

In another study (Janowiak et al. 1992) which used the same wood species as Kilmer et al. (1998) but two different preservative systems (CCA and pentachlorophenol), and compared elevated-temperature and room temperature curing for PRF, very similar glue line shear strengths were reported. They suggested that the need for higher curing temperatures indicated that PRF cure is slowed by the presence of preservative. Furthermore, they observed that preservative treatment with CCA did not adversely affect bonding of the four hard wood species. However, oil-borne pentachlorophenol displayed statistically significant lower glue line properties in their experiment.

According to Raknes (1963), the presence of a preservative in the wood can influence the formation of the adhesive bond in one or more of the following ways;

a) by producing too high a moisture content in the wood
b) by altering the pH of the adhesive
c) by inhibiting the condensation reaction.
d) by delaying water removal from the glue line

e) by preventing the adhesive from wetting the wood surface

He concluded that CCA treated beech wood may be satisfactorily bonded with RF and PRF type adhesive systems, even at high preservative concentrations (Raknes, 1963). He also reported that the preservatives used seem in many cases to delay hardening of the adhesive systems, but this can be corrected by use of suitable adhesion conditions. Considerable differences in bonding were noted comparing the different preservative systems; however, preservative concentration showed little impact on adhesion properties in this particular experiment (Raknes 1963).

Selbo reports in his work that adhesive joints in laminated beams made with resorcinol, phenol resorcinol, and melamine-resin glues are not harmed when post-treated with commonly used wood preservatives (Selbo 1967). He recorded several decreased values in shear strength ranging from 2% to 21% depending on the adhesive systems, wood species and type of preservative. He also concluded that creosote provided excellent protection against checking of laminated beams exposed to the weather for two decades and that there was no significant difference in the performance of three types of glues (resorcinol, phenol resorcinol and melamine) used in these beams.Truax et al. (1953) discussed the effects of preservatives and treatment on the strength of gluelines, and interference with of the glueline with the penetration of preservatives into the wood. They also questioned the difference between pre- and post-treatment methods on glulam bonding and durability.

In preservative treated stress-laminated bridge decks for highway bridge applications, Ritter et al. (1990) observed that water-borne preservatives are not widely used because of concerns about the dimensional stability of the wood laminations. Oil-borne preservatives, such as creosote and pentachlorophenol (PCP) are the primary types of wood preservatives used in structural highway applications. For these preservatives, the preservative and/or oil carrier provides some moisture resistance that limits dimensional change caused by moisture content fluctuations. On the other hand, waterborne preservatives, such as CCA, provide no moisture barrier and lead to increased dimensional changes very critical to maintaining pre-stressed bar force in the deck (Ritter et al. 1990).

Kainz et al (1996) concluded that there was less fluctuation in "stressing bar force" in decks treated with oil-borne preservatives than in decks treated with waterborne preservatives. They recorded very similar stressing bar force fluctuations for all decks treated with the oil-borne preservatives with a maximum variation of 1000 lbs. during the four summer months. Water-borne preservative treated decks, however, exhibited greater changes in relative bar force (2500 lbs.) over the same period (Kainz et. al 1996).

3.2.3. Changes in Surface Characterization of Treated Wood

Surface characterization can be achieved by evaluation of contact angles to provide a measure of substrate surface energy which correlates to the wettability and bondability of different surfaces. Contact angle reflects the physical and chemical affinity between a surface and a liquid such as an adhesive. As a result, contact angle analysis has been used to characterize the wettability of wood surfaces and then to predict their performance when bonded with adhesives (Collet 1972, Hse 1972, Gardner et al. 1991).

Most of the literature found in this area focuses on CCA treated wood since CCA is the most commonly used preservative and a significant body of research exists on surface properties of recycled CCA treated wood. Maldas and Kamden (1998a, b) have reported on the modification of red maple surface properties following treatment with CCA as follows:

a) Wood cell walls are covered with 1-5μm solid deposits, which are rich in chromium, copper and arsenic.

b) O/C ratio of CCA treated samples is increased due to the added oxygen atoms from the CCA on the surface, and at the same time reduced presence of carbon or C1.

c) The surface pH of untreated wood was 6.6 (± 0.13) compared to 5.9 (±).17 for CCA treated wood.

d) The surface roughness profiles for CCA treated wood changed considerably compared with those of untreated wood. (Average roughness for water-treated wood was 1.72 R_a, for CCA treated wood 2.48 R_a).

In another similar study on artificially weathered CCA-treated southern pine (Zhang et al. 1997), CCA treatment resulted in improved RF resin wettability, as expressed by the lower contact angle of RF with the CCA treated wood, compared to untreated southern pine surfaces. Total surface tension of the CCA treated wood was greater than the untreated southern pine. Interestingly, the authors also noted that the total surface tension of both the CCA-treated and untreated southern pine increased as a result of the exposure to accelerated-weathering cycles that caused surface oxidation.

Zhang et al. (1997) discussed that CCA treated wood has been shown to be coated with deposits of metallic oxides (Vick and Kuster 1992) causing a microscopically rough surface. This roughness, coupled with some polar affinity of the oxides with RF resin, may result in the improved wetting of CCA surfaces beyond that occurring with untreated wood surfaces. The wax content of some commercial CCA treatments has previously been offered as an explanation for the higher water contact angle of CCA treated wood as compared to untreated wood. But a greater magnitude contact angle change for water than for RF adhesive indicated that CCA treatment affects water repellency more than the adhesive wettability of the wood. In terms of bond strength evaluation, Zhang et al (1997) reported approximately 20 percent shear strength loss as a result of CCA treatment. The percent of wood failure was not significantly affected when CCA treated and untreated wood were compared. Accelerated-weathering did not greatly reduce the bonding properties of the CCA treated southern pine. The authors concluded that aged CCA treated southern pine should have reasonable bonding properties assuming that the proper adhesive and bonding technology were employed (Zhang et al. 1997).

Shaler et al. (1988) reported that CCA-treated laminates met AITC requirements for glueline performance in shear strength and cyclic delamination when the manufacturers pressing conditions and recommended resin system were used. The mean percentage wood failure of CCA/CCA joints, however, failed to meet the required 70 percent value .

In a scanning electron microscopy (SEM) study of CCA treated southern pine wood Vick and Kuster (1992) and Vick 1994 found that the lumen surfaces were completely covered by a heavy deposition of hemispherically shaped material ranging in diameter from around 1.0 μm to essentially invisible at a magnification of 5000x. Theoretically this would allow little opportunity for molecular-level contact of the adhesive with lignocellulosic constituents of the cell walls. Phenolic components of adhesives are rich in polar hydroxyl groups that can form hydrogen bonds with polar functional groups on lignocellulosic constituents in the cell walls. But in the case of treated wood, as proposed by Vick and Kuster, the insoluble CCA metal oxides that already occupy functional sites may block hydrogen- or perhaps covalent bonding sites that normally might bond with the resin. Despite the presence of insoluble deposits blocking contact between adhesive and wood, Vick and Kuster (1992) concluded that mechanical interlocking by a deeply penetrating phenolic adhesive can produce delamination-free bonds to CCA-treated southern pine even after severe cyclic aging tests.

Vick and Christiansen (1993) produced differential scanning calorimeter (DSC) thermograms indicating that a solution of CCA preservative caused a strong exothermic reaction with phenol-formaldehyde adhesive in which a portion of the adhesive reacted at lower than normal temperatures. Individual metallic ions of Cr (VI), Cr (III), Cu (II) and As (V) in solutions of model compounds also reacted with the adhesive, but only Cr (VI) reacted in the same low temperature range as the solution of CCA preservative. However, when the CCA preservative was chemically “fixed” within the wood no accelerated reactions of the adhesive were evident (Vick and Christiansen 1993).

3.2.4.Compatible Adhesive-Preservative Systems

A preliminary evaluation of adhesive-preservative compatibility by Winandy and River (1986) found that a phenol-resorcinol resin would provide acceptable bonding with pentachlorophenol treated wood . In this same study, phenol-resorcinol resin cured at ambient temperature was incompatible with CCA treated wood. Although early indications showed promising results for CCA-phenol-resorcinol compatibility, industrial experience and laboratory studies seemed to indicate otherwise (Winandy and River 1986). The authors concluded that their proposed vacuum-pressure soak-dry (VPSD) shear test with evaluations of shear strength and wood failure characteristics after multiple VPSD cycles is an effective and more informative test than the standard cyclic delamination test method (ASTM D-2559). They made conclusive statements as follows:

- "Wood failure and in particular, deep wood failure (failure well beyond the depth of adhesive penetration) is significantly higher in the penta-treated specimens than the CCA-treated specimens"

-"No significant differences are detected in delamination as a result of the type or retention level of preservative treatment" (Winandy and River 1986)

Vick et al. (1990) have worked on the compatibility of non-acidic waterborne preservatives (such as DDAC, DDAC with copper, DDAC with carbamate, sodium fluoride and ammonium hydrogen difluoride) with phenol-formaldehyde adhesives. They reported that none of these non-acidic waterborne preservatives interfered with the adhesion of a PF adhesive with aspen veneers treated at retentions of 0.2, 0.4, and 0.6 pcf ammoniacal copper zinc arsenate did not interfere with adhesion at lower retentions, but at higher retention levels, bond integrity fell below standards. ACB was found not compatible with PF adhesive at any retention level (Vick et al. 1990).

Sellers and Miller (1997) reported that an expensive, unmodified RF adhesive could be used to bond CCA-treated lumber satisfactorily for exterior exposure glulam products. They also reported the success of an emulsion-isocyanate adhesive in dry block shear testing; however, this adhesive failed in standard delamination tests (Sellers and Miller 1997).

3.2.5.Trials to Improve Adhesion of Treated Wood

Charles B. Vick has been a pioneer in the field of coupling agents for adhesion studies of wood, and he successfully patented his hydroxymethylated resorcinol coupling agent (HMR) in 1996 for use in producing high durability wood bonds. Coupling agents are chemical molecules with dual functionality. In use, one part of the molecule will promote adhesion to one surface (e.g. a wood surface) while another part of the molecule will adhere to the surface of another material. (e.g. an adhesive polymer). Vick (1995) reports that when CCA-treated southern pine laminates were primed with HMR and bonded with epoxy, phenol-resorcinol, emulsion polymer/isocyanate, and polymeric diisocyanate adhesives, the bonds met the delamination requirements of ASTM D-2559. He also studied the effects of the HMR coupling agent with PRF, melamine urea and melamine adhesives on CCA-treated southern pine lumber. In all tests the HMR coupling agent greatly enhanced the durability of adhesion in southern pine lumber laminates treated with CCA at retention levels of 0.4 and 0.6 pcf. The PRF adhesive met the 5% maximum delamination requirement of ASTM D-2599 (Vick 1995 and 1997a, b). In his theory, the mechanism by which the HMR coupling agent bonds to CCA treated wood is somewhat different from that employed in the bonding of untreated wood. He reports, "It appears that because of the relatively small molecular size of the monomeric hydroxymethylated resorcinol species and their highly polar nature, the species physicochemically adsorbs and mechanically interlocks within the microstructure of metallic oxides. Therefore, the metallic oxide surface is converted to a highly polar and reactive surface by depositing multi molecular layers of the HMR coupling agent".

3.3. Materials and Methods

3.3.1. Wood Species and FRP Type.

All beams were manufactured from southern yellow pine lumber. Generally, specimen material was cut from nominal 2" x 6" (5 x 15.3 cm), medium density, flat sawn sapwood boards. The boards were straight-grained and free of defects. Southern yellow pine was chosen because it is extensively used in glulam production today and the sapwood is relatively easy to treat with a wide range of wood preservatives.

One type of FRP material was used in this experiment: E-Glass / phenolic pultruded composite. This FRP material, identified as K-1, was developed by the Advanced Engineered Wood Composites Center at the University of Maine and manufactured by Strongwell Corporation, MN. The FRP material consisted of reinforced unidirectional (0°) E-glass continuous fiber rovings, and E-glass chopped strand mat (CSM) (0.75 oz / sq.ft) made of randomly oriented short fibers. The short-fiber CSM was initially bonded with melamine resin binder to form a mat suitable for the pultrusion process. In the pultrusion process, the continuous fiber rovings were oriented in the core and integrated with exterior CSM layers using a phenolic resin matrix. A variation of the pultrusion process was applied in which the continuous rovings were impregnated in phenolic resin, while the CSM mats were pulled dry into the die. As a result of this processing scheme, a resin-starved surface layer that improves bonding to wood was produced. The corresponding average volume contents for the fabricated FRP plate were; Vf = 54%, Vm=21%, and Vv= 25% where Vf = fiber volume fraction, Vm = matrix volume fraction, Vv = void volume fraction.

3.3.2. Wood Preservatives.

Five wood preservative systems (acidic and basic waterborne, and oil-borne including organometallic) were tested (Table 3.1). CCA is currently facing severe restrictions in the US and in other areas of the world. However, it currently is still the most widely used acidic water borne preservative in the world and was used at several loadings targeting above ground, ground contact, and marine application retentions.

Table 3.1. Type and percent concentrations (weight/weight) of preservatives used. A range of CCA-C concentrations were used to target the above ground, ground contact and marine application retention levels for wood recommended by AWPA (AWPA 1999a, Book of Standards).

Preservative	**CCA-C[1]**	**CDDC[2]**	**Cu-N[3]**	**PCP[4]**	**Creosote[5]**
Solution Concentration	1, 2.5, 5, 10%	2.5%	1.0%	5%	100%
Target retentions (pcf)	0.25, 0.40, 1.5, 2.5	NR	0.16	0.6	20

[1] Distilled water carrier. Chromated copper arsenic type C; Arsenic acid 17.0%, chromic acid 23.75% and copper oxide 9.25%

[2] Distilled water carrier. Dual treatment process (ISK Biosciences, Memphis, TN.) consisting of a monoethanolamine treatment followed by sodium dimethyldithiocarbamate treatment.

[3] Mineral spirits carrier. Copper naphthenate ; naphthenic acid, copper salt 60 - 80%, mineral spirits 15-25%

[4] Diesel fuel carrier. Pentachlorophenol; pentachlorophenol 90-94%, 2,3,4,6-Tetrachlorophenol 0-1.5%, hydroxypolychlorodibenzo ethers 4-7%.

