

# Chapter 1

## INTRODUCTION

Fiber reinforced polymer matrix composites for structural applications are comprised of continuous or long chopped fibers embedded in a polymer matrix (usually a thermoset material). Such composites have high strength to weight ratios and excellent corrosion resistance relative to steel<sup>1,1</sup>. The function of the matrix is to protect the brittle reinforcing fibers and to transfer load to the fibers. Commonly employed polymer matrix materials include thermosets such as epoxies, unsaturated polyesters and vinyl esters, and also selected thermoplastics such as poly(ether ether ketone), poly(ethylene terephthalate), and poly(phenylene sulfide). Carbon fibers, primarily derived from pyrolysis of poly(acrylonitrile), can provide high modulus or stiffness with a density of 1.8 g/cm<sup>3</sup>. In many aerospace and civil applications, other fiber types include ceramics, E-glass, aramids (Kevlar), and high molecular weight polyethylene (Spectra). A third constituent, the “interphase”, is now known to drastically affect composite performance<sup>1,2</sup>. The interphase is a region of finite mass located at the fiber/matrix interface. This region has gradients in physical properties that greatly influence the performance of the final composite. One method to modify and control the physical properties of this interphase region is by applying a coating (sizing) material to the surface of the carbon fiber prior to impregnation with the matrix material. The process of applying a sizing to a carbon fiber surface is referred to as sizing.

Recent research has demonstrated that thermoplastic sizings in carbon fiber reinforced epoxy matrix composites can improve composite performance, especially durability and lifetime. Lesko et al. compared mechanical properties of epoxy matrix composites reinforced with carbon fibers sized with two different materials<sup>1.3&1.4</sup>, an epoxy, and a low molecular weight poly(vinylpyrrolidone) (14,000 M<sub>n</sub>) thermoplastic sizing. The matrix was untoughened 3501-6. They compared several mechanical properties at two different sizing levels. The most significant interphase material effects

were in the composites' dynamic performance. The composites had a  $[0^\circ/90^\circ]_{8s}$  cross-ply layup. Quasi-static notched compression strength for both sets of composites were found to be almost equal at 314 and 313 MPa respectively for the poly(vinylpyrrolidone) and epoxy sized composites. In spite of their almost identical compression strengths, the compression-compression, R=10 fatigue tests showed marked differences. For example, at an applied load of 70% of ultimate compression strength (UCS), the poly(vinylpyrrolidone) interphase composite was found to have an order of magnitude higher life as compared to the epoxy interphase composite. This is remarkable considering the fact that the quasi-static compression strengths were nearly identical. The transition from low cycle fatigue to high cycle fatigue characteristics in both cases were however seen to occur over a very narrow load range. In order to study the role of the interphase in the fatigue failure process, extensive damage evolution and propagation studies were conducted. It was observed that the initiation and growth of longitudinal  $0^\circ$  splits that extended tangentially from the edge of the notch occurred at about the same rate for both the interphases. This was done by stopping the fatigue test at particular intervals and performing x-ray radiography. However, the ability of the Poly(vinylpyrrolidone) interphase to resist the other major form of damage, namely surface ply buckling (SPB), was far greater than the epoxy interphase. For example at 70% UCS, the poly(vinylpyrrolidone) interphase composite initiated SPB at 10,000 cycles as compared to 3,000 cycles for the epoxy interphase. In addition, once SPB initiated, the growth rate as measured through high speed video monitoring was much slower for the poly(vinylpyrrolidone) interphase. Finally, the length of SPB at which unstable growth occurred was greater for the poly(vinylpyrrolidone) interphase composite as compared to the epoxy composite. All of the above are consistent with the longer lifetimes that the poly(vinylpyrrolidone) interphase composites had over the epoxy composites for a given load level. From this study, it was concluded that the *apparent* critical K (stress intensity factor) for the poly(vinylpyrrolidone) interphase might have been higher. It is not merely the longitudinal splitting or the inherent material strength of the composite that controls the fatigue behavior but more precisely the toughness or damage

tolerance of the interphase material. These results demonstrate that it should be possible to engineer an optimal sizing material to tailor selected composite properties.

The methodology followed in the present work involves comparing the effects of a relatively brittle polymeric sizing with a relatively ductile sizing material in a vinyl ester matrix. Fibers were sized with poly(vinylpyrrolidone) and polyhydroxyether which is a more ductile polymer. An unnotched fatigue test was found to distinguish quite well between the polymer sizing agents and an unsized fiber control. This work is a necessary starting point for further studies of the effects of polymer sizing agents on damage initiation and propagation.

## **EXPERIMENTAL SECTION**

### **Materials**

#### ***Carbon Fiber***

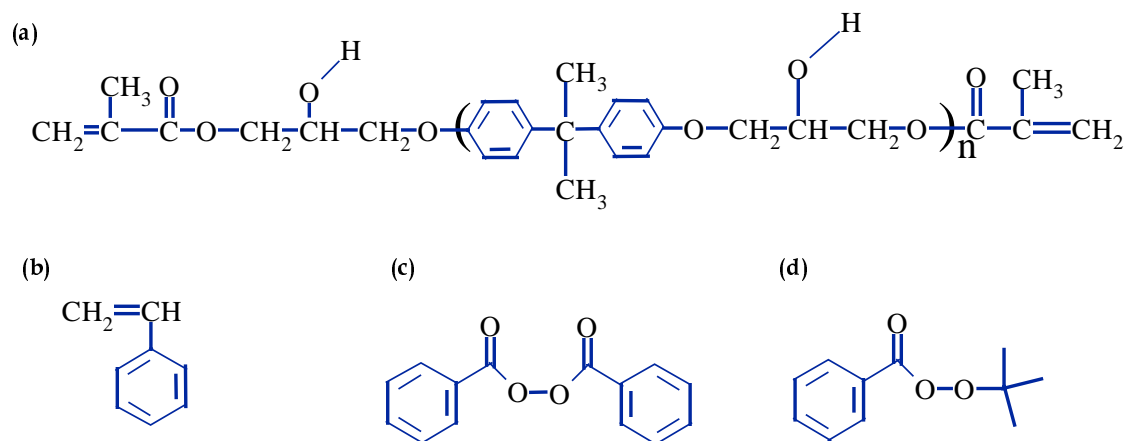
The fibers used in these experiments were Hercules AS-4 12K carbon fiber tow. AS-4 12K unsized but surface treated (lot # 1187-4E) was used as a feedstock for the sizing process.

#### ***Resin or Matrix Material***

The vinyl ester matrix material (Derakane 441-400) was obtained from the Dow Chemical Co. (Figure 1). Literature from the company indicates that the polymer has an ultimate tensile strength of 82.72 MPa and a strain to failure of 7-8%. The Derakane 441-400 matrix consisted of 70 weight percent pure vinyl ester and 30 percent styrene monomer. The vinyl ester component of the resin had an  $M_n$  of approximately 680 g/mol ( $^1\text{H}$  NMR) and was terminated with methacrylate functional groups.

#### ***Matrix Initiators***

The benzoyl peroxide and t-butylperoxybenzoate initiators were obtained from Aldrich and Elf Atochem, respectively, and were used as received.



**Figure 1:** Chemical Structures of Charged Derakane Resin (a) vinyl ester resin (b) styrene (c) benzoyl peroxide and (d) t-butylperoxybenzoate.

