Chapter 6

INTRODUCTION

Carbon fiber composites have traditionally been used in high-end aerospace applications. Presently however, the scenario is quite different, with industries such as offshore oil exploration, civil infrastructure etc. increasing their use of composite materials. In order for composites to find acceptance in civilian markets like infrastructure, the cost of the processing steps and raw materials must be reduced while maintaining or improving their performance. The overall goal of the Designed Interphase Group at Virginia Tech is to improve the performance of continuously reinforced carbon fiber/vinyl-ester composites without increasing their cost.

Pultrusion represents one of the most cost-effective means of rapidly producing continuous fiber reinforced composites with a thermoset matrix. Because civilian markets often require uncomplicated parts of constant cross-section, pultrusion represents one of the most economical means of producing composites for these applications.

Sizings, a thin coating applied to the surface of the carbon fiber before impregnation with the matrix have been shown to affect the mechanical performance of the composite[6.1-6.4]. Even a matrix dominated property like compressive strength can be affected by the sizing constituent[6.5]. A sizing can affect composite performance by altering the processability of the carbon fiber and/or by altering the manner in which load gets transferred from one failed fiber to another. The processability of a carbon fiber is composed of three distinct characteristics: (1) fiber protection (2) fiber alignment and (3) fiber wettability. Unsized carbon fiber is extremely brittle and susceptible to damage. Traditionally, a sizing is placed on the surface of the fiber to protect it from damage. In addition, a sizing can alter the handling characteristics of the tow such as pliability. The pliability of the tow directly influences the fiber alignment/waviness in the final composite. Fiber alignment is an essential parameter in determining composite mechanical performance especially in compression[6.6-6.8]. A sizing also alters the surface free energy of the carbon fiber thus altering the thermodynamic driving force for wetting[6.9]. The manner in which load gets transferred from a failed fiber to surrounding fibers is controlled by two characteristics: (1) fiber/matrix adhesion and (2) graded matrix properties/interphase formation. In the composite community, the term fiber/matrix adhesion is typically quantified by an interfacial shear strength (ISS). However, the physical parameters affecting ISS are not exclusively interfacial. For instance, Cox[6.10] derived a theoretical expression relating ISS to fiber and matrix properties assuming a no-slip fiber/matrix boundary condition. In this classic treatment, the ISS was found to be proportional to the square root of the product of the fiber tensile modulus and matrix shear modulus. Rao and Drzal[6.11,6.12] experimentally confirmed the matrix shear modulus dependence. Therefore, a sizing can alter ISS through modification of fiber properties through enhanced fiber protection, modification of interfacial properties through improvements in fiber/matrix interaction, and modification of matrix properties through matrix plasticastion or interphase formation. An interphase can form from the interdiffusion of the sizing and the matrix that results in a concentration gradient extending radially from the fiber. The interphase ultimately affects the way damage is propagated in the composite system.

Traditionally, on-axis unidirectional composite properties such as 0° tension and longitudinal flexure are thought to be fiber dominated. In other words, the role of the matrix and the interfacial zone are believed to be secondary to the fiber properties. Reifsnider et al.[6.5] derived a theoretical expression for uni-directional tensile and compressive strength as a function of ISS that predicted a maximum in strength at intermediate values of ISS. The trends predicted by this model have been verified by Madhukar[6.2,6.3]. However, the model only predicts a 5% variation in strength as a function of ISS above a critical value of ISS (5 ksi for the conditions tested). Below the critical ISS value, the strength becomes a strong function of ISS. In order to achieve ISS values below the critical ISS, the fiber/matrix adhesion would have to be essentially nonexistent. Due to the compatibility of the matrix and sizing materials tested in this study, it is believed that all the system will have adequate fiber/matrix adhesion. Therefore, any effect on on-axis composite performance will probably not be attributable to variations in fiber/matrix adhesion. This can be verified experimentally by investigating composite fracture surfaces via spectroscopy.

As was discussed above, static compressive strength is also relatively insensitive to changes in ISS above the critical ISS. The static compressive strength of uni-directional composite materials is strongly affected by the fiber properties and the degree of fiber alignment[6.6-6.8]. Fiber waviness has been shown to have a detrimental effect on compressive strength. As will be explained later in the processing section, the thermoplastic nature of the Phenoxy™ and K-90 PVP sizing materials utilized in this study significantly alter the fiber waviness due to their inherent stiffness.

In previous work completed by this author[6.4], Hexcel carbon fibers sized with Phenoxy™ and K-17 PVP were made into composites utilizing a Derakane 441-400 vinyl-ester matrix and a Resin Film Infusion (RFI) processing method. The RFI method can best be described as a "batch" pultrusion where processing related differences between sizing systems are minimized. The results of this study showed that static strength based mechanical properties, both on-axis and off, were not significantly affected by variations in the sizing constituent. However, tensile/compressive fatigue limits were significantly altered by a change in sizing. For instance, a 20-fold increase in lifetime was observed in the Phenoxy™ system compared to the unsized case.

In the present study, Hexcel carbon fibers were sized with Phenoxy™ and K-90 PVP sizing materials and composites were produced from a pultrudable Dow Derakane™ vinyl-ester resin and a small scale pultruder. Comparisons were made with Hexcel carbon fibers sized with the industrial standard sizing G'. The fibers were compared in terms of their pultrusion processability, composite surface finish quality, on-axis mechanical performance, short beam shear, fatigue lifetime, and environmental durability. In addition, a series of fundamental modeling studies were performed to better characterize the phenomenological events associated with a sizing's effect. These included micro-mechanical and interphase formation modeling. The paper presented herein details the processing, composite quality, on-axis mechanical performance, and short beam shear experiments. The remaining sets of experiments and the modeling work will be presented in papers to be published in the near future.

Typically, the industrial composite manufacturer is only concerned with the handling and wetting characteristics of the fiber and isn't concerned with the complex mechanisms of fiber/matrix adhesion. However, the academic community has focused its efforts primarily upon how a sizing effects fiber/matrix interfacial bond strength and interphase formation. The overall objective of this first paper is to determine whether thermoplastic sizing materials optimized for interaction and adhesion with carbon fibers and the corresponding Derakane™ vinyl-ester resin are processable via pultrusion. Because processability of a sized fiber is of paramount importance to the composite manufacturer, the establishment of processability precludes all other criteria for prospective sizing materials developed in academic settings.

EXPERIMENTAL

Materials

Hexcel AS-4 12K unsized carbon fiber (lot # D1317-4C) was sized at Virginia Tech with two different thermoplastic materials: a polyhydroxyether-Phenoxy™ and a K-90 PVP™.

The Phenoxy™ sizing material (PKHW-35 lot # 217013) (Figure 1a) was obtained from Phenoxy Associates, Rock Hill, SC. 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 K-90 PVP sizing material (LUVISKOL lot # 20421501) (Figure 1b) was obtained from BASF. The M_n of this material was 1,250,000 g/mol and it had a Tg of 180°C[6.13].

Hexcel AS-4D G' sized 36K fiber (lot # D1383-5K) was used as the control fiber for these trials. The G' sizing present on this fiber is Hexcel's commercial sizing for the vinyl-ester matrix. The precise chemical structure of the G' is not known but it is known to be an unreacted epoxy oligomer.