[5] As original solution. Complex mixture of hydrocarbons 100%

The other four preservatives were tested at one retention level only to determine the effect of different preservative systems on bond durability and accelerated aging properties of preservative treated wood/wood and wood/FRP interfaces. The retentions tested were typically those appropriate for ground contact and marine treatments. Since in some cases FRP reinforced treated beams are installed in water front applications or salt or brackish water splash zones, it was important to include marine retention treatments (e.g 2.5 pcf CCA).

3.3.3. Resin System. A commercial phenol-resorcinol-formaldehyde (PRF) adhesive was used to laminate untreated (for post-treatment) and preservative treated (for pre-treatment) SYP lumber. The PRF adhesive system was mixed using 70 percent resin (Resorsabond ® 4242. Georgia Pacific Resin, Inc.), 12 percent paraformaldehyde hardener (Resorsabond ® 4554) and 18 percent distilled water according to the manufacturer's recommendations. The adhesive was spread at the rate of 36.4 kg per 92 m^2 (80lb./MSGL).

3.3.4. Preparation of Specimens

Two types of cyclic delamination laminates were prepared:

a) Pre-treated laminations: The individual laminates were treated first and glued together with FRP to make reinforced beam sections.

b) Post-treated laminations: The beam sections were made up from untreated lumber and FRP reinforcement and treated with the wood preservatives outlined in Table 3.1.

All cyclic delamination specimens were 3 inch- (7.6 cm) long cross sections cut from wood/wood or wood/FRP beams and these specimens were tested according to the ASTM D-2559 guidelines (ASTM 2000). Wood/wood beams were prepared by bonding five ¾ in. (1.9 cm) thick, 4.5 in. (11.43 cm) and 12 in. (30.5 cm) long laminations with PRF resin. Three sections were cut from each beam for each treatment combination.

Wood/FRP beams were prepared and cut in a manner similar to the wood/wood beams described above except that E-glass/phenolic FRP plates were bonded between each of the five wood laminates (Figure 3.2). Previous researchers have tested several different specimen configurations, such as the use of top and bottom FRP laminates only (Qiao et al. 1998, Vick 1996) or FRP applied to the top face of a vertically laid glulam beam for bridge decking applications (Lopez-Anido et al. 2000). This modified design employed in our work was used so that all glue lines were representative of FRP to wood bonding. Since the ASTM D-2559 does not specify a particular cyclic delamination specimen design for FRP/wood laminations, the greater FRP/wood bond line percentage, as opposed to the bonding of a single FRP layer in laminated beam, allowed more opportunity to visualize delaminations in the beam.

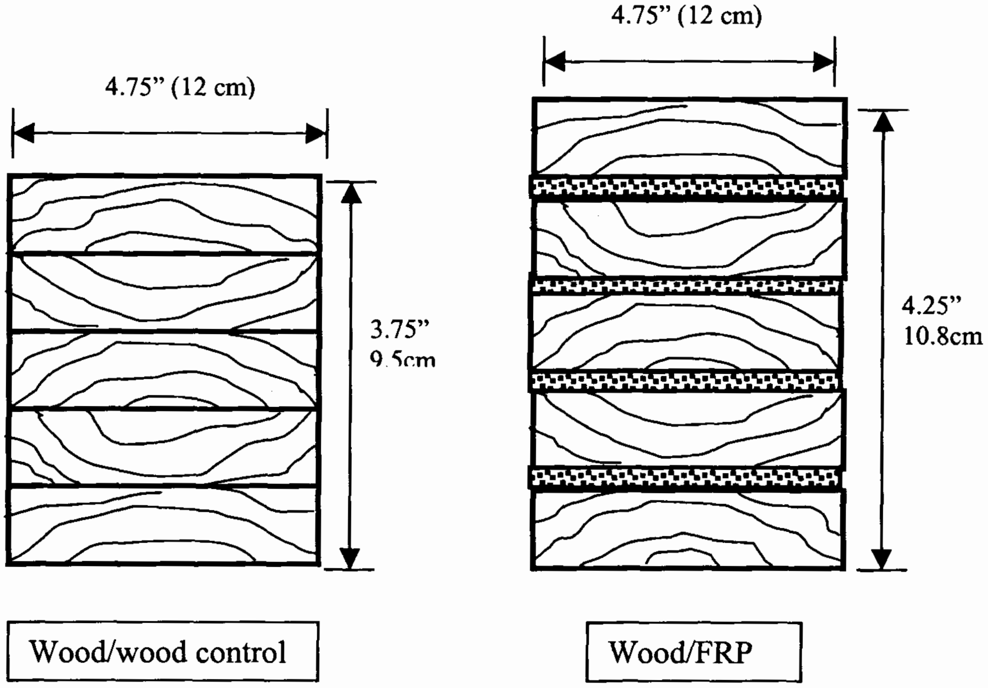

Figure 3.2. Cross section configurations of wood/wood and FRP/wood cyclic delamination specimens.

All FRP plates were primed with the same PRF adhesive 24-hours prior lamination. The average rate of application for the dry primer was 0.0047g/cm^2. Prior to the laminating process, both faces of the FRP plates were wiped with acetone and ethanol to remove possible surface oils and other contaminants.

3.3.5. Preservative Treatments.

All pressure treatments were performed in a 118" x 20" diam. (3m x 0.5m diam.) pressure treatment vessel. Two different pressure treatment schedules were used. For water-borne preservatives a full-cell process which included an initial vacuum of -84.7 kPa (25" Hg) for 10 minutes followed by a pressure of 1.034 MPa (150 psi.) for 15 minutes was applied. For the oil-borne preservatives, an empty cell process that included only 15 minutes of 1.034 MPa (150 psi) pressure was used. Because of the very high retentions obtained in preliminary full cell treatments with oil-born preservatives, to reach required retentions an empty cell process was utilized. The beam sections used in preliminary tests were also examined for preservative penetration. An average of 90-100% of the cross-sectional area was treated in the beams, indicating that the empty cell process was adequate for preservative penetration. Water- and solvent-borne preservative treatments (CCA-C, CDDC, CuN) were treated at ambient temperature. Oil-borne preservative treatments (Creosote, PCP) were performed at 149-154°F (65-68°C). All treatments were conducted at AEWC, where the retention levels for each board (when pre-treatment was performed) or reinforced beams (for post-treatment application) were monitored by weighing them before and after the treatment. After treatments, the individual laminates and beam sections were air-dried and then conditioned to an equilibrium moisture content (EMC) of approximately 11 % at 70° F (21° C) and 60% relative humidity (RH). The untreated wood/wood and wood/FRP controls were also conditioned at the same EMC. One hour before bonding, lumber laminates were jointed and knife planed (1mm from each side) to remove surface contamination and oxidation.

The average open assembly time was 10 minutes and the closed assembly time was also 10 minutes. An initial clamping pressure of 100 psi (690 KPa) was applied for both wood/wood and FRP/wood beam sections resulting in resin squeeze-out along the length of the beams for all joints (Figure 3.4).

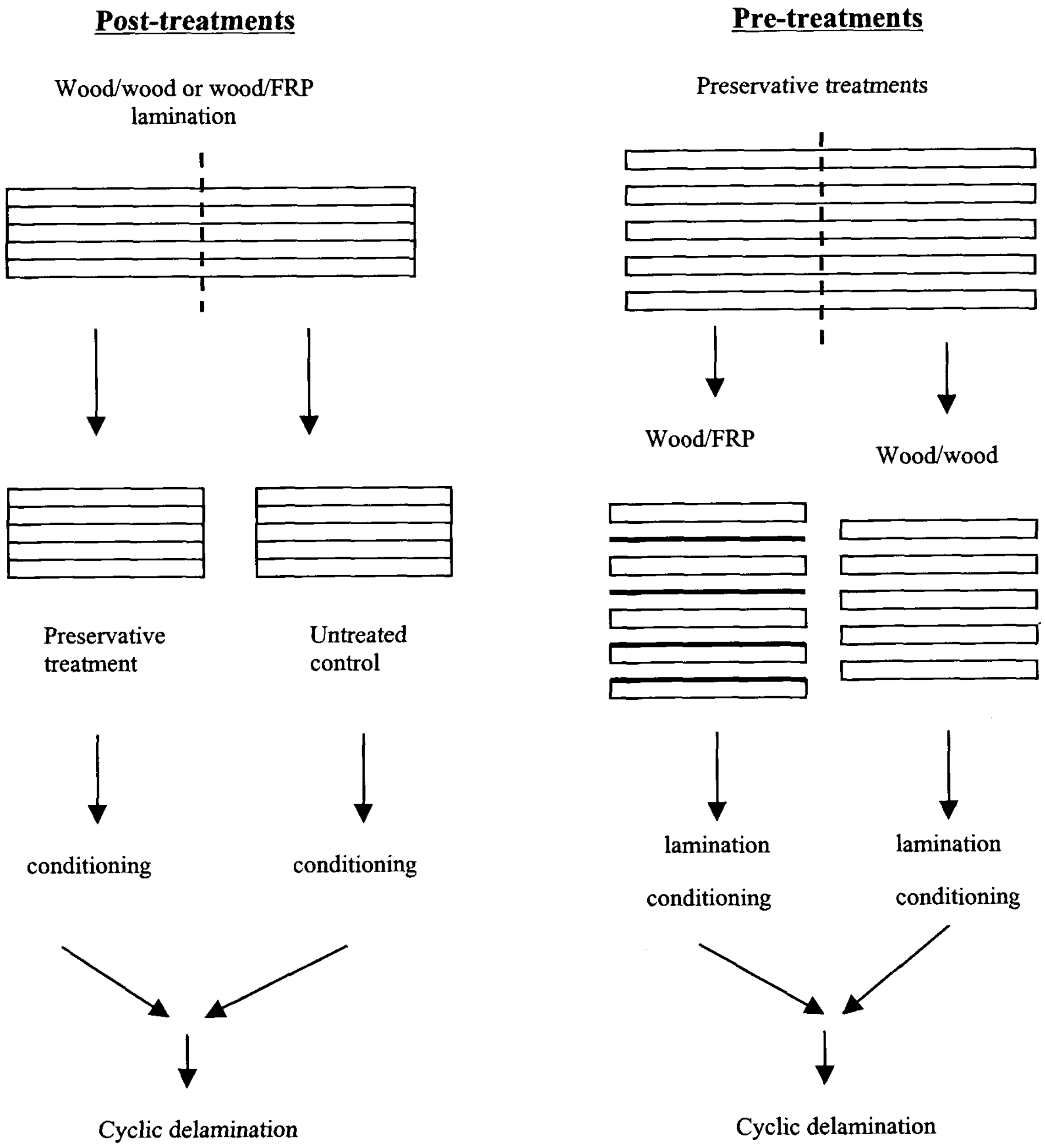

Figure 3.3. Schematic sequence of post- and pre-treated beam lamination techniques used in this study. (Only wood/wood laminations are shown in the left column)

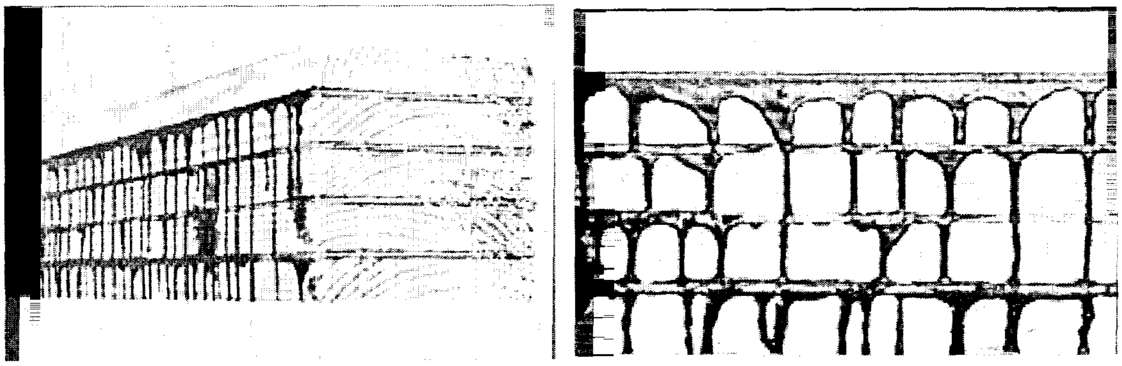

Figure 3.4. PRF resin squeeze-out through lamination joints (laminates were treated with CCA-C).

All laminations were cured in a hydraulic press for 24 hours at room temperature. After curing all beam sections were conditioned an additional 7 days at 70° F (21° C) and 60% RH.

3.3.6. Cyclic Delamination Evaluation of Interface Durability

Three, 3-inch (76 mm) long sections cut from each test joint assembly were subjected to a modified ASTM D2559 cyclic delamination test. The resistance to delamination during accelerated exposure consisted of three cycles of a vacuum-pressure soak (VPS) in water followed by oven drying at 150 °F (65.5 °C) for 22 hours. After the first cycle, randomly selected specimens were monitored for weight change. An average of 63 % weight-gain for the water-borne treated samples and 50 % weight-gain for the oil-borne treatments was recorded. The standard requires a minimum of 50 % weight increase after the first VPS. The specimens treated with oil-borne preservatives had reduced water uptake because the oil-borne wood preservative chemicals already filled some of the cell lumens during the pressure treatments and prevented further VPS water uptake. The second cycle also includes steaming followed by a VPS. Immediately, after the final drying cycle, delamination was measured under 5x magnification along all-end grain surfaces to the nearest 0.05 in. (1.27 mm) with a machinist's scale. Delamination was expressed as a percentage of total bond line length for each specimen computed for each glue line face and for each test joint assembly.

3.3.7. Evaluation of Bond Strength

Evaluation of bond strength between preservative treated southern pine and the FRP was conducted using a modified ASTM D-905 (ASTM 1994c). Only one type of preservative (CCA-C) with four different retentions (Table 3.4) and one wood species (southern pine) were used in this part of the study. One of the modifications of the standard was on the selection of wood species. Although ASTM D-905 recommends hard maple (*Acer saccharum* or *Acer nigrum*) for this test, southern pine was chosen to compare shear strength results to the cyclic delamination tests and surface energy characterization data. The shear block specimens were also modified to test the bond strength between wood and FRP as shown in Figure 3.5.