### ***Sizing Materials***

The PHENOXY polyhydroxyether (PKHW 35) sizing material (Figure 2a) was obtained from Phenoxy Associates, Rock Hill, SC. Data obtained from the company indicates that the polymer has a tensile ultimate strength of 55.16 MPa and a strain to failure of 40-100%. This polymer is therefore a tough polymer. This material was obtained as a 35 weight percent dispersion of approximately 1 micron diameter particles in water. The  $M_n$  of the PHENOXY was 19,000 g/mol (GPC) and it had a  $T_g$  of 97°C (DSC).

The LUVISKOL K-17 poly(vinylpyrrolidone) (lot # 58-0978) sizing material (Figure 2b) was obtained from the BASF Corporation. Although the properties of K-17 are not known, K-90, a higher molecular weight version, has an ultimate tensile strength of 62.06 MPa and a strain to failure of only 0.9%. This indicates that it is an extremely brittle polymer. The  $M_n$  of this material was 14,000 g/mol (GPC) and it had a  $T_g$  of 121°C (DSC).

Deionized water was used in the preparation of the aqueous sizing solutions used in the sizing process. The deionized water came from a NanoPure II™ unit equipped with a 0.2  $\mu\text{m}$  filter and a resistivity typically of 15M $\Omega\text{cm}$  or higher.

### ***Void Determination Materials***

Epoxide resin No.20-8130-032 and epoxide Hardener No. 20-8132-032 were obtained from Buehler for use in preparing composite specimens for scanning electron microscopy.

### ***RFI Consumable Materials***

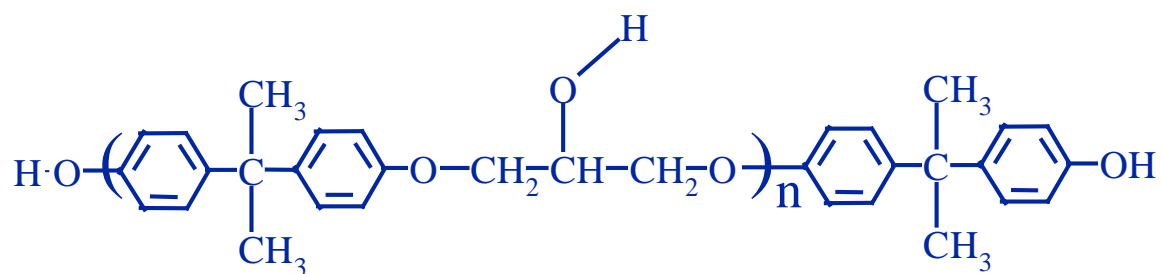
Porous teflon coated fiberglass release cloth was obtained from Airtech for use in the resin film infusion (RFI) process.

### **Materials Characterization**

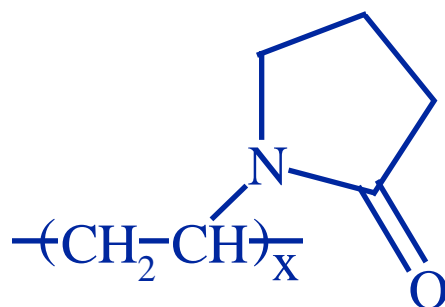
#### ***Viscosity and Glass Transition Temperature***

$^1\text{H}$  NMR spectra were collected using a Varian Unity 400 instrument operating at 400 MHz. GPC was conducted on a Waters GPC/ALC 150-C chromatograph equipped

a)



b)



**Figure 2:** Chemical Structures of (a) polyhydroxyether (PHENOXY) (b) and poly(vinylpyrrolidone) (K-17 PVP).

with the differential refractometer detector (RI) connected in parallel to a differential viscometric detector (DV) Viscotek® model 100. The injector and column compartment, connecting line, and DV detector were individually maintained at the same temperature (60°C). The signals from the RI and DV detectors permitted calculation of intrinsic viscosity and intrinsic viscosity distribution for universal calibration purposes by using Viscotek software Unical 4.04. This calculation assumed that the polymer concentration at the outlet of the SEC columns approached infinite dilution due to separation and column dispersion. N-methylpyrrolidone stirred over P<sub>2</sub>O<sub>5</sub> was prepared according to Cotts and co-workers<sup>1.5&1.6</sup>. HPLC grade N-methylpyrrolidone and P<sub>2</sub>O<sub>5</sub> were obtained from Sigma-Aldrich. The concentration of P<sub>2</sub>O<sub>5</sub> was 0.02 M. Differential Scanning Calorimetry (DSC) was conducted using a DuPont 910 DSC instrument under a nitrogen purge, which was calibrated with indium, lead and poly(dimethylsiloxane) (-123°C). The polyhydroxyether and poly(vinylpyrrolidone) sizing material samples were scanned from 25°C to 300°C, then cooled quickly and scanned a second time. All scanning rates were 10°C/min. No melting endotherms were observed. Glass transition points were taken from the inflection points of the curves from the second scans.

### ***Sizing Level Determination***

The amount of sizing deposited on the carbon fiber was determined via pyrolysis in a nitrogen atmosphere. Approximately 8 grams of sized carbon fiber were used for the analysis. This fiber was first dried in a convection oven above the T<sub>g</sub> of the particular sizing material for eight hours. The fibers were placed in a high temperature Blue-M furnace with a slow nitrogen purge. The fibers were pyrolyzed at 600°C for 30 minutes. In all cases, the pyrolysis cycle was found to be sufficient to completely volatilize the sizing while leaving the fiber unaffected. The amount of sizing material was computed from the differences in mass of the dry sized fiber and the pyrolyzed fiber.

$$S = 100(M_1 - M_2)/M_1 \quad (1)$$

where  $S$  was the weight percent of sizing on the fiber,  $M_1$  was the dry sized fiber mass, and  $M_2$  was the pyrolyzed fiber mass.

### ***Sized Fiber Quality***

The quality of the sized fiber was determined by inspection of the fibers under Scanning Electron Microscopy. The fibers were secured on a standard ESCA mount. The fibers were sputter coated with gold for approximately 2 minutes. Analysis was conducted in an International Scientific Instruments Model SX-40 SEM.

### ***Fiber Volume Fraction***

The fiber volume fractions of the composite panels produced in these experiments were calculated by measuring the density of the composite in air and in isopropyl alcohol. A 4g sample of the composite was dried and weighed. The sample was then immersed in isopropyl alcohol and weighed again. The density of the composite was calculated using Archimedes' principle using the following equation

$$\rho_c = \frac{W_{air}}{(W_{air} - W_{IPA})} * \rho_{IPA} \quad (2)$$

where  $\rho_{composite}$  = density of composite,  $\rho_{IPA}$  = density of isopropyl alcohol,  $W_{air}$  = weight of sample in air and  $W_{IPA}$  = weight of sample in isopropyl alcohol.

The fiber volume fraction was then calculated using the rule of mixtures

$$v = (\rho_c - \rho_{resin}) / (\rho_{fiber} - \rho_{resin}) \quad (3)$$

where v was the fiber volume fraction,  $\rho_{fiber}$  was density of the carbon fiber = 1.8 g/cc,  $\rho_{resin}$  was the cured resin density = 1.162 g/cc, and  $\rho_c$  was the composite density calculated from equation (2). The fiber volume fractions of the panels ranged from 55% to 58%.