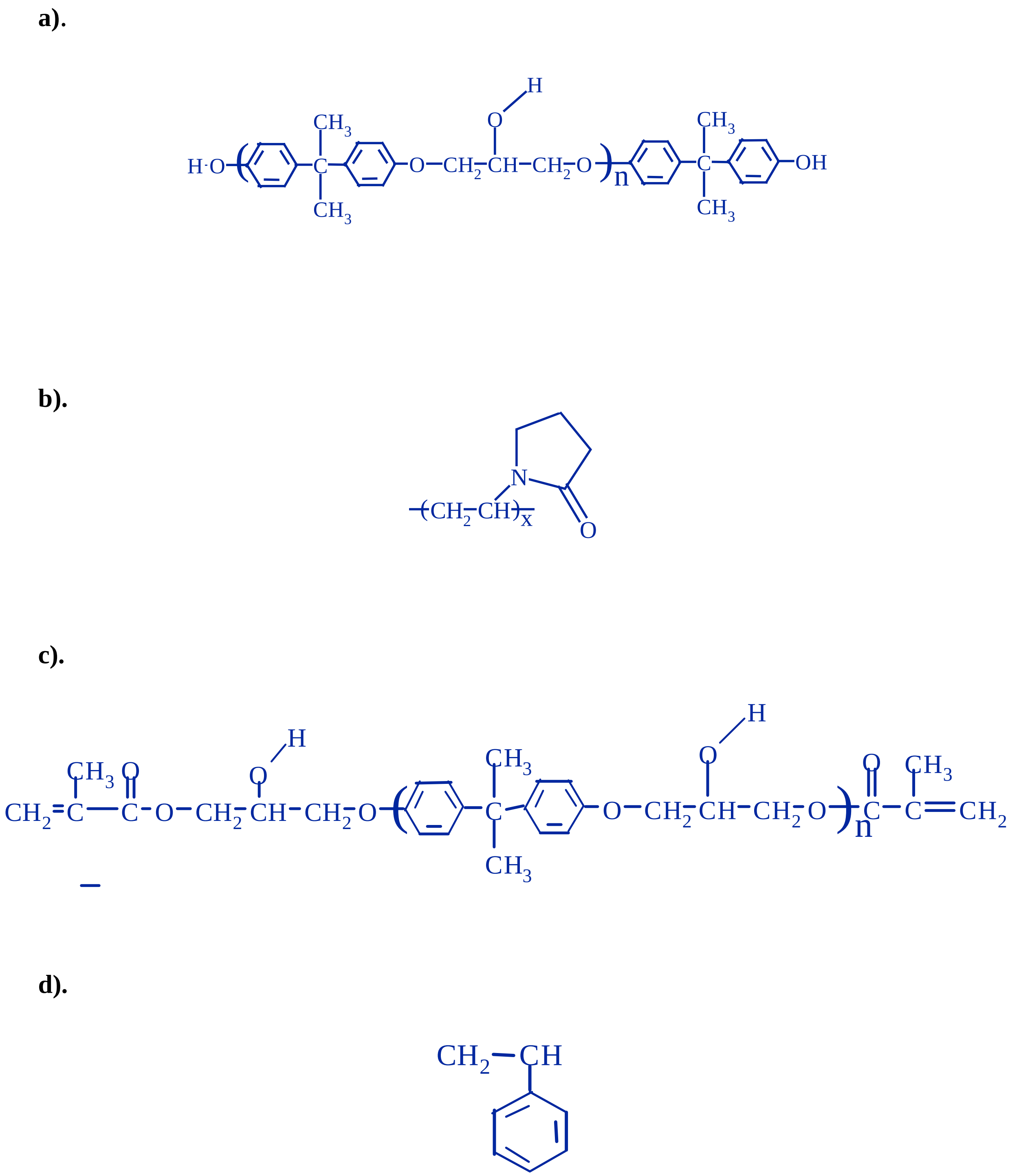

Figure 1 a). Chemical structure of poly(hydroxyether) sizing material. b). Chemical structure of poly(vinylpyrollidone) (PVP) sizing material. c). Chemical structure of vinyl-ester. d). Chemical structure of styrene monomer.

The AS-4D family of carbon fibers utilized for the G’ sizing differs only slightly from the AS-4 family utilized for the thermoplastics sizings (Table 1). The AS-4D family is processed at a higher draw ratio thus decreasing the filament diameter and hence linear density (weight/length). The linear density of the AS-4D is approximately 11% lower than the AS-4. Therefore, less tow ends per 12K bundle of the unsized material were needed to achieve the same fiber volume fraction composite as compared to the G’ sized fiber.

Table 1: Hexcel AS-4 G’ lot # D1383-5K and Hexcel AS-4 unsized lot # D1317-4C carbon fiber mechanical properties.

Hexcel Fiber Type	**G’**	**Unsized**
Lot #	D1383-5K	D1317-4C
Tow Tensile Strength/12K (ksi)	593.8	591.2
Tow Tensile Modulus/12K (msi)	38.1	36.5
Tow SecMod/12K (msi)	35.4	33.8
Tow Strain to Failure/12K (%)	1.56	1.63
Sizing Level (wt%)	0.79	0.00
Linear Density/12K (lb/in)	42.87×10^{-6}	48.16×10^{-6}

Due to the higher draw ratio and improved orientation of the carbon crystals, the AS-4D fiber has a 4% higher modulus (Table 1). The tensile strength is unaffected by the increase in draw ratio. Due to the similarity of the fibers utilized in this study, direct comparisons between the G’ and thermoplastic sized composites could be made after properties were normalized for fiber volume fraction variations. The effect of increased G’ modulus due to the inherent 4% stiffer AS-4D fiber was accounted for in the normalization.

The matrix/resin utilized for pultrusion was a modified Derakane™ 411-35 LI vinyl-ester resin (Figure 1c&d), supplied by the Dow Chemical Company. The pultrudable resin was composed of *approximately* 42 wt% vinyl-ester, 42 wt% styrene monomer, 15 wt% fillers, 0.5 wt% release agents, and 0.5 wt% of a proprietary initiator package. The same resin batch was utilized for all the experimental work presented in this paper.

Deionized water was used to make the sizing solutions/suspensions for the sizing line's dip bath. The deionized water came from a NanoPure II™ unit equipped with a 0.2 μm filter and had a resistivity typically of 15 MΩcm or higher.

Composite specimens were examined with optical microscopy. Before the specimens could be examined utilizing this technique, they had to be mounted in epoxy. The materials utilized to accomplish this potting were Buehler Epoxide resin No.20-8130-032 and Buehler Epoxide Hardener No. 20-8132-032.

Processing

Sizing Solution/Suspension Preparation

Before sizing of the carbon fibers could be conducted, aqueous solutions/suspensions of the sizing materials had to be prepared. In previous work by Broyles et.al[6.4], it was discovered that a sizing level of approximately 1.7 wt% produced good results in a carbon fiber/vinyl ester composite produced via resin infusion molding. For this work, it was decided that this sizing level of 1.7 wt% would be utilized. In order to achieve this final sizing level, the sizing dip bath concentration needed to be approximately 2.0wt%. Therefore, aqueous dip bath solutions/suspensions of 2.0wt% sizing material in deionized water were prepared.

The K-90 PVP sizing material was dried in a convection oven at 110°C for approximately 18 hours before solutions were prepared. Approximately 320g of this dried K-90 PVP was added directly to 15,700g of deionized water. This mixture yielded a 2.0 wt% K-90 PVP in water solution. This solution was then allowed to stir for seven days at room temperature due to the high molecular weight of the K-90 PVP. This solution was then added to the sizing dip bath without further agitation.

The Phenoxy™ material was insoluble in water and was supplied as a 35wt% aqueous suspension. Approximately 143g of the suspension was added to 2360g of deionized water to yield a 2.0 wt% Phenoxy in water suspension. This suspension was allowed to stir rapidly overnight. This suspension was then added to the sizing dip bath and vigorous stirring was applied.

Sized Fiber Preparation

The carbon fibers were sized on a custom made small scale sizing line described in reference[6.9]**.** The unsized carbon fiber tow was pulled off a spool at a set speed ranging from 0.3 to 6.0 cm/sec. The fiber tension was controlled by a nip roller, which was connected to a particle brake. A load cell located at the exit of the sizing dip bath measured the tension. The fibers were then passed through a sizing dip bath that contained the aqueous sizing solution/suspension discussed earlier. In the dip bath, 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 infrared (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. Placement of the thermocouple was such that no background IR interfered with the surface temperature measurement. 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.