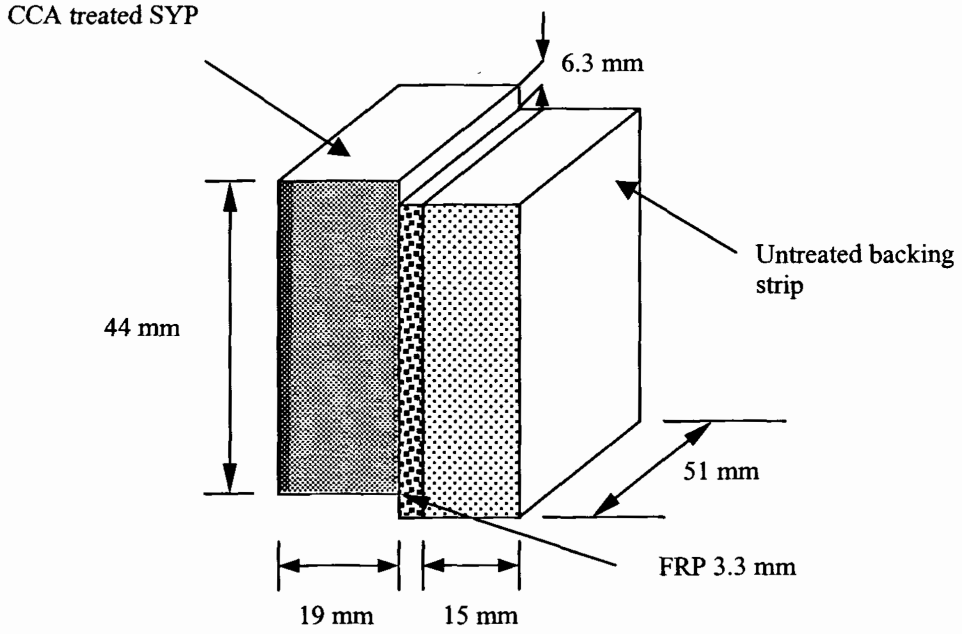

Figure 3.5. Modified ASTM D-905 shear block specimens.

Just prior to billet production, the CCA-C treated southern pine was planed to a thickness of 19 mm. Two 10 mm wide samples were also cut for contact angle and moisture content measurements. A backing piece was also cut and planed to size.

The Resorsabond ® resin was mixed using the ratios described in section 3.1.1.4.

The FRP surfaces were wiped with acetone and alcohol prior to priming. The primed FRP plate (24 hours in advance, an average of 0.008 g /cm^2 dry primer) was placed on electronic balance and 0.043 g/cm^2 of resin was spread over the surface using a steel spatula. The FRP was then placed, resin side down, onto the CCA-C treated southern pine. The orientation of the CCA treated boards was kept the same for each application (pith side facing away from the bond line). The procedure outlined above was repeated one more time on the other side of the FRP in order to attach the backing strip.

The sandwiched billets then were placed in a hydraulic press and a pressure of 689 kPa was applied for 24 hours. After 24 hours, the samples were removed from the hydraulic frame and placed into a conditioning room maintained at 18° C and 65% relative humidity. The billets were allowed to condition for 7 days. The conditioned samples were cut according to ASTM D-905 (Figure 3.5) and then tested using an Instron testing machine and shear tool with a cross head speed of 5mm/min (0.2"/min). Prior to test, the blocks were measured to calculate the shear area. At the end of each test the peak load was recorded. The wood and/or FRP failures were measured after testing using a transparent sheet divided by 1 cm x 1cm squares.

3.3.8. Surface Energy Characterization

The sessile drop contact angle method was used to measure the surface energy of treated southern yellow pine and FRP surfaces. Only two wood preservative systems (CCA-C in distilled water and copper naphthenate [Cu-N] in mineral spirits) with southern pine were utilized for this part of the study. The same full and empty cell treatments outlined in section 3.1.1.3 were applied to both FRP and southern pine specimens. For CCA treatment, a full-cell process which includes an initial vacuum of -84.7 kPa (25" Hg) for 10 minutes followed by a pressure of 1.034 MPa (150 psi.) for 15 minutes was applied. For CuN, an empty cell process with a pressure period of 15 minutes at 1.034 MPa (150psi) pressure was used. The total contact time of the specimens with the solutions was approximately 60 minutes. All samples (both FRP and southern pine blocks) were then exposed to a three-day period of wet fixation. This period was followed by air-drying and conditioning at 65° F and 50 % RH until the specimens reached an equilibrium weight. The preservative treated and untreated SYP blocks were then planed. FRP strips were unprimed to measure the effects of the wood preservative systems alone. All contact angle measurements were completed within 3 h after surface preparation.

Probe liquids (10 μl) were transferred with a micro-pipette onto the differentially treated wood and FRP surfaces. Two seconds after placement of the liquid droplet, a digital (pseudostatic) image of the droplet was captured utilizing a personal computer based frame grabber and camera. Using the digitally recorded images, the contact angles of the drops on both sides (left and right) were measured and averaged with image analysis software (Figure 3.6).

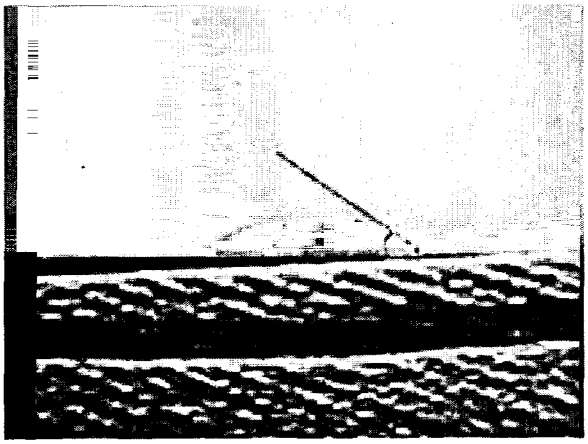

Figure 3.6. Measurement of probe liquid contact angles on differentially treated surfaces of wood and FRP.

The Good – Girifalco (geometric mean) and Chang equations were used to calculate the surface energy of the treated wood surfaces.

Geometric Mean Model: $W = (1 + \cos\theta)\,\gamma_L = 2\,[(\gamma_L^d\ \gamma_s^d)^{1/2} + (\gamma_L^p\ \gamma_s^p)^{1/2}]$

Chang Model: $W = (1 + \cos\theta)\,\gamma_L = P_L^d\,P_S^d - P_L^a\,P_S^b - P_L^b\,P_S^a$

Four different probe liquids (including water) were used in this experiment (Table 3.2). All the chemicals used in this study were HPLC grade with 99% purity or higher.

Table 3.2. Values of surface tension components of the probe liquids used in the contact angle analysis (from Tze and Gardner, 2001).

Probe Liquids	γ_L	γ_L^d	γ_L^p	P_L^d	P_L^a	P_L^b
Diiodomethane	50.8	50.8	0	11.6	-4.11	-4.12
Ethylene glycol	48	29	19	7.5	3.69	-5.44
Formamide	58	39	19	7.3	6.92	-4.64
Water	72.8	21.8	51	6.6	6.88	-7.4

(γ is the surface free energy (surface tension), the subscript L refers to liquid and superscripts d, p, a and b refer dispersive, polar, acid and base forces, respectively.

3.4. Results and Discussion

3.4.1. Retention Results

The reference standard (ASTM D 2559, 2000) used in this study is designed to evaluate wood to wood bonds following accelerated aging. The standard specifies a 5 % maximum allowable delamination for softwood to softwood bonds, and a 8 % maximum allowable delamination for hardwood to hardwood bondlines. Currently, there is no national standard that directly specifies allowable percent delamination in wood/FRP interfaces. Like previous researchers (Vick 1996, Lopez-Anido et al. 2000), ASTM D 2559 was used in this study in a modified manner to shed light on future research on allowable delamination of wood/FRP interfaces.

Table 3.3 provides the average retention values for all preservative systems used in this part of the study. All laminations (representing pre-treatments) and fabricated beam sections (representing post-treatments) for water-borne preservatives were treated using the full cell process outlined in section 3.3.5. Several penetration analyses were performed on cross sections of pre-and post treated members to insure that preservatives contacted the all bond lines. Due to anatomical variations in southern pine and FRP layers, the same treatment schedules (full cell for water bornes and empty cell for oil bornes) resulted in minor differences in retentions.

Table 3.3: Average retentions of the preservative systems used in this study.

Preservative system	**Average retentions (pcf)**	
	Pre-treated	Post-treated (with FRP)
CCA-C	3.21 1.49 0.64 0.29	2.86 1.35 0.53 0.24
CDDC (dual)	0.60	0.64
CuN	0.17	0.17
PCP	0.58	0.61
Creosote	16.85	17.00

3.4.2. Accelerated Aging and Delamination.

3.4.2.1. Post treatment with CCA.

Figure 3.7 shows that increasing CCA retention resulted in an increase in percent delamination values in wood/FRP bonds in post-treated beam sections, while wood/wood bonds were not affected, or showed only a small increase in delamination with increasing CCA retention (Figure 3.7).

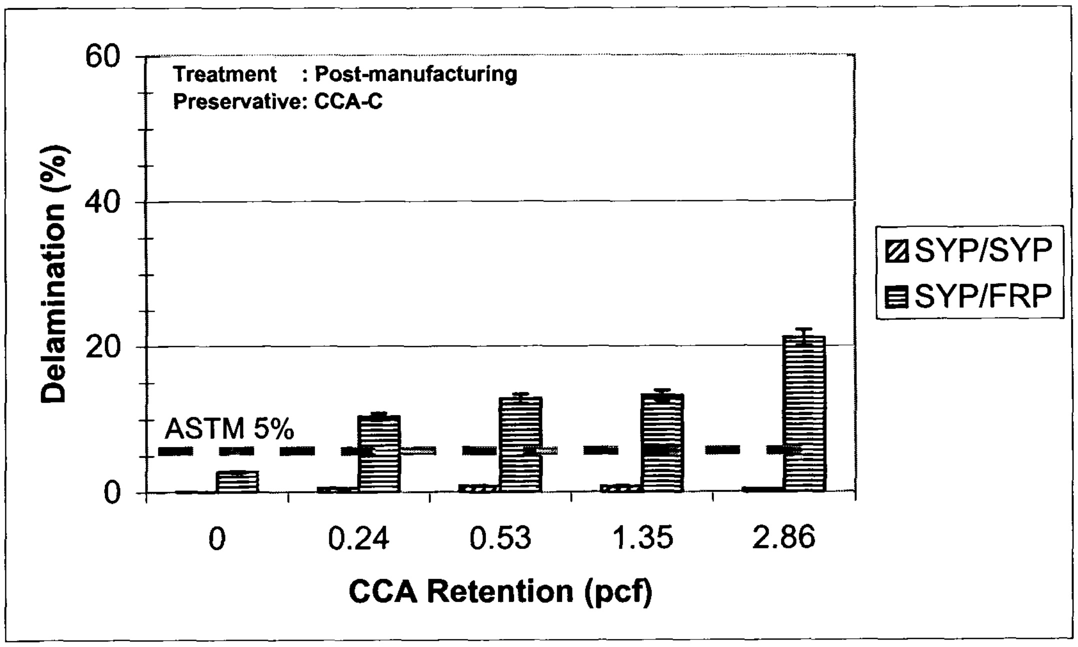

Figure 3.7. Effects of increased CCA retention on delamination of PRF bonds in wood/wood and wood/FRP beam joints after the ASTM D2559 cyclic delamination test (maximum allowable delamination in ASTM D2559: 5 % in softwoods, 8 % in hardwoods for **wood/wood** joints only). The beam sections were **post-treated** with CCA-C at several retentions.

CCA preservative retentions up to 2.86 pcf interfered only minimally with the wood/wood phenolic bonds, and delamination values were less than the 5% ASTM limit indicating that the PRF resin used in this study can produce durable bonds between southern pine laminates at CCA loadings up to marine retention levels. For the wood/FRP bonds, however, increased CCA retention resulted in an increase in delamination rates with maximum (21%) debonding occuring in the 2.86 pcf marine retention laminates. Even though, ASTM D-2559 does not provide an acceptance limit for wood/FRP bonds, if the 5% maximum accepted value for wood-wood (species) bonds were applied, the 21

% delamination, would be considered as failure for acceptable bond quality. An additional step was taken to interpret the CCA post treated wood/FRP delamination results. The cross sections of randomly selected CCA post-treated lamiations were sprayed with Chrome Azurol–S, a chemical copper indicator, to highlight the penetration path of the CCA solution. The FRP chopped strand mat (CSM) area was revealed to produce a deep blue color indicating that the high void content of surface veil allowed heavy penetration and retention of the CCA solutions. This heavy retention in the CSM layer would have exposed the PRF adhesive film between wood and FRP to high concentrations of CCA chemical components during the post-treatment, wet fixation and post conditioning periods. The CCA-C solutions used in this study had a pH range from 1.5-2.5, depending on their concentration, during the 60 minutes of active contact with beam sections throughout the treatments. The pH gradually increased during the three-days of wet fixation and post-treatment conditioning periods (Tascioglu 1997). The high CCA retentions would expose the adhesive film to low pH conditions for a prolonged time causing weakening in the adhesive film. It is possible that the weakening effect contributed to delamination between the wood and FRP when beam sections went through the cyclic delamination mechanical stresses. On the other hand, CCA accumulation in the wood/wood interface region did not occur and this might explain the relatively low wood/wood delamination values in CCA post treated applications.

3.4.2.2. Pre-treatment with CCA.

The CCA pre-treated beam sections displayed a somewhat different delamination pattern than the post-treated beams. In general, the pre-treatment of individual laminates with CCA negatively interfered with the bonding of both wood/wood and wood/FRP interfaces (Figure 3.8).