### ***Quality of Panels (Voids)***

Voids in composite panels were analyzed using an ISI model number SX-40, scanning electron microscope at an acceleration voltage of 20kV. Sections of the composite panel were cut and placed in a Buehler potting cup. Epoxide resin and epoxide hardener were mixed in a ratio of 5:1 by weight and poured into the potting cup. The mixture was cured at room temperature for approximately 6 hours. The cured samples were polished using a Buehler ECOMET 3™ (variable speed) polisher-grinder. The samples were placed in a carousel and attached to the spindle of the AUTOMET 2™ (power head). The



power head ensured controlled loading of the specimens during polishing and resulted in specimens with a high gloss surface.

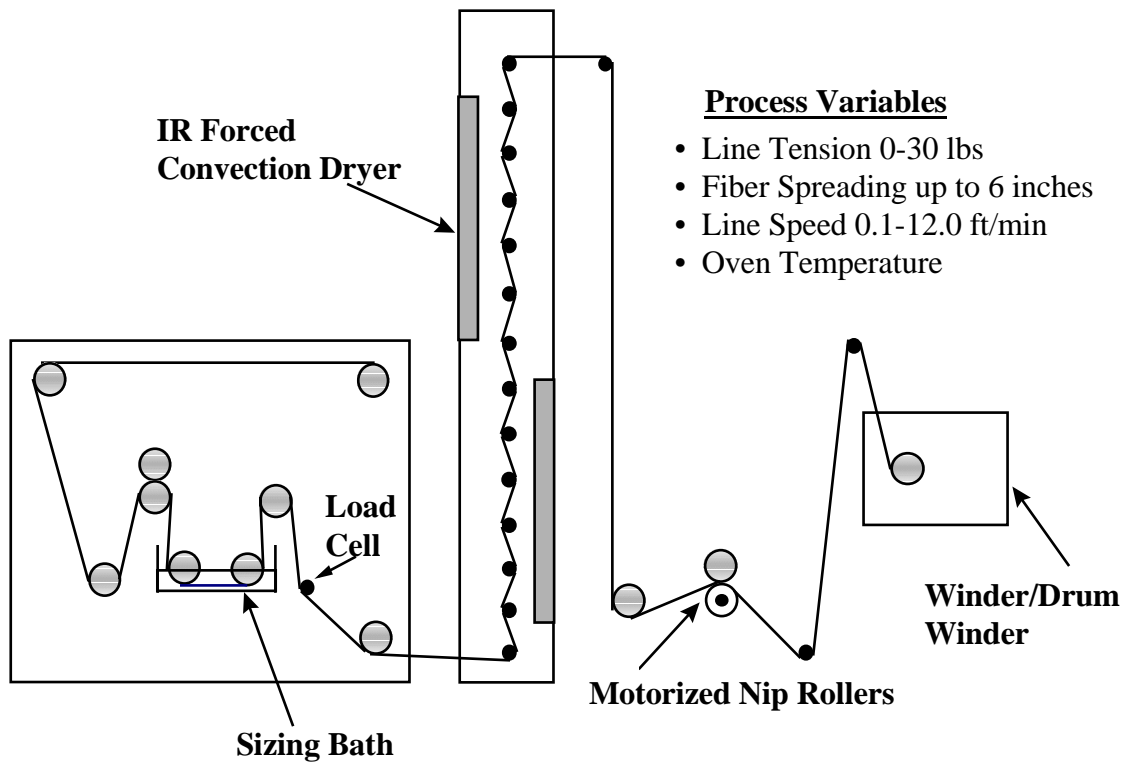
## **Materials Preparation**

### ***Sized Fiber Preparation***

Fibers were sized on a custom made small scale sizing line,<sup>1.7&1.8</sup> (Figure 3). Carbon fiber tow was pulled off a spool at a set speed ranging from 0.3 to 6.0 cm/sec. The fibers were placed under tension by a nip roller connected to a particle brake in the range of 0 to 110 N. The fibers were then passed through the sizing solution where capillary forces provided the driving force for rapid tow wetting. The high fiber tension and extensive use of rollers after the sizing bath spread the tow bundle and also prevented the wet tow from clumping. The spread carbon fiber tow containing the sizing solution was dried online in an IR forced convection dryer.

The emitter surface temperature of the two IR heating panels embedded in the dryer was controllable from ambient temperature up to 500°C. The inlet air temperature was controlled at ambient conditions. The emitter surface temperature directly controlled the surface temperature of the carbon fiber. The surface temperature of the fiber was measured by a hand held thermocouple. A time temperature profile was generated by placing the thermocouple on the fiber surface at various positions in the IR dryer.

The fiber that exited the dryer was wound onto a drumwinder to fabricate a 180cm length of uni-directional single ply fabric. The drumwinder operated by overlapping single tow strands onto a 60 cm diameter drum. The fibers were held in place via tape placed 19 cm apart. Areal weight (fiber mass per unit cross sectional area) of the fabric was controlled by controlling the degree of tow overlap. The fiber on the drum was cut into individual 19 cm by 19 cm plies. The sized fabric produced by this process was stitched perpendicular to the fiber direction at 5 cm intervals to prevent fiber movement in the subsequent processing steps.



**Figure 3:** Custom Small-Scale Sizing Line.

### ***Resin Preparation***

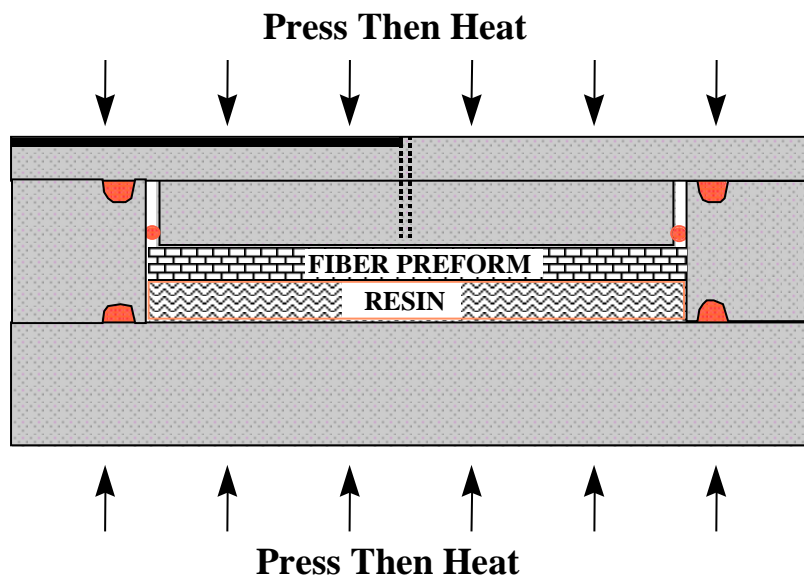
The resin was prepared by dissolving 1.1 wt. % benzoyl peroxide and 0.2 wt. % t-butylperoxybenzoate in Derakane 441-400. The mixture was degassed under vacuum (0.5 atm) with rapid stirring at room temperature until styrene first appeared in the vacuum trap. The amount of styrene lost in this step was found to be negligible. This resin was used for laminate production immediately upon preparation.