The fiber that exited the dryer was pulled through a motorized nip roller where line speed was controlled and line tension was developed. The fiber was then wound onto a standard carbon fiber spool utilizing a constant tension Izumi rewinder. The fibers were then sealed in a plastic bag to prevent moisture from being re-absorbed by the sizing material or the carbon fiber.

Pultrusion

Pultrusion was performed at Strongwell, Inc., utilizing their pilot scale pultruder. Thirty spools of the Hexcel AS-4 12K material sized at Virginia Tech were placed in the creel rack for its processing. Twelve spools of the AS-4 G' 36K material were placed in the creel rack for its processing. The line speed utilized for all trials was approximately 2 feet/minute. The individual tows were directed into the process via a board of perforated Teflon. The fibers were then dipped in the resin bath where the fibers were fully wetted with the resin. After the fibers were pre-formed, they were cured in a die of rectangular cross section.

The die was approximately 30" long and had three zones where temperatures could be monitored and controlled. The three zones were located at the beginning, middle, and end of the die. The first zone required heat input in order to control the surface temperature at approximately 220 °C. The second zone required less heat input to control the surface temperature at 240 °C due to the exotherm associated with the matrix curing. In addition, the third zone required no heat input to control the surface temperature at 240 °C.

After the cure was complete, the composite was air cooled in the roll-out portion of the pultrusion process. The part was then cut utilizing a saw and the final dimension of the composite part was 12.7mm wide by 2.0mm thick by 15.24m long.

Sized Fiber Characterization

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. The fibers were first dried in a convection oven for a period of eight hours. The temperature of the convection oven was set above the T_g of the particular sizing material being tested. After being dried, the fibers were placed in a high temperature Blue-M furnace with a nitrogen purge at a flow rate of approximately 40 cm^3/sec. This led to a purge gas residence time of 30 seconds. Typically 20 minutes were required for heating the chamber from room temperature to the pyrolysis temperature of 600°C. Thus, the pyrolysis chamber typically was purged with gas for about 40 residence times prior to reaching the pyrolysis temperature. This ensured that there was no unwanted oxidation of the carbon fibers. Pyrolysis then proceeded for 30 minutes at 600°C. 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.

Scanning Electron Microscopy (SEM)

The quality of the sized fiber was determined by inspection of the fibers under Scanning Electron Microscopy (SEM). 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. Composite tensile fracture surfaces were also investigated with SEM.

ESCA

Uniformity of the coating was also assessed via ESCA. The sized carbon fiber samples were mounted in a specially designed holder that secured the fibers. The area of examination was about 1mm by 3mm. A survey scan was conducted first to determine the identity of the elements present and then a series of narrow scans were conducted for the primary photoelectron peak of the detected elements. All experiments were conducted utilizing a 400 watt Mg anode.

Composite Characterization

Fiber Volume Fraction

The fiber volume fraction of the composite panels produced in these experiments was determined by two methods. The first method utilized data collected before the composite part was produced and was termed the theoretical fiber volume fraction. The second method utilized data collected after the composite part was produced and was termed the experimental fiber volume fraction.

For the first method, the number of tow ends and their respective linear density allowed the determination of the volume of fiber per unit length entering the pultrusion die. The fiber volume fraction could then be computed from the following equation.

$$\nu_f = (n \cdot l_f)/(A_c \cdot \rho_f) \qquad (2)$$

Where, ν_f is the fiber volume fraction, n is the number of tow ends, l_f is the weight per unit length per bundle, A_c is the cross-sectional area of the composite, and ρ_f is the filament density. The cross-sectional area of the composite, A_c, was determined from the die cross-sectional area (neglecting matrix shrinkage) or from the final composite cross-sectional area (including matrix shrinkage). This method neglects the mass of fiber lost in the pre-processing portions of the pultrusion process, which is negligible in most cases.

For the second method, the density of the composite was determined and a rule of mixtures was used to determine the fiber volume fraction. 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

$$\rho_{composite} = W_{air}/(W_{air} - W_{IPA})\,\rho_{IPA} \qquad (3)$$

Where, $\rho_{composite}$ is the density of the composite, ρ_{IPA} is the density of Isopropyl alcohol, W_{air} is the weight of sample in air and W_{IPA} is the weight of sample in isopropyl alcohol. The fiber volume fraction was then calculated using the rule of mixtures

$$\nu = (\rho_{composite} - \rho_{resin})/(\rho_f - \rho_{resin}) \qquad (4)$$

Where, ν is the fiber volume fraction of the composite, $\rho_{composite}$ is the density of the composite calculated from equation (2), ρ_f is the density of the carbon fiber and ρ_{resin} is the density of the cured resin. Equation (3) assumes that the composite has zero void volume. The difficulty in applying equation (3) is that the resin density, ρ_{resin}, is not known exactly. However, if it is treated as a constant between the different fiber systems, then fiber volume fraction comparisons can be made.

Visual Inspection of the Cut Composite

Composite specimens for mechanical testing were cut using a Felker table saw. The cut specimens were examined visually for defects. This included looking for dry fibers at the cut end of the sample, surface roughness, carbon deposit in the cutting water etc.

Optical Microscopy

Voids and fiber packing structure in the pultruded composites were analyzed using an Olympus Optical Microscope. Sections of the composite panel were cut and placed in a potting cup. Buehler epoxy 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 8 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.

Ultrasonic C-Scan

As a quality control step, linear ultrasonic C-scans were performed on all the composite materials. These tests were performed on a Sonix HS1000 HiSPEED instrument. A 15MHz, 32mm. focal length sensor was used. Data was analyzed using the FlexSCAN-C software provided with the instrument. The scans were gated both to the midplane as well as the bottom surface of the specimens.

MECHANICAL TESTING

Tension Tests

Quasistatic tension tests were performed on all the composites to assess the tensile strength, modulus and strain to failure. These tests were performed on a servo-hydraulic

MTS test frame in load control mode. A loading rate of 200 pounds per second was applied. This loading cycle was programmed into the Microprofiler™, which controlled the machine once a test was begun. A pair of MTS, 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. 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. The total specimen length was 15.24 cm and a gage length of 5.08 cm was used. In order to protect the specimens from crushing inside the grips, high pressure laminated glass-epoxy tabs were adhesively bonded to the specimens. A special fixture was used to align the tabs and specimens prior to bonding. Both, the tabs as well as the specimen surfaces to be bonded were grit blasted in order to prepare the surface for bonding and a two-part epoxy (3M's DP40) was used as the adhesive. The adhesive was cured in an oven for 1 hour at 50°C under load so as to prevent any movement. 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. The signal from the extensometer was amplified using a 2310 Vishay Measurements Group amplifier box. The knife-edges on the extensometer were made to rest in the aluminum tabs on the specimen and fastened via rubber bands. These aluminum tabs were bonded on the specimen using a silicone (GE 2310 RTV) adhesive. LabView® software was used to monitor the load, stroke and strain signals during the tests.

Flexure and Short Beam Shear Testing

Flexure tests were performed in accordance with ASTM D790-90[6.14]. Specimens were cut using a Felker cutting saw using water as a coolant. The specimens were 30 mm long by 2 mm thick. The specimens were mounted in a three-point bend fixture and loaded at a rate of 0.8 mm/min by an Instron 4104 test frame.

Short beam shear tests were performed in accordance with ASTM D 2344-84[6.15]. The specimens were 11 mm long by 2 mm thick. The specimens were mounted in a three-point bend fixture and loaded at a rate of 1.3 mm/min by an Instron 4104 test frame.

For both tests, a 5KN load was used to monitor load and LabView®, a National Instruments Corporation data acquisition software, was used to monitor load versus displacement.