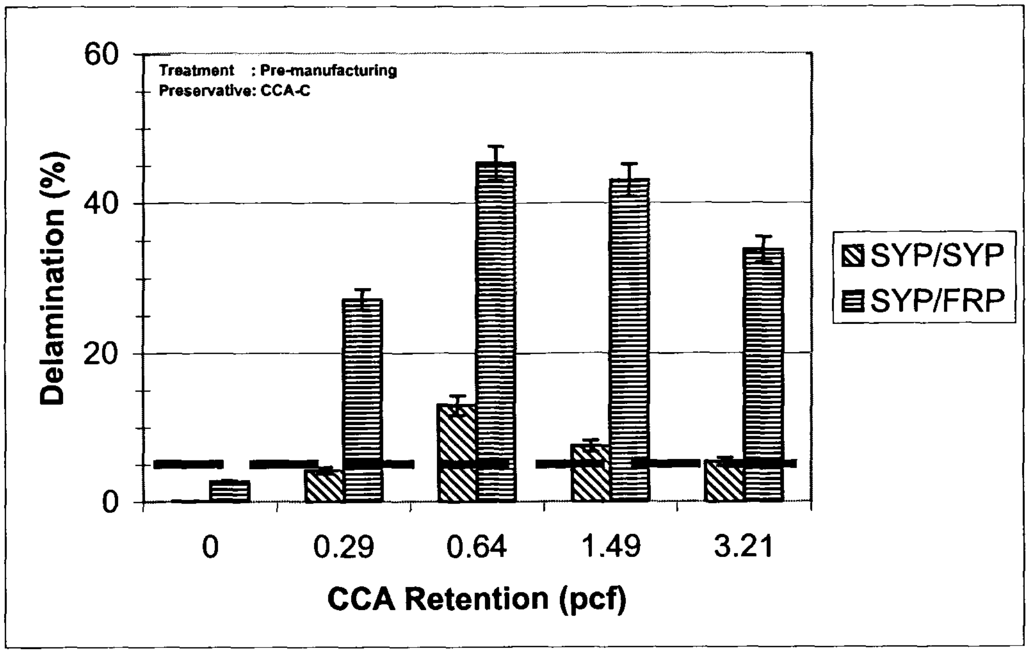

Figure 3.8. Effects of increased CCA retention on delamination of PRF bonds in wood/wood and wood/FRP beam joints after the ASTM D2559 cyclic delamination test (maximum delamination allowable in ASTM D2559: 5 % in softwoods, 8 % in hardwoods for wood/wood joints only). The individual laminates were **pre-treated** with CCA-C at several retentions.

Increases in retention from 0 pcf to 0.29 pcf and from 0.29 pcf to 0.64 pcf resulted in increases in percent delamination from 0 % to 4.25% and 13 % respectively for CCA pre-treated wood/wood interfaces (Figure 3.8). Very similar delamination values were reported for CCA pre-treated wood/wood (southern yellow pine) interfaces after exposed to the ASTM cyclic delamination tests (Vick 1995). Vick (1995) reported a 12.4 percent delamination on southern yellow pine wood/wood bonds with PRF adhesive at a 0.6 pcf

CCA-C retention level. In our work, as retention increased beyond 0.64 pcf, a reduction in both wood/wood, and wood /FRP delamination was recorded (Figure 3.8).

Surface energy analysis results (see preceding chapter) of CCA-C treated southern pine indicates that the likely explanation for the bimodal delamination response to CCA retention levels is that the total surface energy of CCA-C treated southern pine actually increases with increased retention (Figure 3.14). Increased surface energy promotes better wettability and bonding between surfaces which can produce a reduction in delamination values. The wood/FRP delaminations were above the acceptable 5 % ASTM limit, but again, since there is no ASTM standard for wood/FRP bonding, there are no "realistic" limit values to compare. Interestingly, the reduced delamination at high CCA loadings was also observed in wood/FRP interfaces as CCA retention increased in pre-treated wood (see section 3.4.2.1).

3.4.2.3. Post-treatment with CDDC.

The other water-borne wood preservative system used in this study was CDDC. CDDC is a high pH (10-11) dual chemical treatment. Our post-treatment results showed both wood-wood, and wood-FRP beams had delamination greater than 5%. When treated to a 0.6 pcf retention level (Figure 3.9). The average delaminations were recorded at 8% and 16% for wood/wood and wood/FRP interfaces, respectively.

The high sensitivity of phenolic resins to strong bases (Bauccio, M. 1991 and Schweitzer, P. 2000) is well documented. Exposure of cured phenolic resin lines to highly basic solutions such as CDDC (pH 10-11) during the treatment, wet fixation and post conditioning processes could therefore potentially weaken the PRF adhesive film and bonding quality.

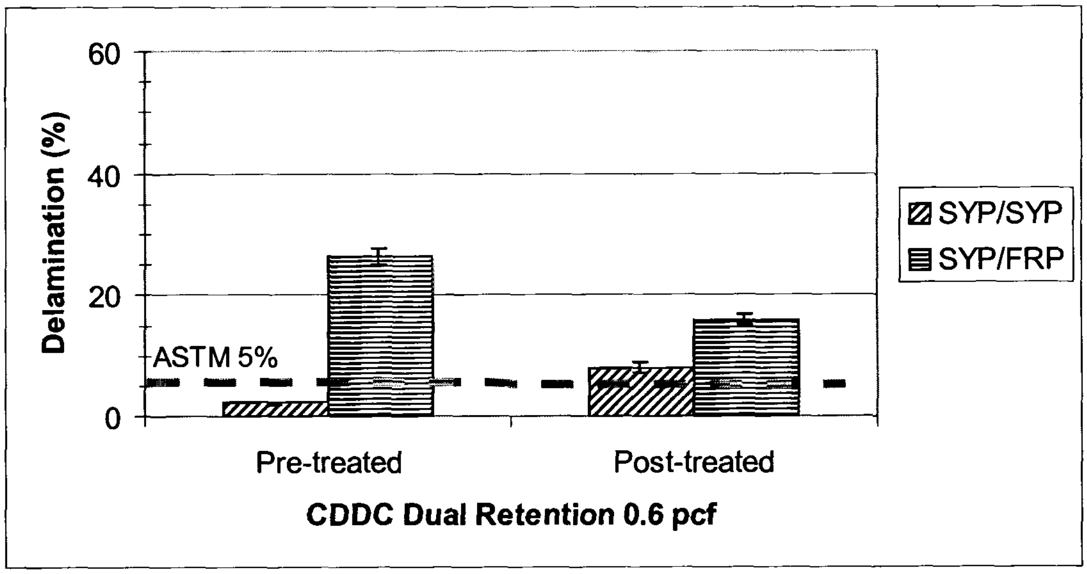

Figure 3.9. A comparison of delamination of pre- and post-treated joints treated with CDDC at 0.6 pcf retention level.

Deterioration of bond line strength would result in increased delamination between wood and the FRP layer when beam sections were exposed to mechanical stresses during the robust cyclic delamination test.

3.4.2.4. Pre-treatment with CDDC.

While pre-treatment of individual southern pine laminates with CDDC at the 0.6 pcf level resulted in only limited debonding in wood/wood bondlines, wood/FRP interfaces showed 26% delamination suggesting that CDDC is incompatible for use as a pre-treatment preservative if the wood is intended for FRP applications.

3.4.2.5. Post-treatment with Oil-borne Preservatives.

No wood/wood delamination greater than 5% was observed in any beam section post-treated with the oil borne preservatives (creosote, CuN or PCP) in the cyclic delamination test (ASTM D-2559). (Figures 3.10, 3.11, 3.12). Phenolic resins have been reported to have excellent resistance to aromatic hydrocarbons and coal tar (Bauccio 1994), therefore the prolonged exposure of cured phenolic bond lines to creosote, copper naphthenate and pentachlorophenol in diesel fuel should have had only a limited effect on wood/wood bond durability. In addition, unlike the waterborne preservative treatments, the oilborne treatments would have reduced the effects of mechanical stresses generated during the cyclic delamination test by reducing the water uptake in laminates. The post-treated wood/FRP bond lines, however, produced 11.8 %, 12 % and 23.8 % delamination for creosote, copper naphthenate and pentachlorophenol, respectively, (Figures 3.10, 3.11, 3.12). Because most of the delamination failure observed was in the glue line this suggests again that retention of high levels of preservative in the FRP surface CSM layer may have caused some deterioration of the adhesive bond.

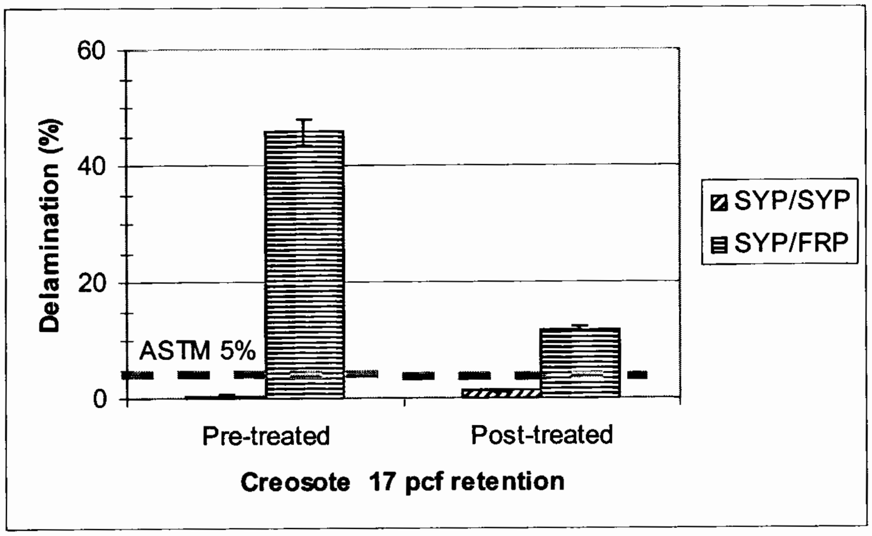

Figure 3.10. A comparison of the delamination of pre- and post-treated joints with creosote at a 17 pcf retention level.

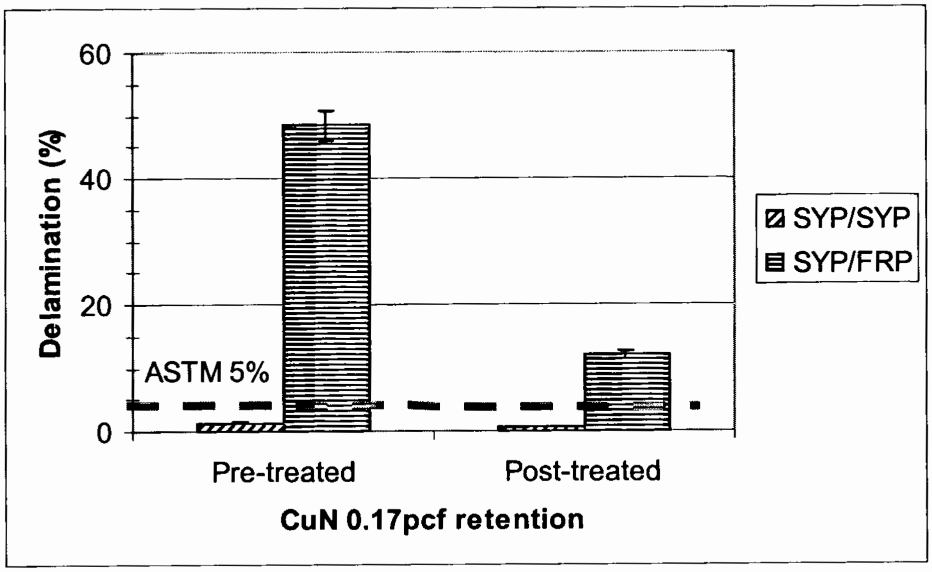

Figure 3.11. A comparison of the delamination of pre-and post-treated joints with CuN at a 0.17 pcf retention level.

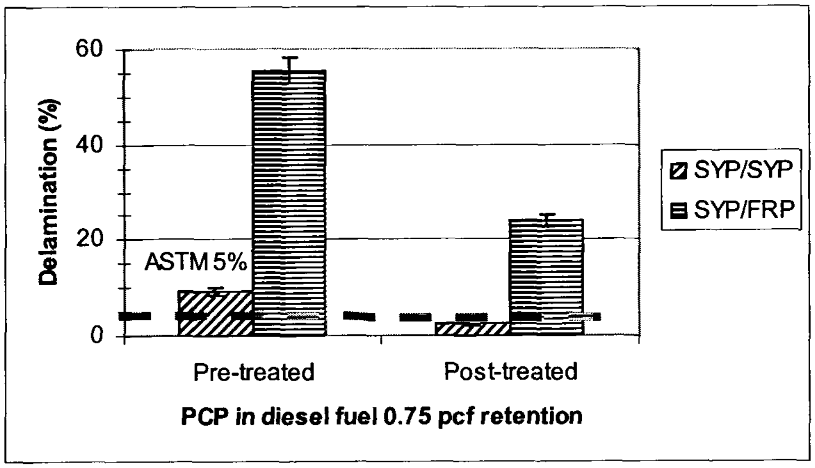

Figure 3.12. A comparison of the delamination of pre- and post-treated joints with PCP at a 0.75 pcf retention level.

3.4.2.6. Pre-treatment with Oil-borne Preservatives.

In general, the pre-treatment of individual wood laminates with oil-borne wood preservatives drastically increased delaminations in wood/FRP bond lines. This may mean that the oily nature of creosote, CuN and PCP severely interferes with the wettability of phenolic resin and therefore reduces the adhesion between the treated wood and FRP joints (Figures 3.10, 3.11, 3.12). The surface energy analyses also support the surface energy reduction in CuN treated SYP (see preceding section). Interestingly the same phenolic resin produced acceptable bond durability in wood-wood joints pre-treated with creosote or CuN at 17 and 0.17 pcf retention level respectively. Since only one retention was tested for each preservative, it is difficult to predict delamination patterns for higher retentions. The higher retentions might increase the delamination values of pre-treated wood-wood delaminations. Surface preparation, jointing and knife planing of treated wood surfaces just prior to lamination might help to produce acceptable bonds. Generally, planning is performed in the industry for southern pine just prior to gluing. The ANSI / AITC standard requires a resurfacing of individual treated laminations just prior to gluing. The resurfacing of treated laminations should remove as little wood as possible while making the surface clean, planed, and uniform in thickness suitable for gluing (AITC 1998, Kaseguma 2002).

3.4.3. Shear Strength

The mean shear strength of the bond line for the pultruded FRP material and untreated southern pine was 10.10 MPa (1465 psi). The FRP and untreated southern pine can produce bonds with phenol resorcinol formaldehyde adhesive (Resorsabond®), which exceeds the 7.59 MPa (1100 psi) ANSI/AITC constructional adhesive performance limit (ANSI/AITC , 1998). The shear strength results with CCA treated southern pine were variable, but in no case did the values drop below the 7.59 MPa ANSI/AITC limit (Table 3.4 and Figure 3.13).

Table 3.4. Adhesive shear strength and percentage wood failure results of CCA pre-treated southern pine and FRP interfaces bonded with phenol resorcinol formaldehyde (PRF) adhesive.