### ***Laminate Preparation***

The method utilized for composite panel production was **Resin Film Infusion (RFI)** or Matrix Film Infusion. A custom mold (Figure 4) was designed for the RFI process. The bottom of the mold was covered with a porous, teflon coated, fiberglass release cloth. Approximately 100 g of the initiator charged resin was poured into the mold cavity. The stitched sized fabric produced by the process described earlier was cut to the exact size of the mold. After cutting to size, the stitched fabric weighed approximately 15 g per ply. Approximately seven plies or 105 g of fiber was placed on top of the resin. The orientation of the individual plies was varied to obtain either unidirectional or  $[0^\circ/90^\circ]_{7s}$  cross-ply composite panels. The top surface of the fibers was covered with another piece of the porous Teflon<sup>™</sup> release cloth. A hole was placed in the center of the release cloth to allow resin to exit the cavity.

The piston plate (top of the mold) was placed on top of the fibers in such a way as to minimize pressure exerted on the fibers. The piston plate was designed with three distinct features. First, an o-ring around the piston plate was used to minimize resin leakage from the sides of the mold. Secondly, a 3 mm diameter hole in the center of the piston plate allowed excess resin to exit through the top of the mold. Finally, a trough was designed around the edges of the piston plate to allow excess resin to collect.

After the mold was assembled, it was placed in a Wabash (model 9112) 25 MPa vacuum hot press that had been covered with a 2 mm aluminum cover plate. The cover plate prevented excess resin from coming into contact with the press. The platens of the hot press were allowed to close at a rate of 6 mm/min. The slow platen closure rate allowed the



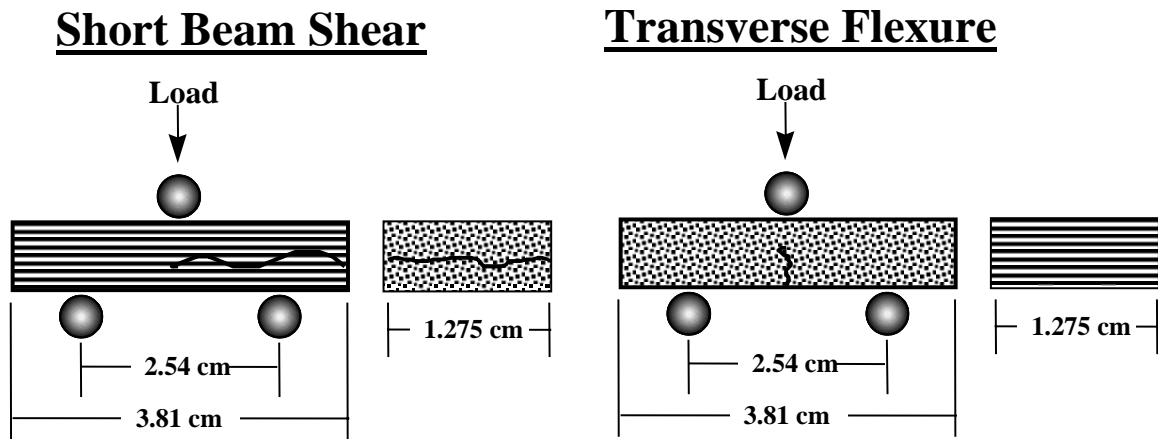
**Figure 4:** Resin Film Infusion Mold.

resin to fully impregnate the individual fabric plies while allowing the air and excess resin to exit. The platen closure pressure was 4000 KPa. After the platens had fully compressed the mold, the platens were briefly opened to allow any trapped air to escape, then re-closed at a pressure of 10 MPa. The platens were then heated to 150°C at a rate of 15°C/min. The platens were held at 150°C for approximately 10 minutes then cooled to room temperature at a rate of -20°C/min. The platens were opened and the composite panel was removed from the mold. Each of the composite panels were produced under the same processing conditions to insure that the same time was available for sizing diffusion.

### ***Mechanical Testing***

Short beam shear (ASTM D 2344-84) and transverse flexural (ASTM D790-90) tests were conducted on unidirectional composite samples. Specimens were cut in two stages in accordance with the ASTM standards. The first rough cuts were made using a Felker cutting saw. The final cuts were made using a Buehler ISOMET™ low speed cutting saw and a Buehler diamond wafering blade. The final specimen dimensions were 3.8 cm X 1.3 cm. The specimens were mounted in a three-point bend fixture and loaded at a rate of 1.3 mm/min using an Instron 4104 instrument. A 5KN load cell was used for both the short beam shear and transverse flexural strength tests. LabView®, a National Instruments Corporation data acquisition software, was used to monitor load versus displacement. Failure was noted when cracking appeared along the length of the specimens in the short beam shear tests and across the thickness in the transverse flexural tests (Figure 5).

Notched quasi-static compression and fatigue tests were conducted on notched, cross-ply (0°/90°)<sub>7s</sub> specimens. Specimens were rough cut with the Felker cutting saw and then ground to 15.2 cm X 2.54 cm. A 6.4 mm diameter hole was drilled in the center of the specimen to create the notch. Aluminum extensometer tabs were attached to the specimen using silicone grease such that the extensometer rested across the notch. An MTS Model 632 extensometer with a gage length of 2.54 cm and a maximum strain limit of 4% was used to monitor strain. Grit 100 sandpaper was wrapped around the specimen ends to protect them from being crushed by the test machine grips. An MTS instrument with a pair of



**Figure 5:** Schematic of the short beam shear and transverse flexure test specimens

Model 647 hydraulic wedge grips, a 448.82 test controller, a 418.91 Microprofiler™, a 413.81 master controller and a 464.80 data display unit were utilized. An external Vishay Measurements Group Model 2310 amplifier box was used to acquire the strain signals. A 5.08 cm test gage length was used. The specimens were loaded into the grips at a grip pressure of 7 MPa and specimen alignment was ensured by the use of a spirit level. Quasi-static compression tests were conducted to evaluate the ultimate compression strengths of the materials. Compressive load was applied at a rate of 57 kg/sec. This loading cycle was programmed into the Microprofiler™ which controlled the machine once a test was begun. The knife edges on the extensometer were made to rest in the aluminum tabs on the specimen and fastened via rubber bands. LabView® software was used to monitor the load, stroke and strain signals during the tests. The stroke interlocks on the machine were set tightly to prevent damage to the extensometer upon specimen failure.

Fatigue tests were conducted in a similar manner on the MTS test frame. Load was applied in a sinusoidal, fully reversed ( $R=-1$ ) manner at a frequency of 10 Hz. The magnitude of the applied load was computed as a percentage of the ultimate compression strength for the material. The Microprofiler™ was used to control the programmed loading cycle and the test controller was used to monitor the number of cycles.

## **RESULTS AND DISCUSSION**

### **Sizing of Carbon Fibers**

#### ***Processing***

An aqueous solution of 1.0 wt% K-17 PVP, and an aqueous dispersion of 1.0 wt% PHENOXY were prepared and were used in the sizing process to produce sized fiber.