Compression Testing

In-plane compressive properties were evaluated by performing compression tests in accordance with ASTM 3410[6.16]. This test introduces the compressive load into the specimen through shear at the wedge grip interface. An Illinois Institute of Technology Research Institute, IITRI compression test fixture was used. Meticulous care was take to ensure that the surfaces of the specimens were parallel to each other, which is a requirement by the standard. In order to achieve this, specimens 15.24 cm long were placed in a fixture and two 7 cm long tabs were surface treated and bonded on one side. The specimens were then ground in the machine shop in order to maintain a reference surface. The second sets of tabs were then bonded on and final grinding was done both on the surfaces and the edges. A gage section of 1.27 cm was used which was considered to be short enough to prevent Euler buckling at the same time, long enough to allow for the decay of stresses to uniaxial compression and minimize Poisson restrain effects due to the grips. Next, strain gages (type: CEA 06 125 UN-350) from Micromeasurements™ were glued on the front and back surfaces of the gage section. This is required by the standard in order to compare front and back surface strains during the test to check for bending. A 100 KN, Instron load-frame along with a 100 KN load cell was used for the tests. A cross-head displacement rate of 1.5 mm/minute was used in accordance with the standard. Each specimen was carefully inserted into the rectangular wedges with the help of an alignment cradle that was held between the faces of a bench top vice. A torque of 150 inch-pound was used to tighten the faces of the wedges onto the specimen tabs. The strain gage lead wires were then hooked up to the amplifier box and the strains zeroed. The specimen and the wedges were then gently lifted off the cradle and lowered into the bottom wedge housing assembly of the IITRI fixture, which rests on the lower platen of the test frame and contains a mating wedge cavity. Next, the top wedge housing assembly was lowered carefully to make contact with the second set of wedges. The downward motion continued until failure of the specimen. Perfect alignment was ensured apriory, and was checked for each test by closely monitoring the strains. Once again, LabView®, a National Instruments Corporation data acquisition software, was used to monitor load, front surface strain and back surface strain and displacement against each other.

Normalization for Fiber Volume Fraction Variation

Before comparisons could be made between composite systems, the mechanical properties had to be normalized with respect to fiber volume fraction. The type of normalization used in this section was a rule of mixtures expression that neglected the mechanical response of the matrix. Even though this type of normalization does not rigorously apply to strength based properties where statistical events control the failure, it will still be reasonably accurate for the fiber volume fraction variation observed in these composites. The equation utilized for the normalization was as follows,

$$\sigma_c{}^n = \sigma_c{}^o \cdot \left[\frac{\nu_f{}^n}{\nu_f{}^o} \right] \cdot R \qquad (5)$$

Where σ_c^n is the normalized property (strength or stiffness) at a fiber volume fraction equal to ν_f^n (in all cases, ν_f^n was set equal to 0.656 or the theoretical fiber volume fraction of the G' sized composite), ν_f^o is the original fiber volume fraction of the composite to be normalized, σ_c^o is the original property (strength or stiffness) at a fiber volume fraction equal to ν_f^o, and R is the ratio of the inherent strength or stiffness of AS-4D G' sized fiber to the inherent strength or stiffness of the AS-4 unsized fiber. The value of R is approximately equal to 1.00 (593.8 MPa/591.2 MPa) when the property being normalized is a strength based property. The value of R is approximately equal to 1.04 (38.1 GPa/36.5 GPa) when the property being normalized is a modulus based property. Strain-to-failure values were not normalized due to a lack of knowledge of how to properly complete the normalization.

RESULTS AND DISCUSSION

Processing

Sized Fiber Preparation

In order to completely dry the sized fiber in the sizing line's forced convection dryer, a surface temperature above the sizing materials T_g was needed. In addition, processing the material above its T_g allowed the sizing to soften and fully encapsulate the carbon fiber. For instance, a Phenoxy™ sizing processed below its T_g (< 97°C) resulted in a fiber coated with particulates (Figure 2a). These particulates were merely the 1 micron particles that were originally dispersed in the sizing dip bath suspension. However, if the surface temperature greatly exceeded the Phenoxy's T_g, then a smooth fiber surface was developed (Figure 2b). For the Phenoxy™ sizing, the optimal fiber surface temperature was found to be above 200°C (Figure 2b). As will be discussed later, this temperature was sufficient to completely dry the fiber. Two different processing techniques were utilized for the Phenoxy™ material, which resulted in two different forms of the Phenoxy™ sized fiber. One form was a high-spread Phenoxy™ (HSP) and the other was a low-spread Phenoxy™ (LSP). The HSP sized fiber had a width twice that of the LSP. It was felt that the higher spreading would lower the resistance to tow wetting and hence enhance its processability. The higher degree of spreading was achieved by placing a high temperature blower at the sizing dip bath exit. This allowed for quicker drying which allowed less time for the wet fiber to contract under the forces of surface tension. For the case of fiber sized with K-90 PVP ($T_g \approx 180$°C), the optimal fiber surface temperature was found to be above 200°C. As will be discussed later, this fiber surface temperature resulted in a fiber that had negligible moisture content. This surface temperature was also sufficient to allow the K-90 PVP to fully encapsulate and uniformly coat the carbon fiber (Figure 3). The K-90 PVP sized fiber had a width approximately equivalent to the HSP. The processing parameters used to produce the sized fibers utilized in this study are noted (Table 2).

Pyrolysis of these sized fibers showed that the LSP material had a final moisture content of 0.05 ± 0.02 wt% and a sizing level of 1.56 ± 0.07 wt% (Table 2). The HSP