Preservative	Retention (pcf)	Shear strength (MPa)	Standard deviation	COV (%)	Failure Mode (%)	
					Wood	CSM
Untreated	0	10.10	1.72	17	10	90
CCA 1%	0.37	8.03	1.37	17	7	93
CCA 2.5%	0.93	10.66	1.65	15.5	15	85
CCA 5%	1.78	10.61	1.27	11.9	12	88
CCA 10%	4.16	12.57	1.12	8.9	40	60

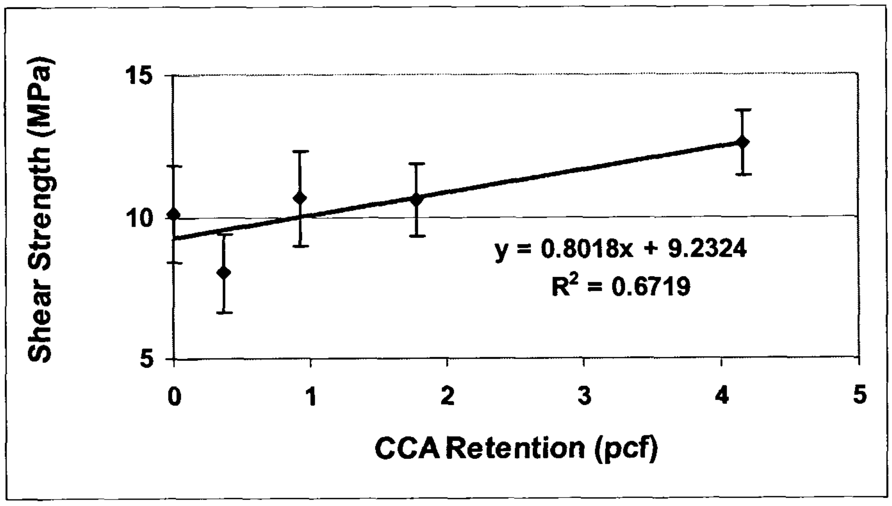

Figure 3.13. Changes in adhesive shear strength with increased CCA retention in southern pine.

Table 3.4 shows that most shear failure occurred between the unidirectional roving fibers and the CSM layer regardless of CCA retention. This suggests that the failure of shear blocks was not limited by the wood/resin interface strength but instead depended on the CSM/unidirectional roving interface.

3.4.4. Surface Energy Characterization

Table 3.5 summarizes the average measured contact angles obtained from differentially treated SYP and FRP surfaces utilizing a series of probe liquids. In general, CuN treatment, an oil-borne preservative, resulted in an increase in contact angle of water while CCA-C treated surfaces reduced the contact angle of water on SYP surfaces. This was expected due to the different physical and chemical characteristics of both surfaces tested. In case of preservative treated FRP surfaces, however, both types of treatment (water- and oil-borne) caused increases in water contact angles on FRP surfaces. The increase in contact angle on surfaces tested represents a reduction of surface energy (Pocius 1997).

Table 3.5. Summary table of measured contact angle averages of the probe liquids used on differentially treated southern pine and FRP surfaces (5 replicates for each liquid). Standard deviations are in parenthesis. Values are in degrees).

Surface	**Probe Liquids**			
Material / Solution	**Diiodomethane**	**Ethylene glycol**	**Formamide**	**Water**
S. pine / untreated	36.4 (2.67)	41.86 (4.42)	34.58 (2.51)	85.17 (9.01)
S. pine / 0.25 % Cu-N	38.21 (4.99)	56.21 (4.30)	48.63 (6.92)	63.33 (5.33)
S. pine / 1 % Cu-N	47.76 (3.52)	68.48 (3.8)	58.43 (6.14)	111.7 (3.52)
S. pine / 1 % CCA	33.34 (3.93)	41.9 (3.04)	48.87 (9.53)	65.53 (5.84)
S. pine / 10 % CCA	27.38 (1.33)	37.46 (4.40)	41.49 (4.19)	59.89 (4.26)
FRP / untreated	20.28 (13.3)	27.16 (3.53)	24.51 (2.11)	24.01 (14.9)
FRP / 1 % CCA	39 (13.6)	84.07 (4.56)	91.87 (7.07)	112.9 (6.98)
FRP / 5 % CCA	48.24 (5.39)	90.35 (15.39)	75.75 (7.56)	115.6 (3.07)
FRP / 1 % Cu-N	45.97 (2.38)	80.34 (5.23)	83.23 (7.58)	90.79 (11.6)
FRP / 2.5 % Cu-N	43.88 (5.31)	74.67 (6.10)	84.23 (4.97)	107.6 (9.98)

Known values of γ_L, γ_L^d, γ_L^p for the probe liquids used (Table 3.2) and their actual measured contact angles on wood and FRP surfaces (Table 3.5) were used to calculate the total surface energy (γs) (mJ/m^2) of solid surfaces, acid-base surface tension (γ_{ab}), and the dispersive component (mJ/m^2) as described by Gardner et al. (1999).

The dispersive energy was determined using the geometric mean equation;

$$(1 + \cos \theta)\,\gamma_L = 2\,[(\gamma_L^d\ \gamma_s^d)^{1/2} + (\gamma_L^p\ \gamma_s^p)^{1/2}]\,,$$

Diiodomethane was used to determine γ_s^d as the second value in the equation assumed zero $[(\gamma_L^p \ \gamma_s^p)^{1/2} = 0]$. Therefore the equation changed as follows;

$$(1 + \cos\theta)\,\gamma_L = 2\,(\gamma_L^d \ \gamma_s^d)^{1/2}$$

$$\gamma_s^d = \tfrac{1}{4}\,\gamma_L\,(1 + \cos\theta)^2 \qquad (\gamma_L = \gamma_L^d \text{ for non-polar liquids})$$

The calculated dispersive surface energy was inserted into the Chang model to compute the Psd value $(\mathrm{mJ/m^2})^{1/2}$ which equals the square root of $2\,\gamma_s^d$.

$$\gamma_s^d = \tfrac{1}{2}\,(P_s^d)^2$$

$$P_s^d = (2\,\gamma_s^d)^{1/2}$$

The Chang model takes into account not only the attractive interactions between acidic and basic molecules but counts the repulsive interaction of a solid or a liquid surface.

$$(1 + \cos\theta)\,\gamma_L = P_L^d P_S^d - P_L^a P_S^b - P_L^b P_S^a$$

$$\gamma_S^{AB} = -\,P_S^a P_S^b$$

$$\gamma_S^{Total} = \gamma_s^d + \gamma_S^{AB}$$

The γ_S = total surface energy ($\mathrm{mJ/m^2}$), γ^{AB} = acid-base surface tension ($\mathrm{mJ/m^2}$), and γ_s^d = non-polar dispersive component ($\mathrm{mJ/m^2}$) values of differentially treated solid surfaces were calculated using the equations listed above. These values are listed in the following summary table (Table 3.6).

Table 3.6. Surface tension components for untreated, CCA and Cu-N treated southern pine and FRP after exposure to post-treatment conditioning.

Material	Treatment	Retention (pcf)	Surface prep.	γ^{AB}	γ_S^d	γ_S
S. pine	Untreated	0	Freshly planed	0.790	41.37	42.16
S. pine	Cu-N	0.06	Freshly planed	0.692	40.49	41.19
S. pine	Cu-N	0.25	Freshly planed	-2.895	35.51	32.61
S. pine	CCA	0.37	Freshly planed	2.188	42.78	44.97
S. pine	CCA	4.16	Freshly planed	2.846	45.09	47.94
FRP	Untreated	0	Unprimed	3.732	50.42	54.16
FRP	Cu-N	0.12	Unprimed	-2.366	40.45	38.08
FRP	Cu-N	0.33	Unprimed	-1.036	37.60	36.57
FRP	CCA	0.10	Unprimed	-1.557	40.10	38.55
FRP	CCA	0.52	Unprimed	-2.982	35.25	32.26

Surface energy calculations reveal that the surface chemistry of southern pine and FRP was greatly altered by preservative treatments (Figures 3.15, 3.16, 3.17). The total surface energy of southern pine decreased by about 1 mJ/m^2 when CuN retention increased from 0 pcf to 0.06 pcf and 10 mJ/m^2 when CuN retention increased from 0.06 pcf to 0.25 pcf (Figure 3.15). This decrease in surface energy was expected because of the oily non-polar nature of Cu-N wood preservative. The CCA treatment of southern pine, on the other hand, displayed the opposite results. Increased CCA retention increased the total surface energy of southern pine. The total surface energy of untreated southern pine increased from 42.16 mJ/m^2 to 44.97 mJ/m^2 with a retention of 0.37 pcf CCA. Approximately a ten fold further increase in CCA retention increased the total surface energy of southern pine to 48 mJ/m^2 (Figure 3.16). These findings are in agreement with Zhang et al. (1997). They reported a total surface energy of 43.35 mJ/m^2 for commercial CCA-C treated southern pine at a 0.4 pcf retention level. The increased surface energy was attributed to the chemical modification of the wood surface by the high surface energy metallic salts (Zhang et al. 1997). The accumulation of these high surface energy metallic salts was shown in this study utilizing a SEM microscope (Figure 3.14).

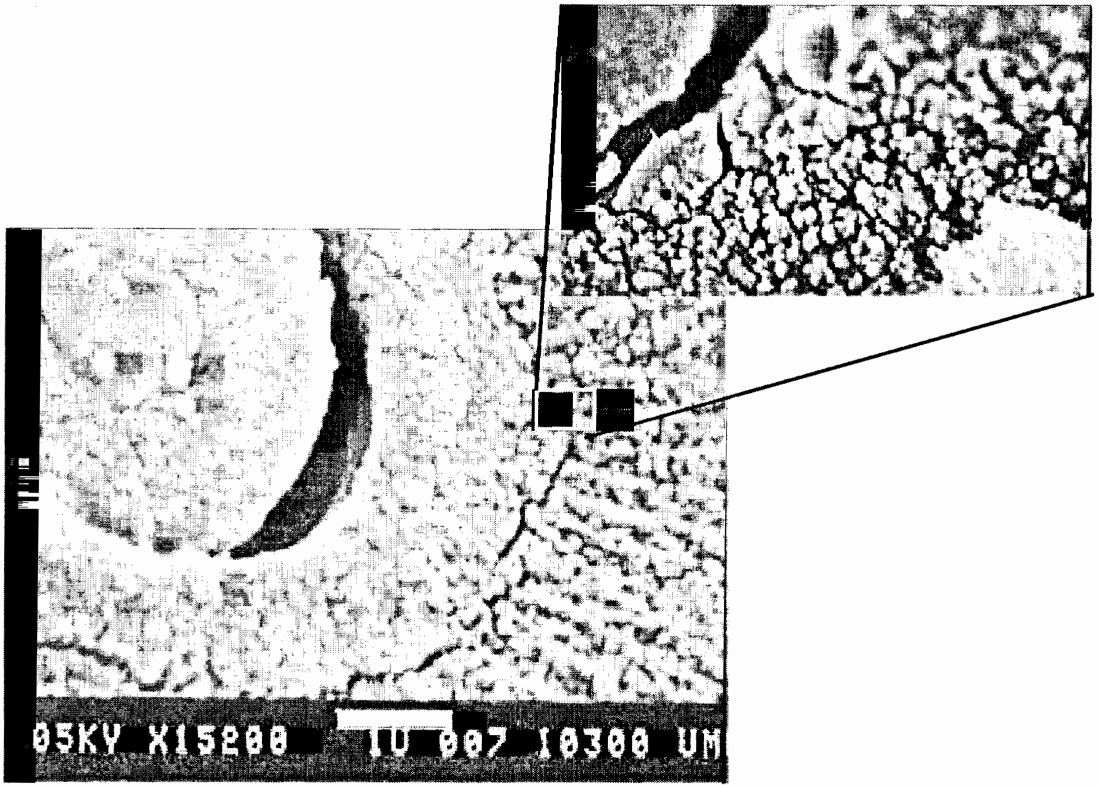

Figure 3.14. SEM micrograph of the surface of a cell lumen and ruptured torus from CCA pressure treated southern pine. Note that the lumen surface is completely covered with hemispherically shaped deposits of high surface energy metallic salts (chromium, copper and arsenic). The pit aperture shows the relative size of the metal deposits to the opening through which the adhesive flowed. Also note the parallel alignment of metallic deposits to pit membrane's microfibril strands at the region of the margo.

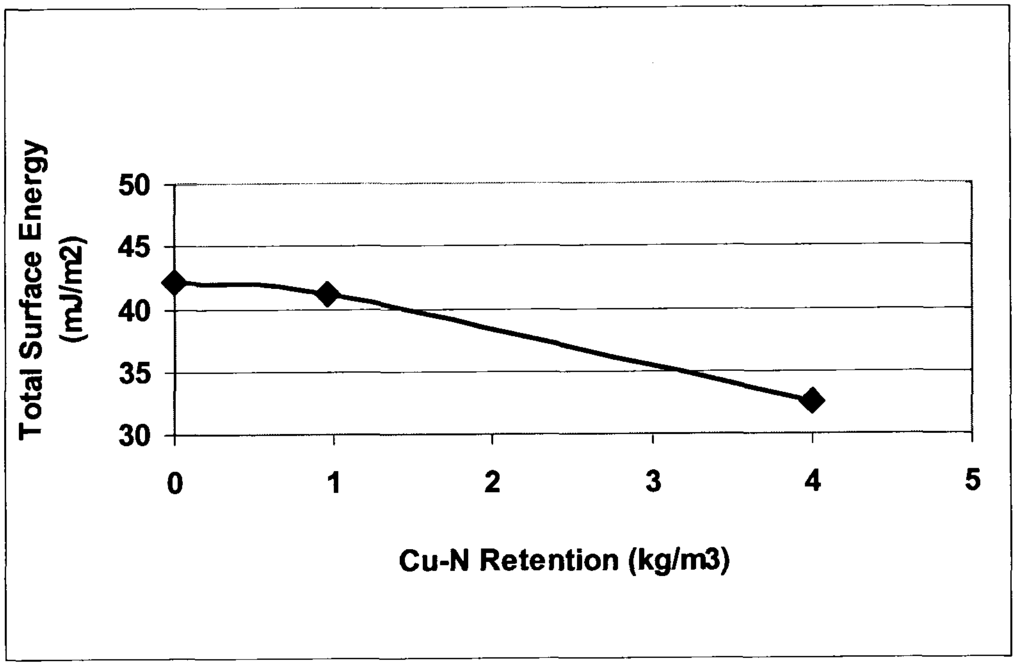

Figure 3.15. Changes in total surface energy characteristics of southern pine as Cu-N retention increases.