The surface temperature history of the sized carbon fiber affected the handling characteristics of the final sized tow. It also affected the morphology of the sizing deposited onto the fiber surface. For each sizing material, an optimal time temperature dryer profile was determined. For the case of fiber sized with poly(vinylpyrrolidone), the optimal fiber surface temperature was found to be above 150°C but below 200°C. The

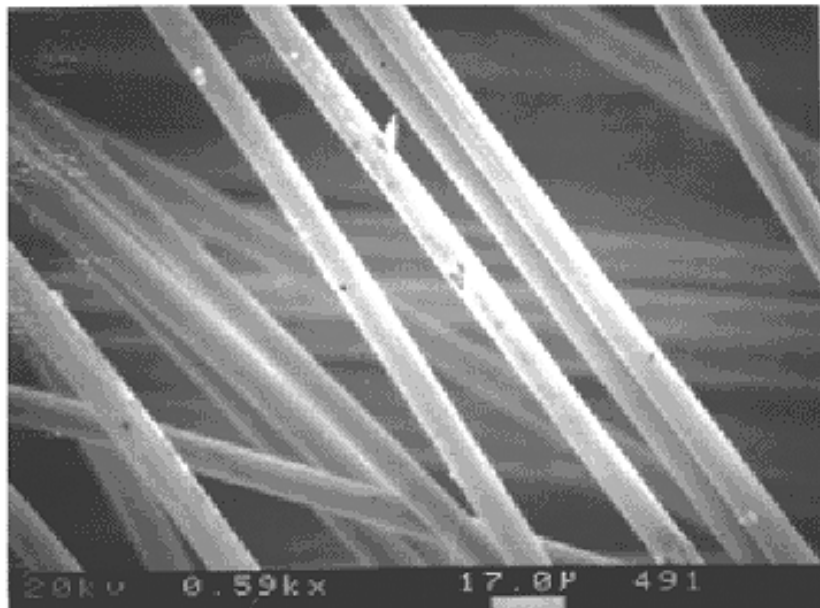
sized fiber was noticeably stiff and rigid when the fiber surface temperature did not exceed 150°C. On the other hand, fiber sized with poly(vinylpyrrolidone) which had been processed above 150°C led to a pliable tow. This pliable tow was more suitable for the subsequent processing operations. Since the  $T_g$  of K-17 poly(vinylpyrrolidone) was 121°C, it was concluded that processing at or above 150°C allowed the poly(vinylpyrrolidone) film to soften and thus evenly coat the individual filaments. Processing the poly(vinylpyrrolidone) below 150°C did not allow the sizing to reach its  $T_g$  and thus prevented the coated fibers from separating from each other due to stresses experienced by the tow during handling in the drying tower. The fibers remained bonded together which resulted in a highly rigid sized fiber. Thus, the fibers sized with poly(vinylpyrrolidone) were processed above their  $T_g$  for the results presented later in this section. The resultant sized fibers showed an extremely smooth surface when examined under SEM (Figure 6a). For the polyhydroxyether sizing, the sized fibers were not completely dried before they were stitched together to make preforms. These preforms were then dried in a convection oven between 150-200°C so that the polyhydroxyether sizing was in the form of films and particles on the fiber surface (Figure 6b). Processing this fiber above its  $T_g$ , resulted in a fiber with a smooth surface similar to that seen with poly(vinylpyrrolidone). When composites were produced from these two sets of polyhydroxyether sized fibers, significant differences were witnessed. The fiber coated with polyhydroxyether particles produced void free composite panels. While composites produced with film coated polyhydroxyether fiber had numerous voids. This resulted in mechanical properties for the particle coated fiber being higher than that for the film coated. For this reason, the mechanical property results for polyhydroxyether sizing material presented later in this paper were processed such that particles adhered to the surface.

#### ***Characterization of Sized Carbon Fibers***

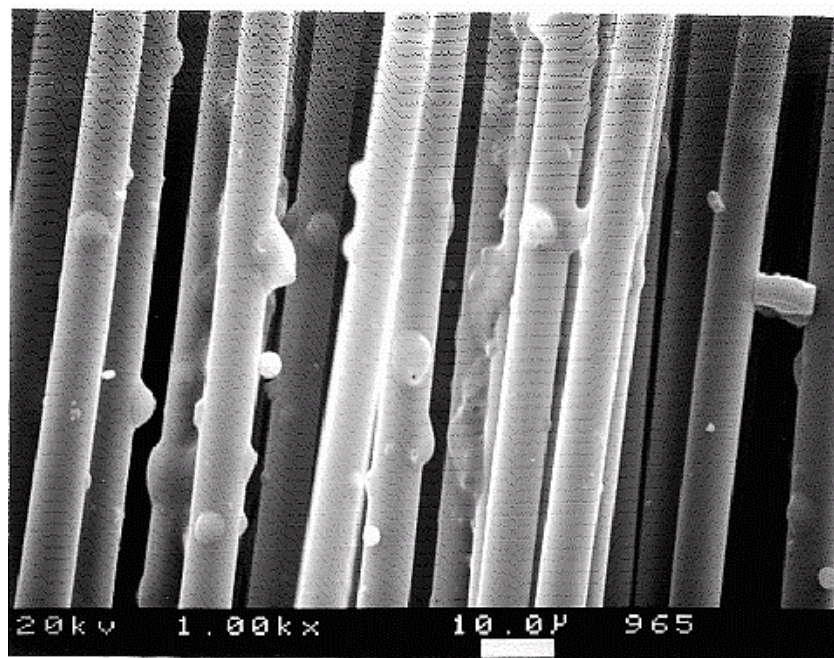
The fibers sized by the process were analyzed via pyrolysis to determine the amount of sizing material present. The K-17 PVP sized fiber coated from a 1.0 wt% sizing solution had a final sizing level of approximately  $0.7 \pm 0.05$  wt%. The polyhydroxyether sized fiber



a)



b)



**Figure 6:** SEM micrographs of (a) sized AS-4 12K with 0.7 wt% poly(vinylpyrrolidone) (b) sized AS-4 12K with 0.6 wt% polyhydroxyether.

## **Composite Panel Production**

### ***Processing***

The three fiber systems described previously (unsized, poly(vinylpyrrolidone), and polyhydroxyether) were processed into composites using the RFI technique. Four sets of unidirectional laminates were prepared for each of the three systems. In addition, four sets of  $[0/90]_{7s}$  laminates were prepared. The resulting composite specimens were analyzed for void content and fiber volume fraction. In these experiments, the composite processing cycle was fixed.

### ***Composite Characterization***

The resin film infusion process produced consistent panels with a low void content as evident from the representative micrograph (Figure 7). The process allowed for the rapid production of numerous composite panels with varying interphase regions.