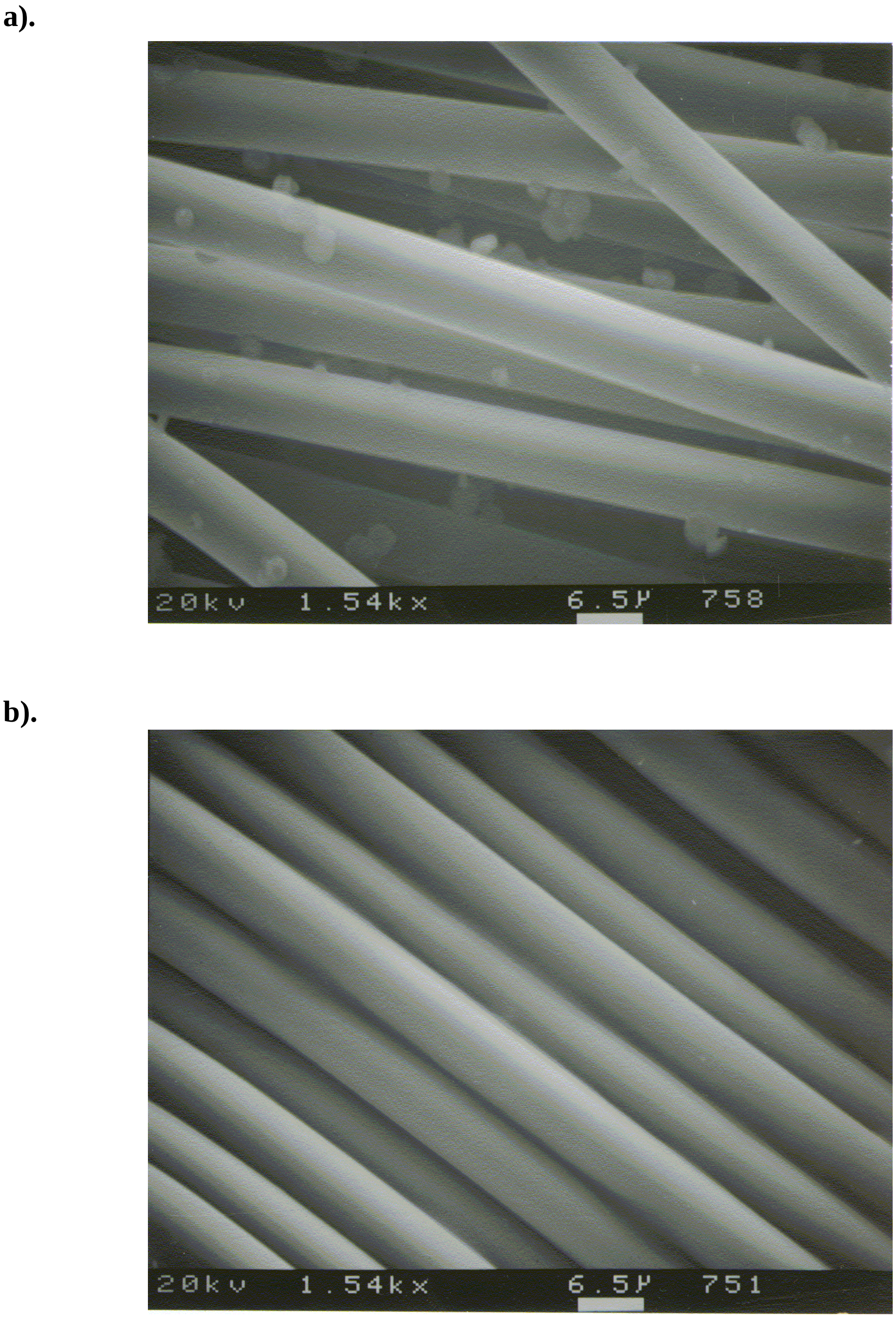

Figure 2 a). Phenoxy particulate sized Hexcel AS-4 12K. Note: Surface temperature did not exceed 97°C or Phenoxy's glass transition. b). Phenoxy film sized Hexcel AS-4 12K. Note: Surface temperature exceeded 97°C or Phenoxy's glass transition.

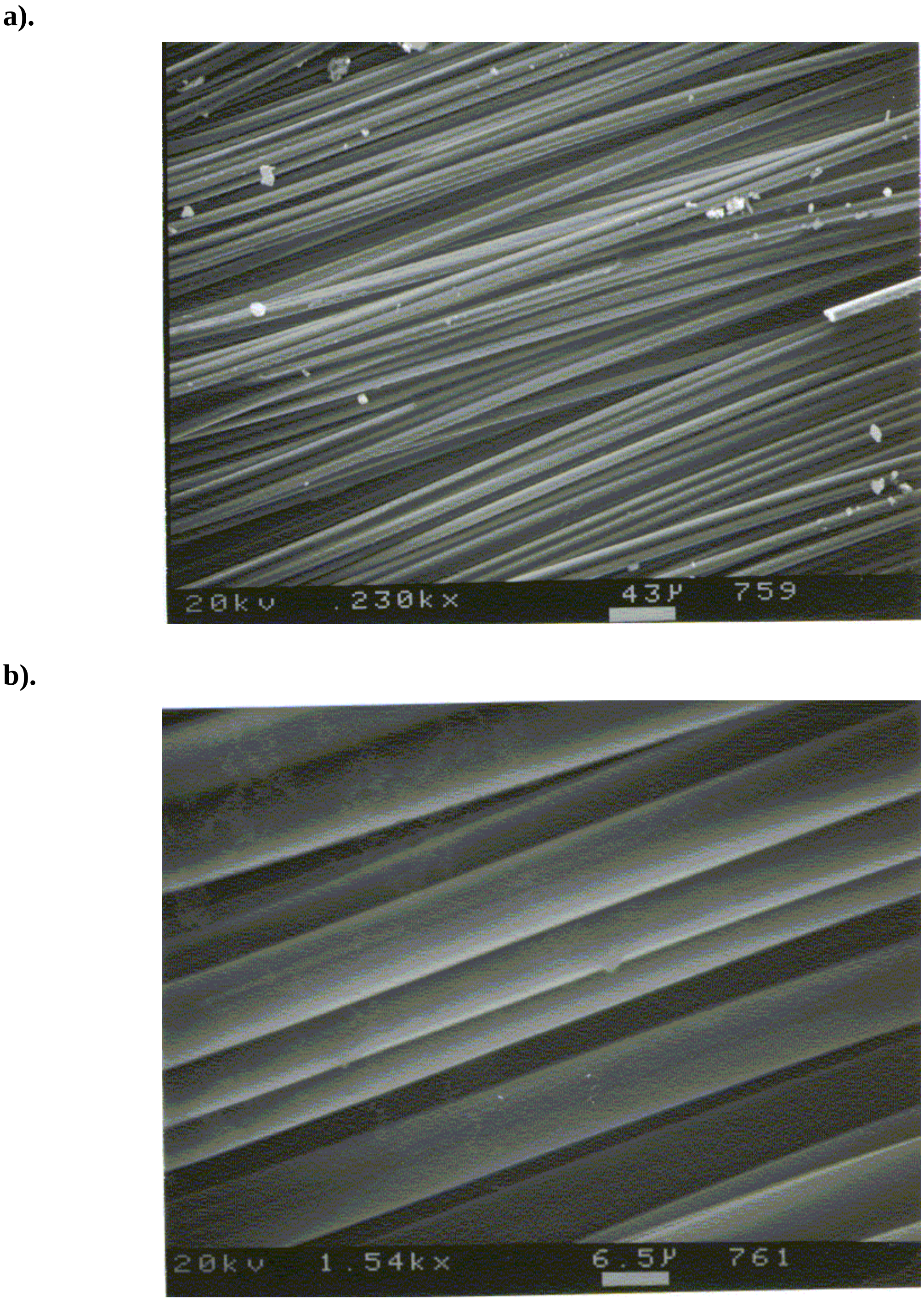

Figure 3 K-90 PVP sized Hexcel AS-4 12K (≈ 1.97 wt%). Note: Surface temperature exceeded 200°C. a). 230 X Magnification b). 1540 X Magnification.

Table 2: Processing parameters used to produce the sized fibers utilized in this study. In addition, sizing characterization information also displayed

Sizing System	**Low Spread Phenoxy**	**High Spread Phenoxy**	***K-90 PVP***
Dip Bath Concentration (wt%)	2.0	2.0	2.0
Auxillary Heat Blower On (Yes/No)	No	Yes	Yes
First IR Heating Panel (°C)	400.0	400.0	415.0
Second IR Heating Panel (°C)	400.0	400.0	415.0
Main Heat Blower On (Yes/No)	No	No	No
Maximum Fiber Surface Temperature (°C)	215.0	225.0	245.0
Line Tension at Dip Bath Exit (lbs)	2.30	2.30	2.30
Tension Setting onto Spool	2.0	2.0	2.0
Approximate Width of Sized Fiber (in.)	1/8	¼	¼
Fiber Moisture Content (wt%)	0.05 ± 0.02	0.13 ± 0.16	0.24 ± 0.06
Dry Fiber Sizing Level (wt%)	1.56 ± 0.07	2.90 ± 0.26	1.97 ± 0.07

material had a final moisture content of 0.13 ± 0.16 wt% and a sizing level of 2.90 ± 0.26 wt%. The K-90 PVP material had a final moisture content of 0.24 ± 0.06 wt% and a sizing level of 1.97 ± 0.07 wt%. The low levels of moisture (<0.30 wt%) indicated that the drying conditions were sufficient to completely dry the fiber. In addition, the low standard deviations on the sizing level indicated the consistency of the sizing process.

ESCA was completed on all the sized fibers utilized for the pultrusion trials (Table 3). In all cases, the theoretical sizing thickness was significantly greater than the penetration depth of the ESCA. In addition, ESCA was completed on the Phenoxy™ and K-90 PVP sizing materials (Table 3). The unsized Hexcel AS-4 carbon fiber surface had an atomic element composition of 88.36% carbon, 8.03% oxygen, and 3.60% nitrogen. The Hexcel G' sized AS-4 carbon fiber surface had an atomic element composition of 84.59% carbon and 15.41% oxygen.

Table 3: ESCA results for Hexcel AS-4 carbon fibers sized with various agents. ESCA results for pure sizing materials are also shown.