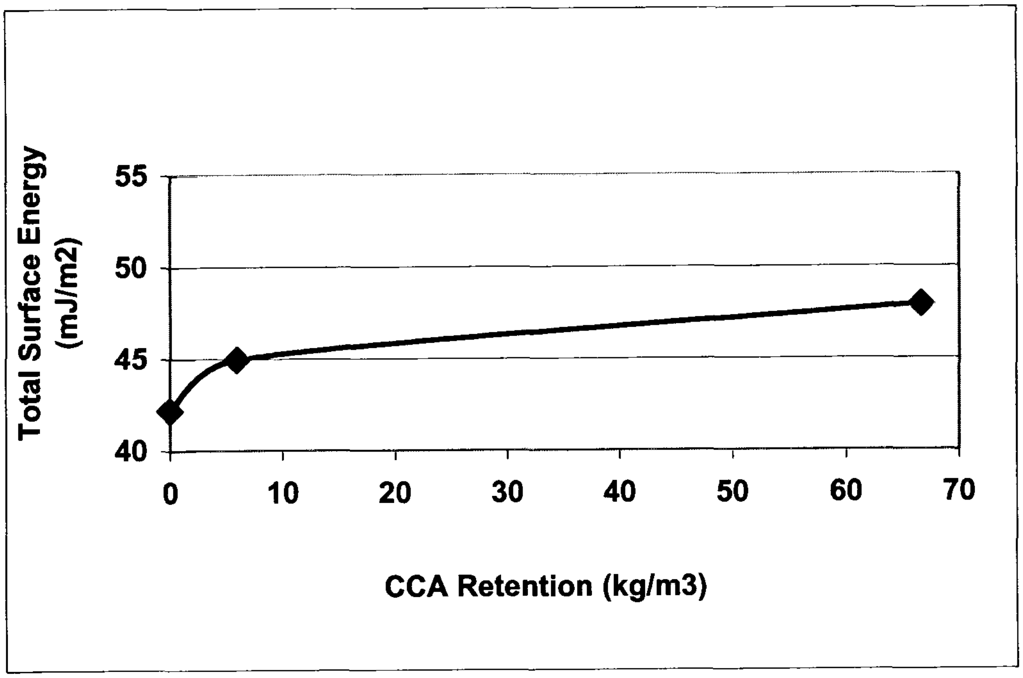

Figure 3.16. Changes in total surface energy characteristics of southern pine as CCA-C retention increases.

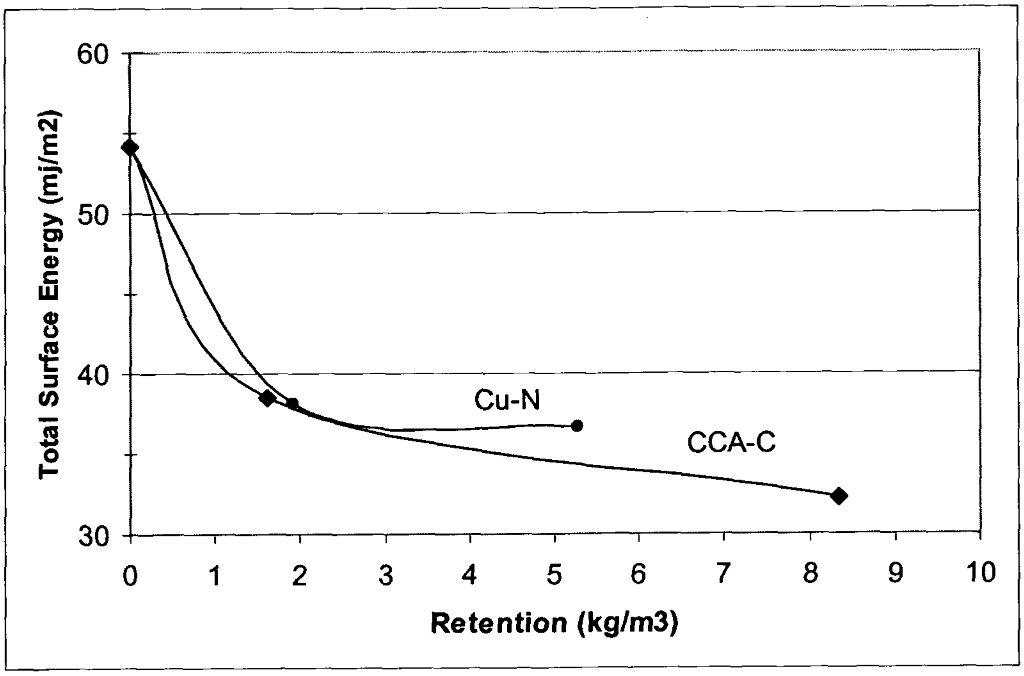

Figure 3.17. Changes in surface energy characteristics of FRP as preservative retention increases.

FRP surfaces, on the other hand, responded similarly to both treatments (CCA and CuN). The total surface energy of pressure treated FRP was drastically reduced with increased retentions of CCA-C and CuN, suggesting that adhesion performance would be negatively altered by these treatments (Figure 3.17). Somewhat different changes were expected since the chemical interactions between preservative chemicals and surfaces are different. These findings are important for long-term durability of pre-treated FRP reinforced beams if FRP plates are also to be treated before lamination. Our results show that CCA-C and CuN treatments of wood laminates or FRP plates will directly affect the physiochemical surface properties and the total surface energy of these materials. These changes in surface energy will be directly reflected the bondability of wood and FRP laminates. The pressure treatment of individual wood laminates with oil-borne preservatives (creosote, CuN, and PCP) resulted in high delamination values for wood/FRP interfaces. Our surface energy analysis supports these findings with total surface energy reductions up to 23 % for southern pine surfaces and up to 40 % for E-glass/phenolic pultruded surfaces. It is interesting to note that the increased total surface energy of pre-treated southern pine laminates with CCA-C, agreed with the delamination results for both wood/wood and wood/FRP interfaces. The average percent delamination of pre-treated wood/wood and wood/FRP bonds declined as the retention of CCA-C has increased.

3.5. Conclusions

The following conclusions have been drawn from this study:

1) Preservative treatments had significant negative impacts on bond durability of wood/E-glass phenolic pultruded FRP sheet bond lines for both pre- and post-treatments. Therefore preservative/pressure treatment should be taken into account in durability studies.
2) All oil-borne treatments at the retentions used in this study negatively interfere with pre-treated wood/E-glass-phenolic interfaces.
3) Increased CCA retentions have increased the delamination of wood/E-glass-phenolic pultruded FRP for post-treated wood/FRP bond applications. The pre-treated applications have also affected negatively for wood/wood and wood/FRP bonds but there was a declining trend in delamination as the retention of CCA increased. This trend was supported with surface energy analysis results.

4) The modified ASTM D-2559 test was successfully used to examine the effects of wood preservative systems on wood/FRP interfaces. Although this standard does not include delamination values of wood/FRP interfaces.
5) Shear block tests (based on modified ASTM D 905) of the bond line between CCA treated southern pine and FRP surfaces also showed that increased retention resulted in an increase in shear strength. This trend may be explained with increased surface energy.
6) Analysis of surface energy characteristics with contact angle measurements revealed that the surface energy of preservative treated southern yellow pine and E-glass/phenolic FRP surfaces was greatly affected by the preservative treatments used in this study. Surface energy characterization through contact angle measurement may be a promising technique for interpreting the durability of wood/FRP interfaces.
7) The FRP reinforced engineered wood industry should consider the effects different preservative systems and pre- or post-manufacturing methods will have on advanced engineered wood composite fabrication and long-term durability. Pre-screening tests with different wood preservative systems should be conducted for compatibility between preservative and composite systems (fibers and matrix) whenever new systems are developed.

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APPENDIX A: Non-Destructive Evaluation (NDE) of Decay Exposed FRP Composite

A.1. Introduction

The application of ultrasonic techniques (acousto-ultrasonics) has been gaining popularity for non-destructive evaluation of various materials including FRP composites over the last decade (Beall et al.1998, Emerson 2000, Franklin et al. 2001). Ultrasonic methodology basically involves either the analysis of signals transmitted through materials along a fixed path to evaluate active changes in a material, or scanning the material to locate defective and weak areas (Beall 1996).

In this work an electronic pulser was used to generate repeatable elastic waves using a piezoelectric transducer. These waves propagate through FRP specimens and are received by a second transducer. The resulting waveforms can be recorded as voltage changes with subsequent waveform analysis performed using different techniques such as Fast Fourier Transform (FFT) to determine the changes in the signal content in the path. These changes result from microstructural modifications including potentially any internal flaws, and loss of material integrity

A.2. Application of Non-destructive Evaluation and Waveform Analysis

Each decay-exposed FRP coupon was tested ultrasonically using a square wave pulser, which excites a 1.0 MHz piezoelectric ultrasonic transducer. The transducer generates an elastic pulse that propagates through the FRP coupon. The ultrasonic transducer is then excited by the received signal, which is sent through a preamplifier and displayed as a voltage versus time waveform on a digital oscilloscope (Figure 4.1). A fast Fourier transform (FFT) was used to analyze the energy distribution and changes in signal content of the decayed and control waveforms.

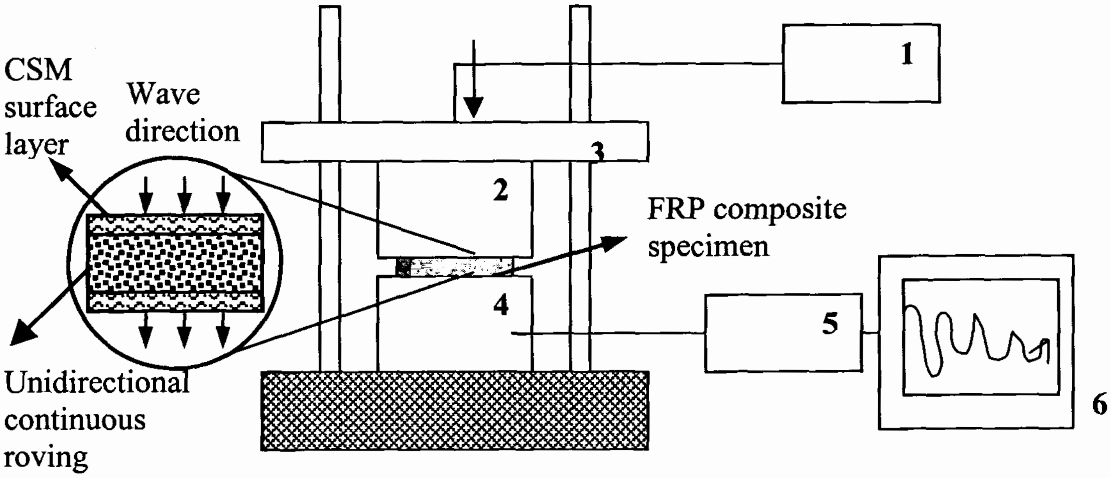

Figure A.1. Details of ultrasonic measurement of FRP coupons. Ultrasonic pulse generator (1), ultrasonic transducer (2), weight bar (3), ultrasonic receiver (4), ultrasonic pre-amplifier (5), digital oscilloscope (6).

4.3. Results and Discussion

The waveform analysis and Fast Fourier Transform (FFT) results (Figures 4.2 and 4.3) showed that, the *G. trabeum* decay-exposed FRP coupons had considerable reduction in FFT magnitude of transferred energy as recorded by the shear transducer. This reduction in FFT magnitude can be attributed to the attenuation of the ultrasonic waves that travel through the FRP material. The average FFT magnitude recorded in the *G. trabeum* exposed FRP coupons was approximately 25% of that for the unexposed or sterile soil-exposed FRP. A 55% reduction in FFT magnitude was recorded in the *T. versicolor* exposed samples with the same transducer. Unexposed and sterile soil-exposed FRP coupons, on the other hand, did not show any reduction in FFT magnitude after 24 weeks of exposure. Internal changes (increased porosity or weakening of the fiber/matrix interface due to fungal growth or secretion of acids, etc.) may be responsible for the observed reduction of sound energy transfer in the *G.trabeum* exposed FRP material.

G.trabeum brown rot fungi are known to use a non-enzymatic degradative system to attack cellulose in wood (Goodell et al. 1997b, Xu and Goodell 2001), and this non-enzymatic degradation with production of powerful oxidants may play a role in FRP degradation.

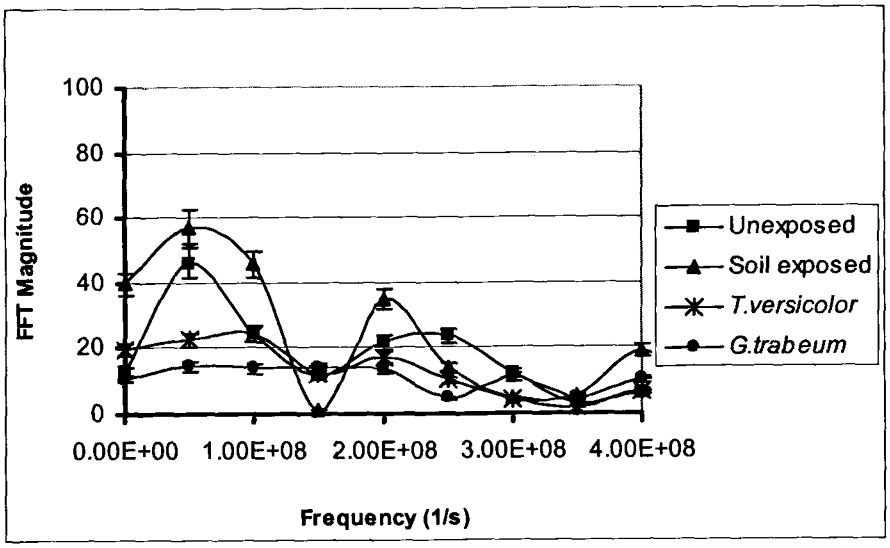

Figure A.2. Comparison of FFT magnitude plots of control (sterile soil-exposed and unexposed) and decay-exposed (*G. trabeum* and *T. versicolor*) FRP versus frequency for shear transducer data. (Each line represents an average of 3 specimens).