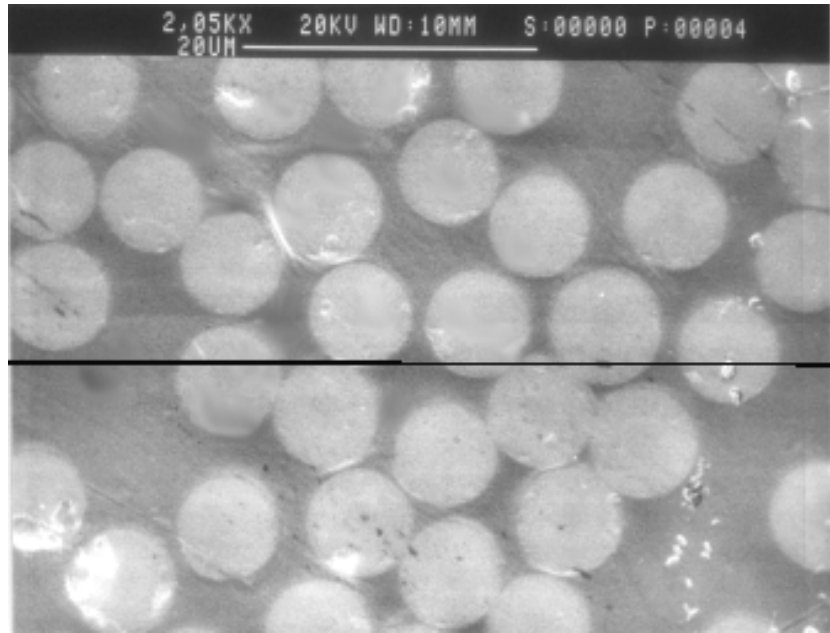
Another strong point of the RFI process was the consistency of fiber volume fraction obtainable (i.e. 58%-61%). For each of the composite panels, fiber volume fraction did not vary significantly within any sizing set and also did not vary significantly between sizing sets. This consistency in fiber volume fraction between composite panels allowed for the direct comparison of mechanical property results without any normalization.

## **Mechanical Testing**

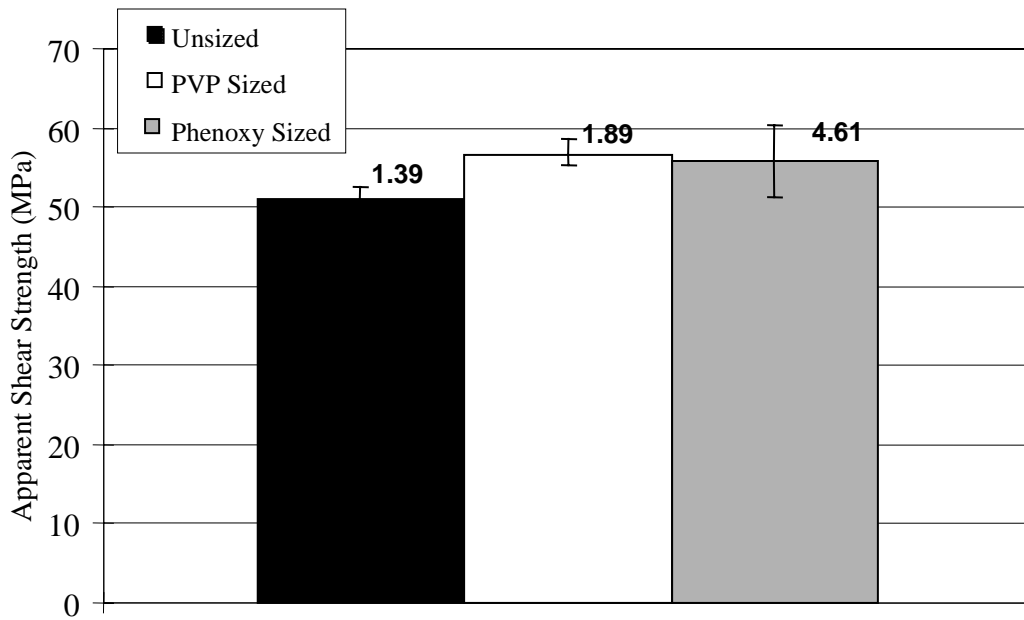
### ***Beam Shear and Transverse Flexure Tests***

Apparent shear strengths were determined for the uni-directional composites produced from unsized, poly(vinylpyrrolidone) sized and polyhydroxyether sized fiber (Figure 8). There was no statistically significant effect of the sizing material on the apparent composite shear strength.

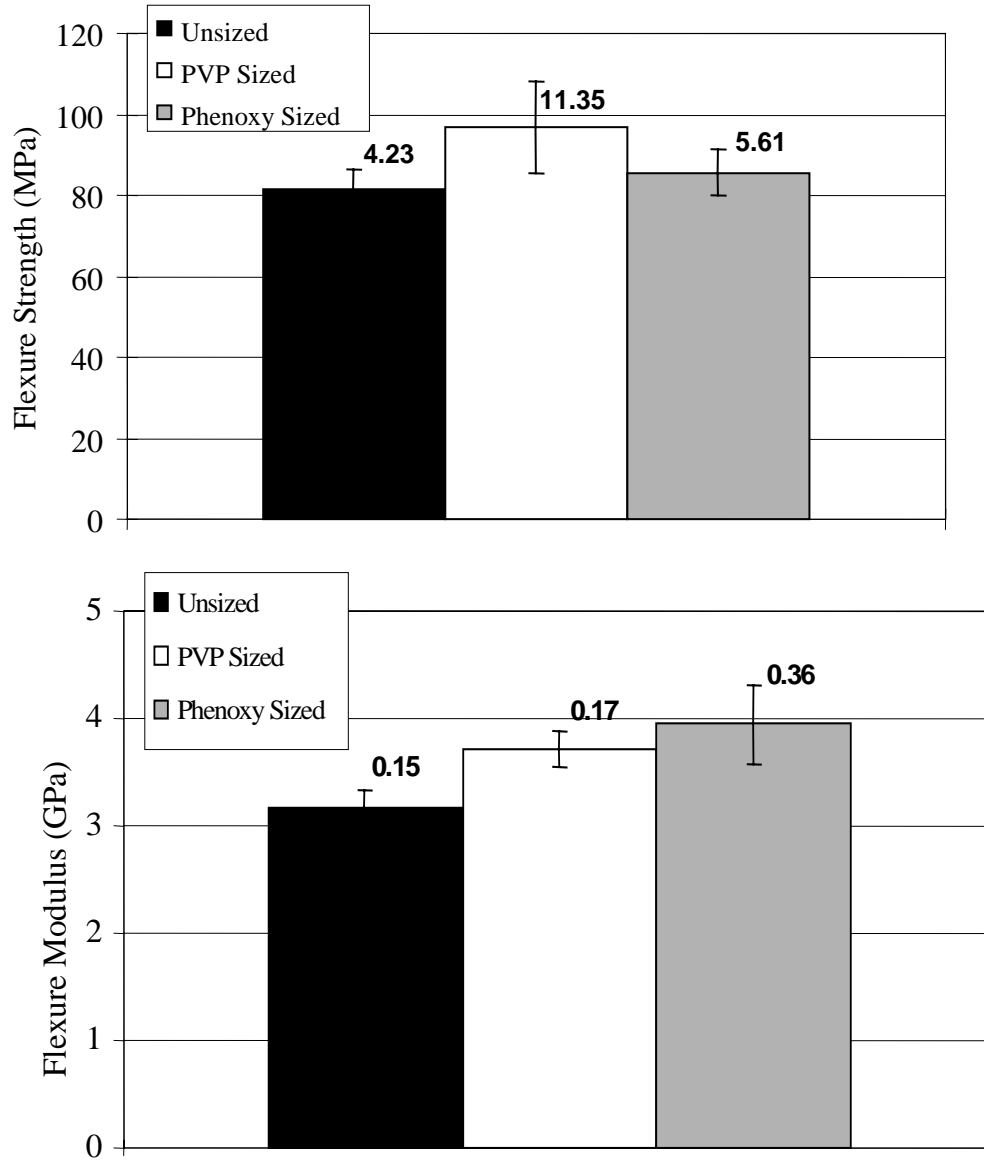
Flexure strength and modulus were determined for the unsized, poly(vinylpyrrolidone) sized, and polyhydroxyether sized fiber composites (Figure 9a and 9b). There was no statistical difference in the flexural *strengths* for the various sizings



**Figure 7:** SEM micrograph of representative cut and polished composite structure.



**Figure 8:** Apparent shear strength comparison plot for various sizing materials. The numbers represent one standard deviation.