Element (%)	**C1s**	**O1s**	**N1s**	**Na1s**	**Si2p**
Unsized Hexcel AS-4	88.36	8.03	3.60	0.00	0.00
G' Sized Hexcel AS-4	84.59	15.41	0.00	0.00	0.00
Pure Phenoxy	81.17	18.29	0.00	0.00	0.54
LSP Sized Fiber	87.10	10.83	2.06	0.00	0.00
HSP Sized Fiber	85.92	11.58	2.49	0.00	0.00
Pure K-90 PVP	76.32	12.52	11.16	0.00	0.00
K-90 PVP Sized Fiber	78.62	11.32	10.07	0.00	0.00

This was an indication that the surface of the G' sized material was completely covered with the oligomeric epoxy sizing because nitrogen was no longer detected. The chemical structure of the Phenoxy™ indicates that this material should contain no nitrogen. The ESCA trace on the pure Phenoxy™ sizing material verified this hypothesis. Therefore, if the surface of the carbon fiber were completely covered with the Phenoxy™ material, then no nitrogen should be present on the surface.

The ESCA traces of both the LSP and HSP sized fibers showed some presence of nitrogen (LSP: 2.06% N HSP: 2.49% N) indicating incomplete surface coverage. There were no apparent differences in the surface atomic element composition between the LSP and HSP sized fibers. In both the cases, the Phenoxy™ sizing did not completely cover the Hexcel carbon fiber surface. The pure K-90 PVP sizing material's ESCA trace showed an atomic composition of 76.32% carbon, 12.52% oxygen, and 11.16% nitrogen. The K-90 PVP sized Hexcel fiber showed a similar atomic surface composition of 78.62% carbon, 11.32% oxygen, and 10.07% nitrogen. Therefore, it can be safely concluded that the K-90 sizing material completely covered the Hexcel fiber.

Pultrusion

As was noted in the experimental section, pultrusion of the Hexcel AS-4 G' material was conducted on Day 1 of the trial. During the processing of the G' sized material, it was noted that the carbon fibers were not protected sufficiently by the G' sizing. The guide and spreader bars damaged the fiber extensively. At the entrance to the resin dip bath, the fibers were compacted between stationary metal bars. The goal of these bars was to force the cylindrical G' tow into a tape configuration that would minimize tow wet-out time. This resulted in tremendous fiber damage and build-up on the dip bath entrance. The extensive fiber fraying and damage that resulted upstream was further exaggerated by the compaction experienced at the die entrance. The resulting composite had a surface finish that was rough and very diffractive to light. Also, fiber breaks and fiber kink-bands could be readily observed in the composite.

Pultrusion of the LSP was conducted on Day 2 of the trials. During the loading of the spools onto the creel rack, it was noted that the Phenoxy™ sized fiber was very stiff and difficult to keep on its respective spool due to memory effects of the high T_g sized fibers. However, after tension was applied to the spools, the Phenoxy™ sized fiber processed efficiently. Because of its stiff and spread configuration, the Phenoxy™ sized fiber displayed no fraying as was observed and is customarily observed with the standard

G’ sizing. Significant fiber loss and damage always occurs with the G’ system because of its cylindrical and soft nature. In addition, because of the inherent compatibility of the Phenoxy™ sizing with the vinyl-ester matrix, rapid wetting of the fibers was observed. The Phenoxy™ sized fiber, protected by the tough thermoplastic sizing, entered the resin dip bath in a spread/tape configuration, minimizing the resistance to wet-out and minimizing the damage caused by the static spreader bars. The Phenoxy™ sized fiber exited the resin dip bath saturated with resin and with no fiber damage as a result of fraying. Also, the fibers were now more pliable as a result of the vinyl-ester matrix possibly softening the thermoplastic Phenoxy™ sizing. The compatibility of the Phenoxy™ sizing with the vinyl-ester matrix may have allowed the Phenoxy™ sizing to swell and relax thus making it more rubbery. The composite that exited the pultruder die had a very different surface finish compared to the Hexcel G’ sized fiber composite. The LSP sized composite had a very smooth surface finish. In addition, the surface appeared very glassy and had no traces of fiber breakage. The internal fibers appeared parallel to the processing direction and no-kink bands were apparent.

Pultrusion of the HSP and the K-90 PVP was conducted on Day 3 of the trials. These materials processed very similarly to the LSP processed on Day 2. The thermoplastic nature of these sizing materials provided a stiff fiber before the resin dip bath and a pliable/rubbery fiber after the dip bath. The resulting composites also had a smooth and glassy surface.

Composite Characterization

Fiber Volume Fraction

The theoretical composite fiber volume fraction was computed for all four fiber systems. Utilizing equation (2) and the corresponding G’ sized AS-4 linear density (Table 1) and fiber density (ρ_f = 1.78 g/cm^3), the G’ sized AS-4 composite had a theoretical fiber volume fraction of approximately 65.6%. Utilizing equation (2) and the corresponding unsized AS-4 linear density (Table 1) and fiber density (ρ_f = 1.78 g/cm^3), the thermoplastic sized AS-4 composites had a theoretical fiber volume fraction of approximately 61.1%.

Table 4: Summary of Results

Property	**G’**	**LS Phenoxy**	**HS Phenoxy**	**K-90 PVP**
Sizing Level (wt%)	0.79[4]	1.95 ± 0.07	2.90 ± 0.26	1.97 ± 0.07
Fiber Volume Fraction[1] (%)	65.6	61.1	61.1	61.1
Fiber Volume Fraction[2] (%)	68.0 ± 0.3	65.0 ± 0.6	61.1 ± 0.6	63.9 ± 0.2
Tensile Strength (MPa)	1673 ± 39	2035 ± 35	1940 ± 72	1964 ± 71
Normalized[3] Strength (MPa)	1673 ± 39	2185 ± 38	2083 ± 77	2109 ± 76
Tensile Modulus (GPa)	120.3	n.a.	105.0	113.3
Normalized[3] Modulus (GPa)	120.3	n.a.	121.7	125.2
Strain-to-Failure (%)	1.47 ± 0.08	1.41 ± 0.09	1.08 ± 0.46	1.33 ± 0.11
Normalized STF (%)	n.a.	n.a.	n.a.	n.a.
Flexure Strength (MPa)	983 ± 67	1186 ± 28	1091 ± 41	1113 ± 20
Normalized[3] Strength (MPa)	983 ± 67	1274 ± 30	1171 ± 44	1195 ± 22
Flexure Modulus (GPa)	102.3 ± 3.4	95.7 ± 1.0	95.1 ± 1.6	94.2 ± 1.2
Normalized[3] Modulus (GPa)	102.3 ± 3.4	106.9 ± 1.1	106.2 ± 1.9	105.1 ± 1.3
SBS Strength (MPa)	43.0 ± 1.4	61.6 ± 0.6	55.5 ± 2.1	55.6 ± 0.3
Normalized[3] Strength (MPa)	43.0 ± 1.4	66.1 ± 0.7	59.6 ± 2.3	59.7 ± 0.3
Compressive Strength (MPa)	747 ± 110	913 ± 98	n.a.	932 ± 84
Normalized[3] Strength (MPa)	747 ± 110	980 ± 105	n.a.	1000.5 ± 90
Compressive Modulus (GPa)	136 ± 13	121 ± 13	n.a.	116 ± 15
Normalized[3] Modulus (GPa)	136 ± 13	135 ± 14	n.a.	130 ± 17

[1] *Theoretical fiber volume fraction determined from fiber denier and density.*

[2] *Calculated from density determination after composite fabrication.*

[3] *Normalized to 65.6% fiber volume fraction from the theoretical fiber volume fraction plus correction for differences in the inherent fiber properties.*

[4] *Data supplied by Hexcel.*

The experimental composite fiber volume fraction was computed for all four fiber systems. Utilizing a cured resin density of 1.16 g/cm^3, this method determined the pultruded composites to have fiber volume fractions that ranged from 61% to 68% (Table 4). The G', LSP, HSP, and K-90 PVP sized composites had fiber volume fractions of 68.0 ± 0.3%, 65.0 ± 0.6%, 61.1 ± 0.6%, and 63.9 ± 0.2% respectively.