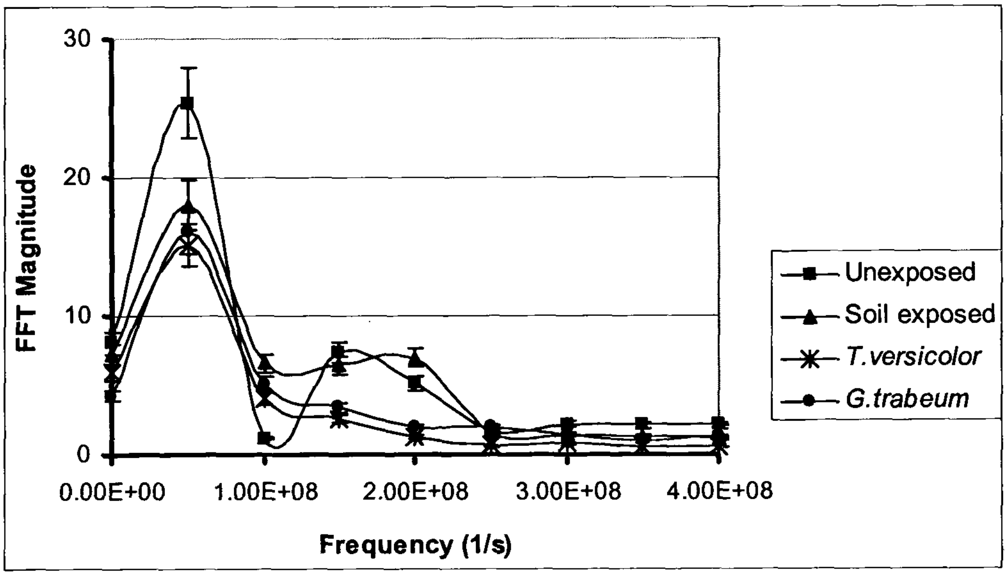

Figure A.3. Comparison of FFT magnitude plots of control (sterile soil-exposed and unexposed) and decay-exposed (*G. trabeum* and *T. versicolor*) FRP versus frequency for longitudinal transducer data. (Each line represents an average of 3 specimens).

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APPENDIX B: Statistical Analysis

B.1. Analysis of Variance (ANOVA) and Comparison of Probabilities of Longitudinal Tensile Strength of Preservative Treated FRP

```
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Variables

 TREATMENT$   UTS

Effects coding used for categorical variables in model.

Categorical values encountered during processing are:
TREATMENT$ (14 levels)
  CCA 10%, CCA 2.5%, Creosote, CuN 0.5%, CuN 2.5%, CuN 8%, Diesel fuel,
  Kodiak High, Kodiak Low, Min. Spirits, Penta 10%, Penta 5%, Untreated, Water

Dep Var: UTS   N: 124   Multiple R: 0.656   Squared multiple R: 0.431


                    Analysis of Variance

Source            Sum-of-Squares  df  Mean-Square   F-ratio     P

TREATMENT$          1.31111E+10   13  1.00855E+09    6.405    0.000

Error               1.73220E+10  110  1.57473E+08

-------------------------------------------------------------------------------

Durbin-Watson D Statistic     1.916
First Order Autocorrelation  0.038
COL/
ROW TREATMENT$
  1 CCA 10%
  2 CCA 2.5%
  3 Creosote
  4 CuN 0.5%
  5 CuN 2.5%
  6 CuN 8%
  7 Diesel fuel
  8 Kodiak High
  9 Kodiak Low
```

```
 10 Min. Spirits
 11 Penta 10%
 12 Penta 5%
 13 Untreated
 14 Water
Using least squares means.
Post Hoc test of UTS
--------------------------------------------------------------------------

Using model MSE of 157472896.132 with 110 df.
Matrix of pairwise mean differences:

              1           2           3           4           5
   1        0.0
   2   5877.371         0.0
   3  27823.193   21945.821         0.0
   4  25263.537   19386.166   -2559.656         0.0
   5  14790.298    8912.926  -13032.895  -10473.239         0.0
   6  18499.343   12621.971   -9323.850   -6764.194    3709.045
   7  28722.673   22845.301     899.480    3459.136   13932.375
   8  -3063.743   -8941.114  -30886.936  -28327.280  -17854.041
   9  -3513.393   -9390.764  -31336.586  -28776.930  -18303.691
  10  17469.969   11592.597  -10353.224   -7793.569    2679.671
  11  20464.426   14587.054   -7358.767   -4799.111    5674.128
  12  10884.500    5007.129  -16938.693  -14379.037   -3905.798
  13  25304.067   19426.695   -2519.126      40.529   10513.769
  14  20461.024   14583.653   -7362.169   -4802.513    5670.726

              6           7           8           9          10
   6        0.0
   7  10223.330         0.0
   8 -21563.086  -31786.416         0.0
   9 -22012.736  -32236.066    -449.650         0.0
  10  -1029.374  -11252.704   20533.711   20983.361         0.0
  11   1965.083   -8258.247   23528.169   23977.819    2994.457
  12  -7614.843  -17838.173   13948.243   14397.893   -6585.469
  13   6804.724   -3418.606   28367.809   28817.459    7834.098
  14   1961.681   -8261.649   23524.767   23974.417    2991.056

             11          12          13          14
  11        0.0
  12  -9579.926         0.0
  13   4839.641   14419.567         0.0
  14     -3.401    9576.524   -4843.042         0.0
```

Tukey HSD Multiple Comparisons.
Matrix of pairwise comparison probabilities:

	1	2	3	4	5
1	1.000				
2	1.000	1.000			
3	0.000	0.017	1.000		
4	0.018	0.198	1.000	1.000	
5	0.387	0.958	0.267	0.870	1.000
6	0.262	0.832	0.941	0.999	1.000
7	0.003	0.054	1.000	1.000	0.488
8	1.000	0.987	0.000	0.004	0.129
9	1.000	0.980	0.000	0.003	0.107
10	0.350	0.901	0.879	0.996	1.000
11	0.137	0.648	0.992	1.000	0.999
12	0.936	1.000	0.187	0.670	1.000
13	0.004	0.081	1.000	1.000	0.679
14	0.038	0.411	0.954	1.000	0.995

	6	7	8	9	10
6	1.000				
7	0.960	1.000			
8	0.090	0.001	1.000		
9	0.076	0.000	1.000	1.000	
10	1.000	0.919	0.133	0.113	1.000
11	1.000	0.994	0.040	0.033	1.000
12	0.997	0.317	0.713	0.668	0.999
13	0.997	1.000	0.001	0.000	0.989
14	1.000	0.977	0.007	0.005	1.000

	11	12	13	14
11	1.000			
12	0.976	1.000		
13	1.000	0.476	1.000	
14	1.000	0.929	0.999	1.000

B.2. Analysis of Variance (ANOVA) and Comparison of Probabilities of Longitudinal Modulus of Preservative Treated FRP

```
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Variables
TREATMENTS$  MOE


 Effects coding used for categorical variables in model.

Categorical values encountered during processing are:
TREATMENTS$ (14 levels)
   CCA 10%, CCA 2.5%, Creosote, CuN 0.5%, CuN 2.5%, CuN 8%, Diesel fuel,
   Kodiak H, Kodiak L, Min.spirits, Penta 10%, Penta 5%, Untreated, Water

Dep Var: MOE   N: 124   Multiple R: 0.390   Squared multiple R: 0.152


                       Analysis of Variance

Source              Sum-of-Squares  df  Mean-Square    F-ratio      P

TREATMENTS$           1.22144E+12   13  9.39570E+10    1.522     0.121

Error                 6.78998E+12  110  6.17271E+10

-------------------------------------------------------------------------


Durbin-Watson D Statistic     1.841
First Order Autocorrelation  0.075
COL/
ROW TREATMENTS$
  1 CCA 10%
  2 CCA 2.5%
  3 Creosote
  4 CuN 0.5%
  5 CuN 2.5%
  6 CuN 8%
  7 Diesel fuel
  8 Kodiak H
  9 Kodiak L
 10 Min.spirits
```

```
 11  Penta 10%
 12  Penta 5%
 13  Untreated
 14  Water
Using least squares means.
Post Hoc test of MOE
-------------------------------------------------------------------------

Using model MSE of 61727123268.398 with 110 df.
Matrix of pairwise mean differences:

              1            2            3            4            5
  1         0.0
  2    37571.429        0.0
  3   182571.429   145000.000        0.0
  4   217714.286   180142.857    35142.857        0.0
  5    62214.286    24642.857  -120357.143  -155500.000        0.0
  6   124142.857    86571.429   -58428.571   -93571.429    61928.571
  7   240571.429   203000.000    58000.000    22857.143   178357.143
  8    42285.714     4714.286  -140285.714  -175428.571   -19928.571
  9    66285.714    28714.286  -116285.714  -151428.571     4071.429
 10    -5714.286   -43285.714  -188285.714  -223428.571   -67928.571
 11   -48571.429   -86142.857  -231142.857  -266285.714  -110785.714
 12  -113142.857  -150714.286  -295714.286  -330857.143  -175357.143
 13    69273.810    31702.381  -113297.619  -148440.476     7059.524
 14   215714.286   178142.857    33142.857    -2000.000   153500.000

              6            7            8            9           10
  6         0.0
  7   116428.571        0.0
  8   -81857.143  -198285.714        0.0
  9   -57857.143  -174285.714    24000.000        0.0
 10  -129857.143  -246285.714   -48000.000   -72000.000        0.0
 11  -172714.286  -289142.857   -90857.143  -114857.143   -42857.143
 12  -237285.714  -353714.286  -155428.571  -179428.571  -107428.571
 13   -54869.048  -171297.619    26988.095     2988.095    74988.095
 14    91571.429   -24857.143   173428.571   149428.571   221428.571

             11           12           13           14
 11         0.0
 12   -64571.429        0.0
 13   117845.238   182416.667        0.0
 14   264285.714   328857.143   146440.476        0.0

Tukey HSD Multiple Comparisons.
Matrix of pairwise comparison probabilities:
```

```
            1       2       3       4       5
 1      1.000
 2      1.000   1.000
 3      0.946   0.992   1.000
 4      0.931   0.985   1.000   1.000
 5      1.000   1.000   0.991   0.985   1.000
 6      1.000   1.000   1.000   1.000   1.000
 7      0.866   0.959   1.000   1.000   0.955
 8      1.000   1.000   0.994   0.988   1.000
 9      1.000   1.000   0.999   0.997   1.000
10      1.000   1.000   0.932   0.918   1.000
11      1.000   1.000   0.758   0.761   0.999
12      1.000   0.997   0.371   0.424   0.960
13      1.000   1.000   0.996   0.992   1.000
14      0.835   0.955   1.000   1.000   0.933

            6       7       8       9      10
 6      1.000
 7      1.000   1.000
 8      1.000   0.966   1.000
 9      1.000   0.989   1.000   1.000
10      0.999   0.846   1.000   1.000   1.000
11      0.990   0.646   1.000   1.000   1.000
12      0.877   0.314   0.996   0.985   1.000
13      1.000   0.973   1.000   1.000   1.000
14      1.000   1.000   0.963   0.990   0.808

           11      12      13      14
11      1.000
12      1.000   1.000
13      0.999   0.956   1.000
14      0.560   0.212   0.965   1.000
-----------------------------------------------------------------------------
```

B.3. Analysis of Variance (ANOVA) and Comparison of Probabilities of Transversal Tensile (TTS) Strength of Preservative Treated FRP

```
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Variables;
TREATMENTS$  UTTS      MOE
```

```
Effects coding used for categorical variables in model.

Categorical values encountered during processing are:
TREATMENTS$ (9 levels)
  CCA-10%, Creosote, CuN-2.5%, Diesel fuel, Kodiak-5%, Min.Spirits, PCP-5%,
  Untreated, Water

Dep Var: UTTS   N: 67   Multiple R: 0.416   Squared multiple R: 0.173


                 Analysis of Variance

Source            Sum-of-Squares  df  Mean-Square   F-ratio     P

TREATMENTS$         461092.100     8   57636.512     1.513    0.173

Error              2209505.002    58   38094.914

-------------------------------------------------------------------------


Durbin-Watson D Statistic     1.962
First Order Autocorrelation   0.005
COL/
ROW TREATMENTS$
 1 CCA-10%
 2 Creosote
 3 CuN-2.5%
 4 Diesel fuel
 5 Kodiak-5%
 6 Min.Spirits
 7 PCP-5%
 8 Untreated
 9 Water
Using least squares means.
Post Hoc test of UTTS
-------------------------------------------------------------------------

Using model MSE of 38094.914 with 58 df.
Matrix of pairwise mean differences:

             1          2          3          4          5
   1       0.0
   2      56.855      0.0
   3     138.356     81.502      0.0
   4     129.449     72.595     -8.907      0.0
```

```
5      166.630    109.775    28.273    37.180     0.0
6       43.873    -12.982   -94.484   -85.577  -122.757
7      137.878     81.023    -0.479     8.428   -28.752
8      -90.143   -146.998  -228.500  -219.592  -256.773
9      183.278    126.423    44.921    53.828    16.648

          6          7          8          9
6       0.0
7      94.005      0.0
8    -134.016   -228.021      0.0
9     139.405     45.400    273.421      0.0

Tukey HSD Multiple Comparisons.
Matrix of pairwise comparison probabilities:

         1         2         3         4         5
1      1.000
2      1.000     1.000
3      0.919     0.997     1.000
4      0.944     0.999     1.000     1.000
5      0.802     0.979     1.000     1.000     1.000
6      1.000     1.000     0.992     0.996     0.958
7      0.921     0.997     1.000     1.000     1.000
8      0.995     0.910     0.481     0.535     0.323
9      0.567     0.907     1.000     1.000     1.000

         6         7         8         9
6      1.000
7      0.992     1.000
8      0.945     0.483     1.000
9      0.850     1.000     0.137     1.000
--------------------------------------------------------------------------------
```