**Figure 9:** Flexure (a) strength and (b) modulus plot for various sizing materials.

tested. However, the flexure *modulus* for the composites containing a sizing did show a marked increase over the composite produced from unsized carbon fiber.

The polyhydroxyether showed a 40% increase in flexural modulus and the poly(vinylpyrrolidone) showed a 20% increase compared to the unsized composite panels. The magnitude of the error bars is possibly due to some fiber misalignment that was noticed in the fracture surfaces of the specimens. The sized specimens (Figure 10b) showed a highly organized fiber arrangement wherein they remained stuck to each other by the matrix. In contrast, the fracture surfaces of the unsized specimens (Figure 10a) indicated more bare fibers caused by matrix debonding from the fiber probably due to poor fiber/matrix adhesion.

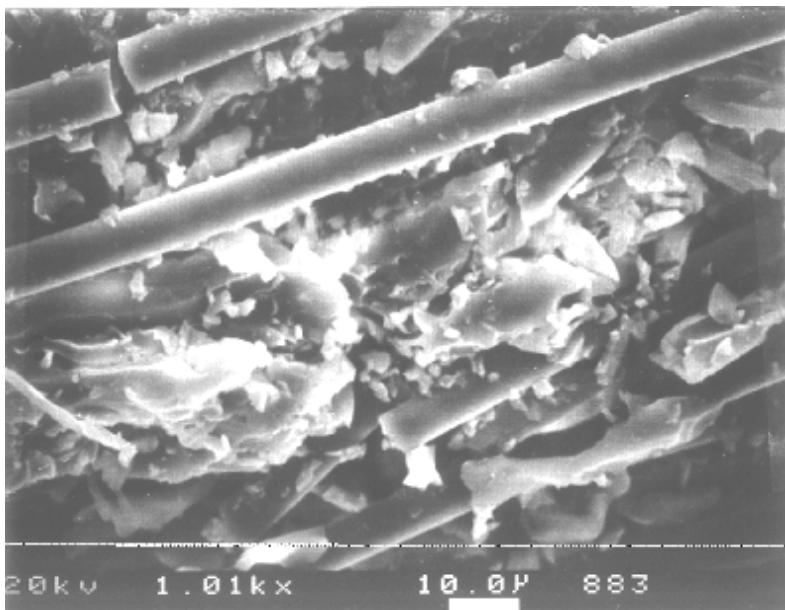
### ***Fatigue and Compression Tests***

The fatigue limit of the composites with poly(vinylpyrrolidone), polyhydroxyether, and unsized interphases was determined (Figure 11). The fatigue limit is defined as the highest load level that can be applied to a specimen in order to achieve a million cycles in fatigue. The stress on the plot was computed based on the ultimate compression strength. Stress levels of 75%, 65%, 55% and 45% were chosen based on the composite in order to get a good idea of the shape of the ‘S-N’ curve. Quasi-static compression strength was determined for the poly(vinylpyrrolidone) sized and polyhydroxyether sized composites (Figure 12). There was no statistically significant effect of the sizing material on the compression strength.

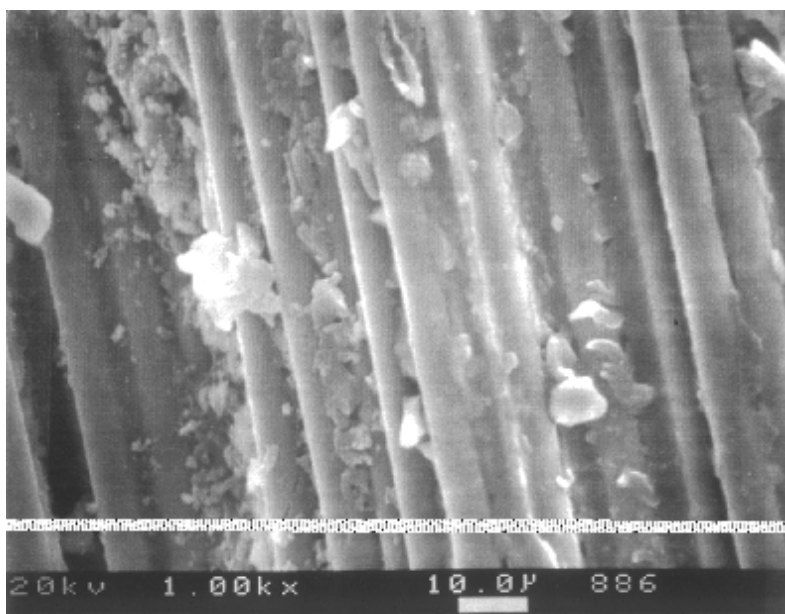
Substantial differences in the fatigue limit were noted between the polyhydroxyether sized material, the poly(vinylpyrrolidone) sized material, and the unsized materials. As seen in Figure 11, the fatigue limit for the polyhydroxyether sized material was about 210 MPa, a 60% improvement in the fatigue limit compared to that for the unsized material, 130 MPa. The fatigue limit for the poly(vinylpyrrolidone) sized material was about 160 MPa, about 20% higher than the limit for the unsized material.

At a given stress level, the type of sizing material had a significant effect on the lifetime of the composites. For example, at a 207 MPa stress level, the composite sized with