Within a fiber/sizing system, the pultrusion process produced composites with a very consistent fiber volume fraction as indicated by the low standard deviations. Because the equivalent of thirty-six 12K tows were utilized for the G' pultrusion and thirty 12K tows were utilized for the other systems (ignoring the differences in linear density between the lots), it was not surprising that the G' system had a considerably higher fiber volume fraction. It was surprising that the HSP experimental fiber volume fraction of 61.1% was so much lower than that of the LSP and the K-90 PVP (65.0% and 63.9%). Because the HSP contained such a high sizing level (2.9 wt%), it is believed that excess Phenoxy™ prevented the vinyl-ester resin from fully penetrating the tow. This left a larger degree of void space that compromised the integrity of the rule of mixtures calculation expressed by equation (4). If the cured resin density could accurately be determined, then the void volume could be calculated from the theoretical composite fiber volume fraction and a modified rule of mixtures that included an air phase in the contribution.

Before mechanical property results could be compared between the various systems, normalization with respect to the theoretical fiber volume fraction was completed.

Visual inspection of cut sections of the pultruded composites revealed a dramatic difference in composite cross-section quality. Upon cutting the composites for mechanical testing, differences were again noted. The G' sized composite system produced a large quantity of dust when cutting was undertaken. The cut G' cross-section displayed numerous dry carbon fibers and was quite rough. The Phenoxy™ (both LSP and HSP) and K-90 PVP sized composite systems cut like a brittle glass and produced no carbon fiber dust during the cutting stage. The cut Phenoxy™ (both LSP and HSP) cross-section was clean and very smooth. The visual observations made both before and after the cutting step reinforced the observations made during the pultrusion trials. The

Phenoxy™ (both LSP and HSP) and K-90 PVP sizings produced a composite with improved fiber wet-out and less fiber breakage.

Optically micrographed cross-sections of the pultruded composites showed some interesting differences amongst the various sizings (Figure 4, 5, 6, and 7). The G' sized composite cross-section showed an extremely uniform fiber distribution (Figure 4) which was an indication of good inter-tow consolidation. No resin rich or poor regions were readily visible. This was also the case for the LSP sized composite (Figure 5). Again, this was an indication of extremely good inter-tow consolidation. However, the HSP sized composite had extensive resin rich and poor regions (Figure 6). The various resin rich areas appeared to form lines that existed parallel to one another. The fiber rich areas had a geometrical shape and size very similar to that of the sized fiber tow that entered the pultruder die. This was an indication of poor inter-tow consolidation. The thick (2.9 wt%) Phenoxy sizing on each of the tow strands prevented the individual tows from inter-consolidating. Although not apparent in the optical micrographs, a large amount of air voids could be present on the inside of the tow because of the thick Phenoxy coating resident on the outside. This was hypothesized earlier when the fiber volume fraction of the HSP calculated from equation (4), appeared to be too low. The mechanical property results for the HSP composites presented later in this paper must be viewed with caution considering the poor inter-tow consolidation and possible presence of voids. The K-90 PVP sized composite also had some resin rich and poor regions (Figure 7) but overall had good inter-tow consolidation.

Ultrasonic C-Scan

Ultrasonic c-scan showed good consolidation and no apparent differences between the composites made from the differently sized carbon fibers could be ascertained.

Mechanical Properties

The mechanical property results for the pultruded composites are summarized in Table 4. All the mechanical property results discussed in the following sections except the tensile strain-to-failure results were normalized from the theoretical fiber volume

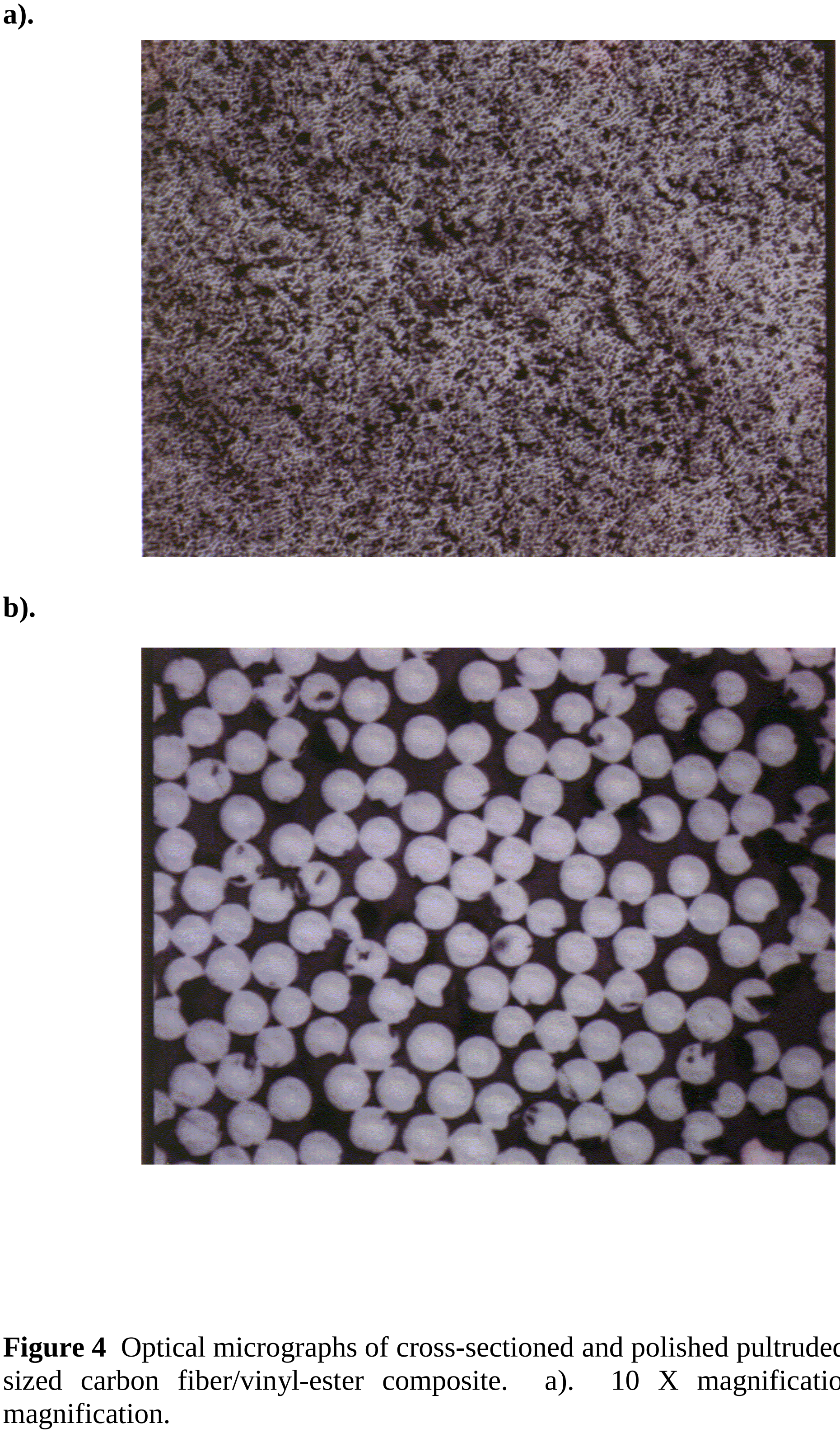

Figure 4 Optical micrographs of cross-sectioned and polished pultruded Hexcel AS-4 G' sized carbon fiber/vinyl-ester composite. a). 10 X magnification b). 100 X magnification.