B.4. Analysis of Variance (ANOVA) and Comparison of Probabilities of Transversal Modulus of Preservative Treated FRP

```
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Variables
TREATMENTS$  UTTS       MOE

Effects coding used for categorical variables in model.
```

```
Categorical values encountered during processing are:
TREATMENTS$ (9 levels)
  CCA-10%, Creosote, CuN-2.5%, Diesel fuel, Kodiak-5%, Min.Spirits, PCP-5%,
  Untreated, Water

Dep Var: MOE   N: 67   Multiple R: 0.376   Squared multiple R: 0.141


                    Analysis of Variance

Source           Sum-of-Squares  df   Mean-Square   F-ratio     P

TREATMENTS$         139488.749    8   17436.094      1.192    0.320

Error               848753.110   58   14633.674

-------------------------------------------------------------------------------


Durbin-Watson D Statistic     1.891
First Order Autocorrelation  0.049
COL/
ROW TREATMENTS$
 1 CCA-10%
 2 Creosote
 3 CuN-2.5%
 4 Diesel fuel
 5 Kodiak-5%
 6 Min.Spirits
 7 PCP-5%
 8 Untreated
 9 Water
Using least squares means.
Post Hoc test of MOE
-------------------------------------------------------------------------------

Using model MSE of 14633.674 with 58 df.
Matrix of pairwise mean differences:
```

```
              1          2          3          4          5
     1       0.0
     2     -12.563      0.0
     3      13.071     25.634      0.0
     4      34.816     47.379     21.744      0.0
     5     -56.509    -43.946    -69.580    -91.324      0.0
     6     -20.834     -8.271    -33.906    -55.650     35.674
     7     -24.580    -12.017    -37.651    -59.396     31.929
     8      71.957     84.520     58.886     37.142    128.466
     9     -83.733    -71.171    -96.805   -118.549    -27.225

              6          7          8          9

     6       0.0
     7      -3.746      0.0
     8      92.792     96.537      0.0
     9     -62.899    -59.153   -155.691      0.0

Tukey HSD Multiple Comparisons.
Matrix of pairwise comparison probabilities:

              1          2          3          4          5
     1      1.000
     2      1.000      1.000
     3      1.000      1.000      1.000
     4      1.000      0.998      1.000      1.000
     5      0.994      0.999      0.975      0.889      1.000
     6      1.000      1.000      1.000      0.994      1.000
     7      1.000      1.000      1.000      0.991      1.000
     8      0.976      0.940      0.993      1.000      0.611
     9      0.871      0.945      0.754      0.509      1.000

              6          7          8          9
     6      1.000
     7      1.000      1.000
     8      0.901      0.880      1.000
     9      0.973      0.981      0.220      1.000
--------------------------------------------------------------------------------
```

B.5. Analysis of Variance (ANOVA) and Comparison of Probabilities of Interlaminar Shear Strength (ILSS) of Preservative Treated FRP

```
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Variables
TREATMENT$   ILSSTRENGTH

Effects coding used for categorical variables in model.

Categorical values encountered during processing are:
TREATMENT$ (14 levels)
  CCA 10%, CCA 2.5%, Creosote, CuN 0.5%, CuN 2.5%, CuN 8%, Diesel fuel,
  Kodiak High, Kodiak Low, Min. Spirits, Penta 10%, Penta 5%, Untreated, Water

Dep Var: ILSSTRENGTH   N: 149   Multiple R: 0.694   Squared multiple R: 0.482


                  Analysis of Variance

Source            Sum-of-Squares  df  Mean-Square    F-ratio      P

TREATMENT$        4588209.885     13  352939.222     9.675      0.000

Error             4924808.620    135   36480.064

-----------------------------------------------------------------------------


Durbin-Watson D Statistic      2.028
First Order Autocorrelation   -0.042
COL/
ROW TREATMENT$
 1 CCA 10%
 2 CCA 2.5%
 3 Creosote
 4 CuN 0.5%
 5 CuN 2.5%
 6 CuN 8%
 7 Diesel fuel
 8 Kodiak High
 9 Kodiak Low
```

```
10 Min. Spirits
11 Penta 10%
12 Penta 5%
13 Untreated
14 Water
Using least squares means.
Post Hoc test of ILSSTRENGTH
-----------------------------------------------------------------------------

Using model MSE of 36480.064 with 135 df.
Matrix of pairwise mean differences:

            1          2          3          4          5
  1       0.0
  2     -18.584      0.0
  3    -239.814   -221.230      0.0
  4      40.304     58.889    280.119      0.0
  5    -138.780   -120.196    101.034   -179.084      0.0
  6      56.957     75.542    296.772     16.653    195.737
  7    -116.647    -98.062    123.168   -156.951     22.133
  8    -499.330   -480.746   -259.516   -539.634   -360.550
  9    -429.711   -411.127   -189.897   -470.016   -290.931
 10      -5.573     13.011    234.241    -45.878    133.207
 11      56.962     75.547    296.777     16.658    195.742
 12      53.016     71.600    292.830     12.711    191.796
 13     100.748    119.333    340.563     60.444    239.528
 14       1.923     20.507    241.737    -38.382    140.703

            6          7          8          9         10
  6       0.0
  7    -173.604      0.0
  8    -556.287   -382.683      0.0
  9    -486.668   -313.064     69.619      0.0
 10     -62.530    111.073    493.757    424.138      0.0
 11       0.005    173.609    556.292    486.673     62.536
 12      -3.942    169.662    552.346    482.727     58.589
 13      43.791    217.395    600.078    530.459    106.322
 14     -55.034    118.569    501.253    431.634      7.496

           11         12         13         14
 11       0.0
 12      -3.947      0.0
 13      43.786     47.733      0.0
 14     -55.039    -51.093    -98.826      0.0
```

Tukey HSD Multiple Comparisons.
Matrix of pairwise comparison probabilities:

	1	2	3	4	5
1	1.000				
2	1.000	1.000			
3	0.113	0.206	1.000		
4	1.000	1.000	0.023	1.000	
5	0.960	0.988	0.991	0.775	1.000
6	1.000	1.000	0.113	1.000	0.859
7	0.991	0.998	0.952	0.901	1.000
8	0.000	0.000	0.054	0.000	0.005
9	0.000	0.000	0.454	0.000	0.073
10	1.000	1.000	0.137	1.000	0.971
11	1.000	1.000	0.010	1.000	0.649
12	1.000	1.000	0.013	1.000	0.680
13	0.991	0.962	0.000	1.000	0.114
14	1.000	1.000	0.011	1.000	0.875

	6	7	8	9	10
6	1.000				
7	0.939	1.000			
8	0.000	0.002	1.000		
9	0.000	0.034	1.000	1.000	
10	1.000	0.994	0.000	0.000	1.000
11	1.000	0.811	0.000	0.000	1.000
12	1.000	0.835	0.000	0.000	1.000
13	1.000	0.230	0.000	0.000	0.986
14	1.000	0.964	0.000	0.000	1.000

	11	12	13	14
11	1.000			
12	1.000	1.000		
13	1.000	1.000	1.000	
14	1.000	1.000	0.958	1.000

B.6. Analysis of Variance (ANOVA) and Comparison of Probabilities of Interlaminar Shear Strength (ILSS) of Decay Exposed FRP

```
SYSTAT VERSION 7.0
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SYSTAT Rectangular file C:\SYSTAT\DECAYILS.SYD,
Variables:
 EXPOSURES$  ILSS

Effects coding used for categorical variables in model.

Categorical values encountered during processing are:
EXPOSURES$ (4 levels)
  G.trabeum, Soil exposed, T.versicolor, Unexposed

Dep Var: ILSS   N: 47   Multiple R: 0.526   Squared multiple R: 0.277


                    Analysis of Variance

Source          Sum-of-Squares  df  Mean-Square   F-ratio     P

EXPOSURES$          730541.227   3   243513.742     5.493   0.003

Error              1906428.187  43    44335.539

-------------------------------------------------------------------------


Durbin-Watson D Statistic     1.869
First Order Autocorrelation   0.061
COL/
ROW EXPOSURES$
 1 G.trabeum
 2 Soil exposed
 3 T.versicolor
 4 Unexposed
Using least squares means.
Post Hoc test of ILSS
-------------------------------------------------------------------------

Using model MSE of 44335.539 with 43 df.
```

```
Matrix of pairwise mean differences:

               1          2          3          4
     1       0.0
     2     329.622      0.0
     3     136.482   -193.140      0.0
     4     285.394    -44.228    148.912      0.0

Tukey HSD Multiple Comparisons.
Matrix of pairwise comparison probabilities:

               1          2          3          4
     1       1.000
     2       0.004      1.000
     3       0.481      0.120      1.000
     4       0.016      0.947      0.323      1.000
-------------------------------------------------------------------------------
```

B.7. Analysis of Variance (ANOVA) and Comparison of Probabilities of Post Decay Moisture Content of Decay Exposed FRP

```
SYSTAT VERSION 7.0
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Variables:
 EXPOSURES$   MC

Effects coding used for categorical variables in model.

Categorical values encountered during processing are:
EXPOSURES$ (4 levels)
   C.globusum, G.trabeum, Soil exposed, T.versicolor
1 case(s) deleted due to missing data.

Dep Var: MC   N: 28   Multiple R: 0.928   Squared multiple R: 0.862
```

```
               Analysis of Variance

Source         Sum-of-Squares  df  Mean-Square   F-ratio     P

EXPOSURES$              29.500  3       9.833    50.012    0.000

Error              4.719   24      0.197

-------------------------------------------------------------------------------

*** WARNING ***
Case          9 is an outlier       (Studentized Residual =         3.841)

Durbin-Watson D Statistic      2.930
First Order Autocorrelation  -0.472
COL/
ROW EXPOSURES$
  1  C.globusum
  2  G.trabeum
  3  Soil exposed
  4  T.versicolor
Using least squares means.
Post Hoc test of MC
-------------------------------------------------------------------------------

Using model MSE of 0.197 with 24 df.
Matrix of pairwise mean differences:

                  1          2          3          4
          1       0.0
          2       2.293      0.0
          3      -0.387     -2.680      0.0
          4       0.481     -1.811      0.869      0.0

Tukey HSD Multiple Comparisons.
Matrix of pairwise comparison probabilities:

                  1          2          3          4
          1       1.000
          2       0.000      1.000
          3       0.380      0.000      1.000
          4       0.205      0.000      0.006      1.000
-------------------------------------------------------------------------------
```

B.8. Analysis of Variance (ANOVA) and Comparison of Probabilities of Post Decay Surface pH of Decay Exposed FRP

```
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Variables:
 EXPOSURES$   SURFACEPH

Effects coding used for categorical variables in model.

Categorical values encountered during processing are:
EXPOSURES$ (5 levels)
  C. globusum, G. trabeum, Soil exposed, T. versicolor, Unexposed

Dep Var: SURFACEPH   N: 120   Multiple R: 0.798   Squared multiple R: 0.636


                    Analysis of Variance

Source          Sum-of-Squares  df  Mean-Square    F-ratio      P

EXPOSURES$              65.921   4       16.480     50.331    0.000

Error             37.655   115      0.327

-------------------------------------------------------------------------------

*** WARNING ***
Case        102 is an outlier      (Studentized Residual =      -3.857)

Durbin-Watson D Statistic     1.419
First Order Autocorrelation   0.283
COL/
ROW EXPOSURES$
  1 C.globusum
  2 G.trabeum
  3 Soil exposed
  4 T.versicolor
  5 Unexposed
Using least squares means.
Post Hoc test of SURFACEPH
-------------------------------------------------------------------------------

Using model MSE of 0.327 with 115 df.
Matrix of pairwise mean differences:
```

```
          1        2        3        4        5
   1     0.0
   2    -1.596    0.0
   3     0.384    1.980    0.0
   4    -0.678    0.918   -1.062    0.0
   5     0.307    1.903   -0.077    0.985    0.0

Tukey HSD Multiple Comparisons.
Matrix of pairwise comparison probabilities:

          1        2        3        4        5
   1     1.000
   2     0.000    1.000
   3     0.145    0.000    1.000
   4     0.001    0.000    0.000    1.000
   5     0.345    0.000    0.990    0.000    1.000
-------------------------------------------------------------------------------
```

B.9 Analysis of Variance (ANOVA) and Comparison of Probabilities of Shear Strength of CCA Treated Southern Pine/FRP Interfaces (Figure 3.13)

```
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Variables:
 TREATMENT$   SHEARSTG

Effects coding used for categorical variables in model.

Categorical values encountered during processing are:
TREATMENT$ (5 levels)
   CCA1%, CCA10%, CCA2.5%, CCA5%, Untreated

Dep Var: SHEARSTG   N: 60   Multiple R: 0.723   Squared multiple R: 0.522


                    Analysis of Variance

Source          Sum-of-Squares  df  Mean-Square    F-ratio      P

TREATMENT$           2654584.767    4  663646.192     15.034     0.000

Error           2427819.664    55   44142.176
```

```
-------------------------------------------------------------------------------


Durbin-Watson D Statistic     1.763
First Order Autocorrelation   0.072
COL/
ROW TREATMENT$
  1 CCA1%
  2 CCA10%
  3 CCA2.5%
  4 CCA5%
  5 Untreated
Using least squares means.
Post Hoc test of SHEARSTG
-------------------------------------------------------------------------------

Using model MSE of 44142.176 with 55 df.
Matrix of pairwise mean differences:

               1          2          3          4          5
       1       0.0
       2     374.001      0.0
       3     380.439      6.438      0.0
       4     658.148    284.146    277.709      0.0
       5     299.557    -74.445    -80.882   -358.591      0.0

Tukey HSD Multiple Comparisons.
Matrix of pairwise comparison probabilities:

               1          2          3          4          5
       1       1.000
       2       0.001      1.000
       3       0.000      1.000      1.000
       4       0.000      0.014      0.017      1.000
       5       0.008      0.907      0.879      0.001      1.000
-------------------------------------------------------------------------------
```

BIOGRAPHY OF THE AUTHOR

Cihat Tascioglu was born in Istanbul, Turkey, on January 4, 1970, and graduated from 50. Yil Tahran High School in 1987. He studied forest industrial engineering at the University of Istanbul in Sariyer, Istanbul from 1988-1992. Cihat worked as quality control engineer in Konak International Wood Ltd., in Istanbul and as research assistant in Abant Izzet Baysal University in Bolu, Turkey before returning to his graduate studies. He graduated from the State University of New York, College of Environmental Science and Forestry at Syracuse in May, 1997, with a Master of Science degree in Wood Products Engineering. He is a member of the Forest Products Society (FPS), American Wood Preservers' Association (AWPA), Society of Wood Science and Technology (SWST), and International Research Group on Wood Preservation (IRG).

His research interests are wood preservation and biodeterioration, durability, wood preservative compatibility and biodegradation of fiber reinforced polymer (FRP) materials used for wood reinforcement.

Cihat entered the graduate program in Forest Resources at The University Maine in 1998, and served as a graduate research assistant in the University's Forest Management Department and Advanced Engineered Wood Composite (AEWC) Center from 1998 until May 2002. Cihat is a candidate for the Doctor of Philosophy degree in Forest Resources from The University of Maine in May, 2002.