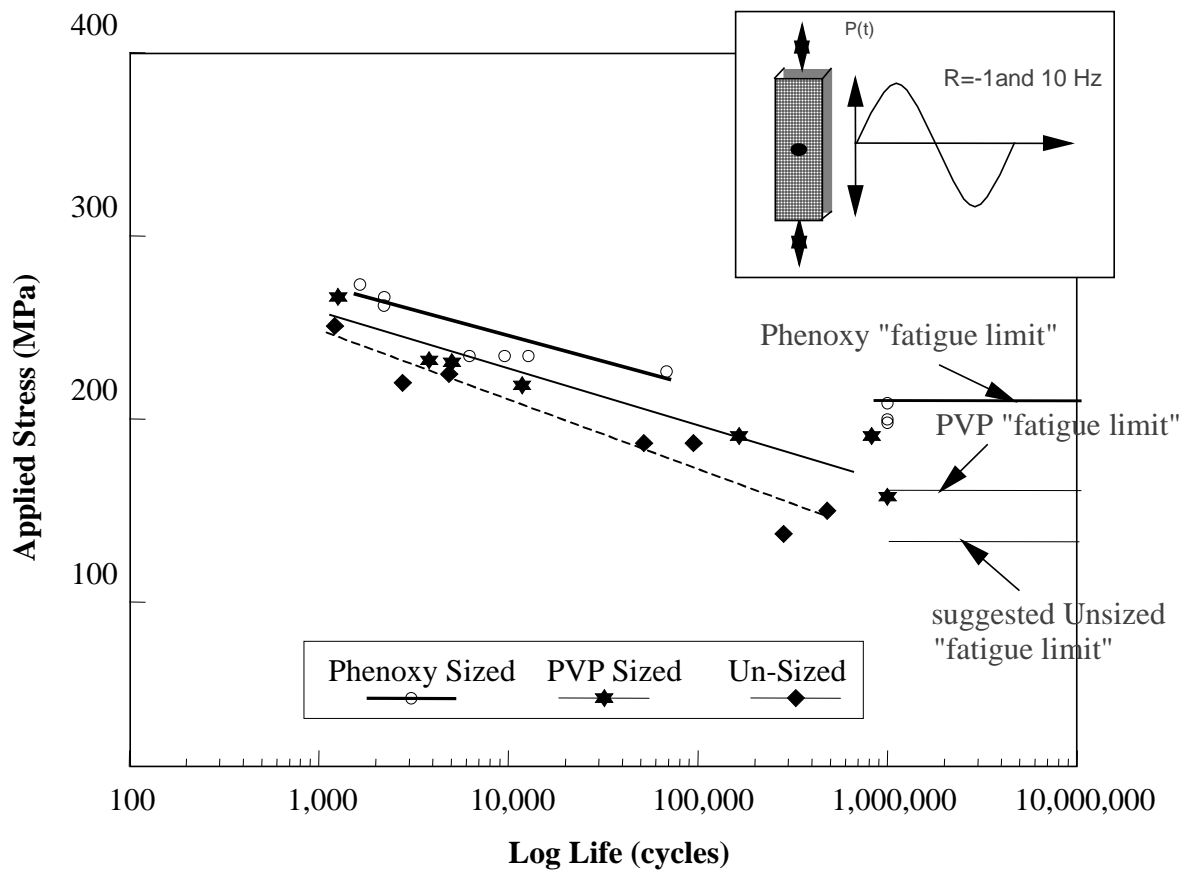
a)



b)

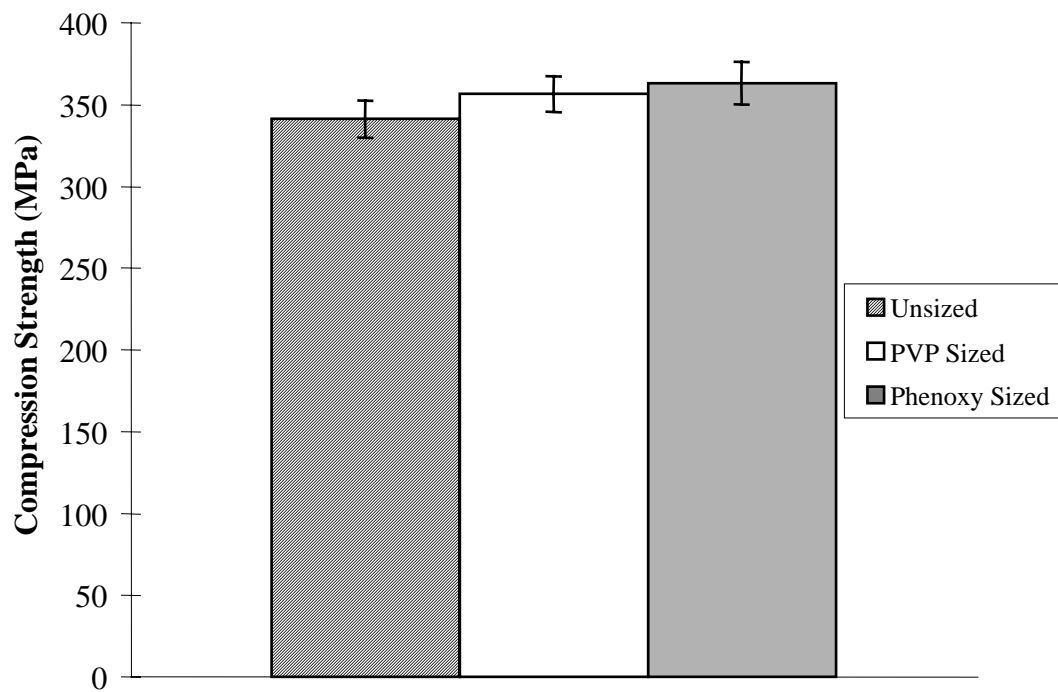


**Figure 10:** Micrograph of (a) unsized and (b) poly(vinylpyrrolidone) sized fracture surfaces.



**Figure 11:** Fatigue Limit 'S-N' Curve for various sizing materials.





**Figure 12:** Quasi-static Compressive Strength for various sizing materials.

polyhydroxyether lasted for 200,000 loading cycles, the composite sized with poly(vinylpyrrolidone) lasted for 50,000 loading cycles, and the unsized material lasted for only 9,000 loading cycles. This drastic difference in the fatigue and the lifetime limits can be explained by the physical nature of the sizings present in the interphase region. The polyhydroxyether was a relatively tough thermoplastic material compared to the more brittle poly(vinylpyrrolidone). Experiments are underway to relate more precisely the sizing material properties to interphase effects at the micro- and macroscales.

## CONCLUSIONS

Carbon fiber-vinyl ester composites were made from sized carbon fibers that were formed into a unidirectional fabric. This fabric was processed into composite panels using a Resin Film Infusion (RFI) technique. Two dissimilar sizing agents were studied - a brittle thermoplastic K-17 poly(vinylpyrrolidone) (PVP) and a ductile thermoplastic polyhydroxyether (Phenoxy Resin). The processing conditions were shown to effect the handling characteristics of the fiber. Processing above  $T_g$  for the poly(vinylpyrrolidone) sizing resulted in a high quality, pliable sized fiber. The polyhydroxyether sizing was processed in such a way as to coat the fiber with a mixture of films and particles. RFI provided a fast and easy way to manufacture consistently good panels with uniform fiber volume fractions and relatively low void content.

Fatigue tests demonstrated clear differences between the two polymeric sizings and the unsized fiber control. Large differences were noticed in the fatigue limit of the composites. The polyhydroxyether sizing resulted in a 60% improvement in the fatigue limit as compared to the unsized composite. The fatigue limit for the poly(vinylpyrrolidone) sized material was about 20% higher than the limit for the unsized material. A 20-fold increase in lifetime was demonstrated at a 207 MPa loading level for the ductile polyhydroxyether sized composite compared to the unsized case. The brittle poly(vinylpyrrolidone) sized composite panel showed a 6-fold increase in lifetime compared to the unsized case. Negligible differences in the shear strength, flexural strength, and static compressive strength were observed for the different interphase agents. To

understand the reason for these effects, it is necessary to understand how damage is initiated and propagated in these materials.

In future work, the interdiffusion of the sizing and matrix material will be measured and used in a model to predict mechanical property gradients across the interphase. Micromechanical modeling <sup>1.9&1.10</sup> can then be used to predict both initiation and propagation of damage in a composite system under a particular loading scheme. It has been shown before <sup>1.11</sup> that the inelastic properties tend to have a larger impact on the micromechanical models than the elastic properties. Once this is done for the different interphases, laminate level responses can then be addressed.