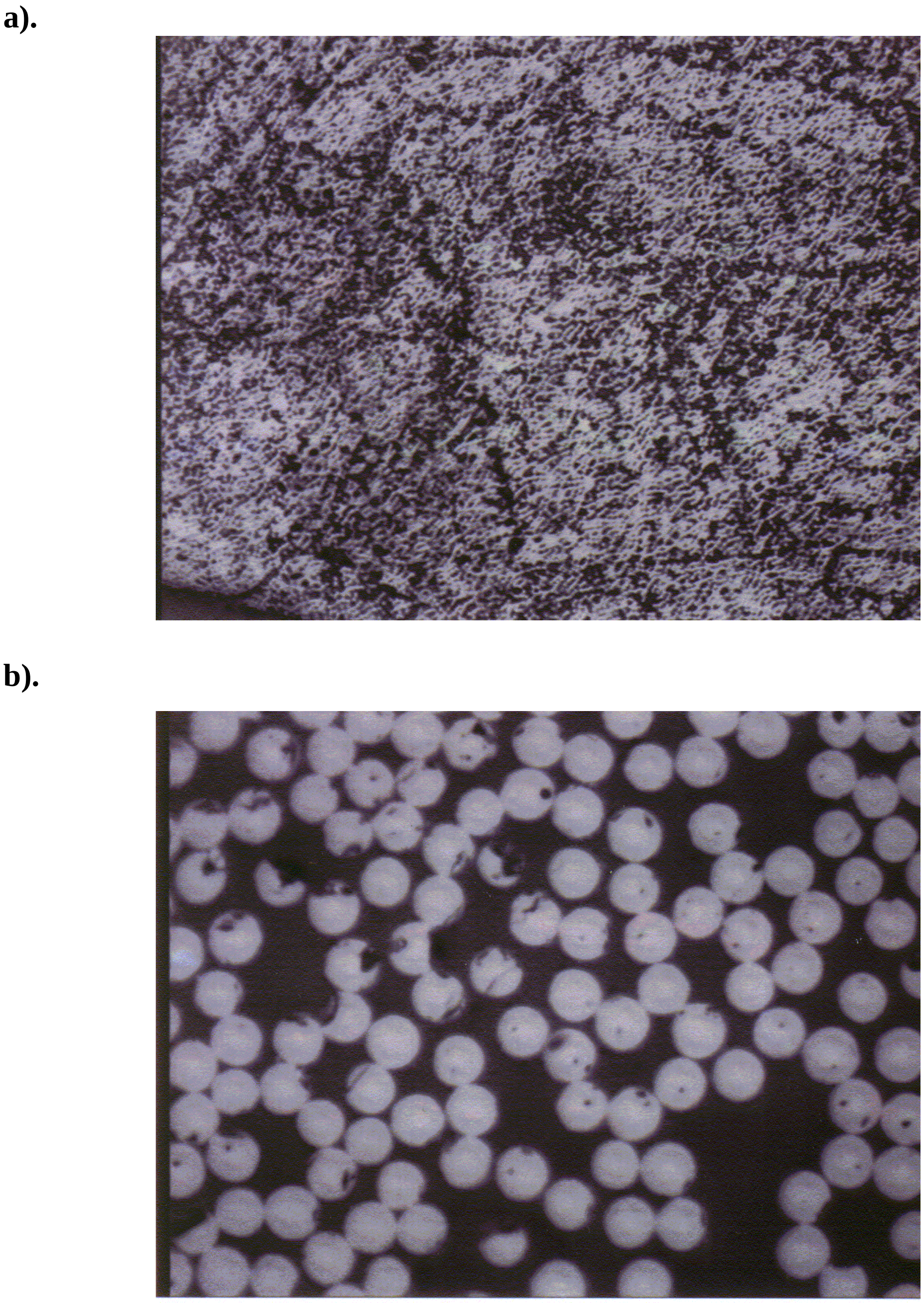

Figure 5 Optical micrographs of cross-sectioned and polished pultruded Hexcel AS-4 low spread Phenoxy sized carbon fiber/vinyl-ester composite. a). 10 X magnification b). 100 X magnification.

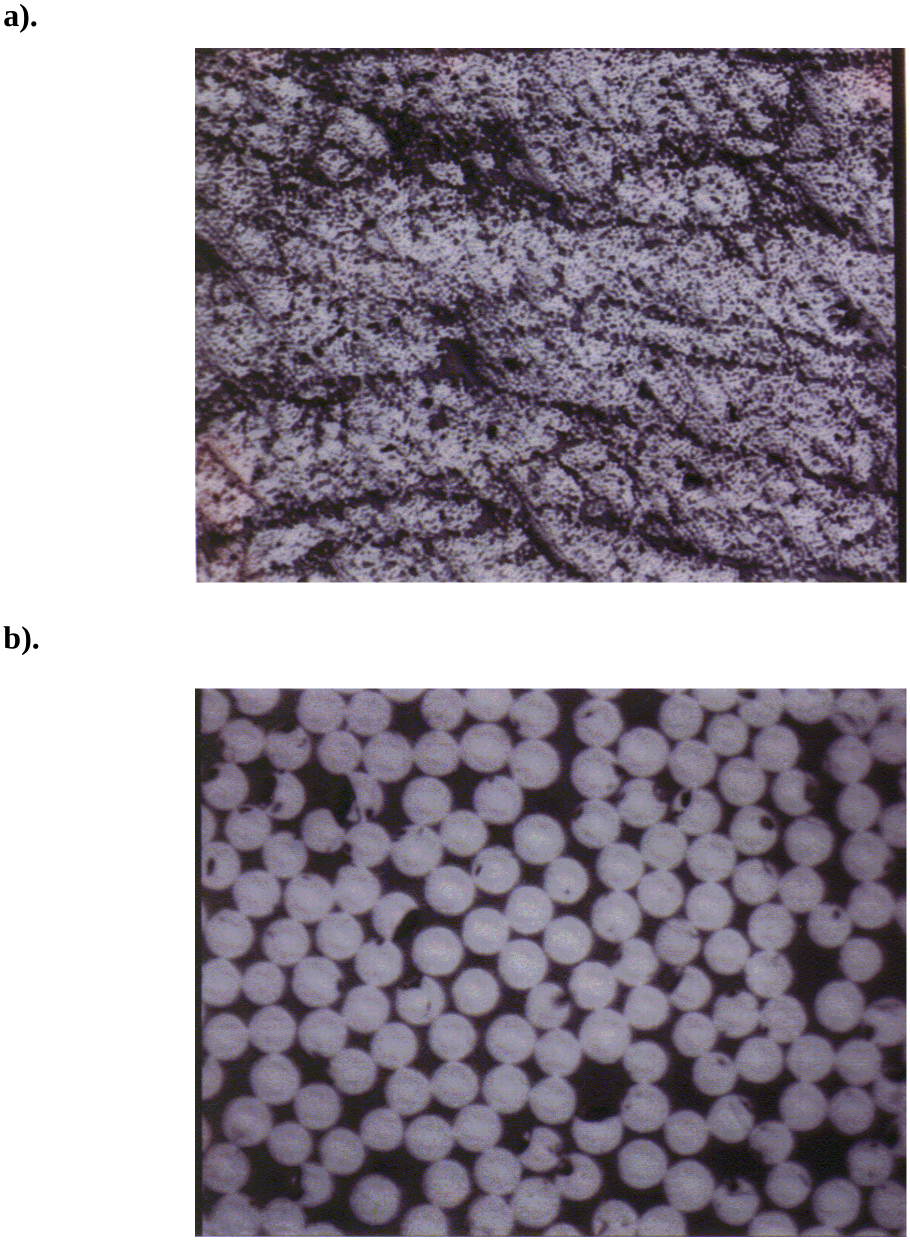

Figure 6 Optical micrographs of cross-sectioned and polished pultruded Hexcel AS-4 high-spread Phenoxy sized carbon fiber/vinyl-ester composite. a). 10 X magnification b). 100 X magnification.

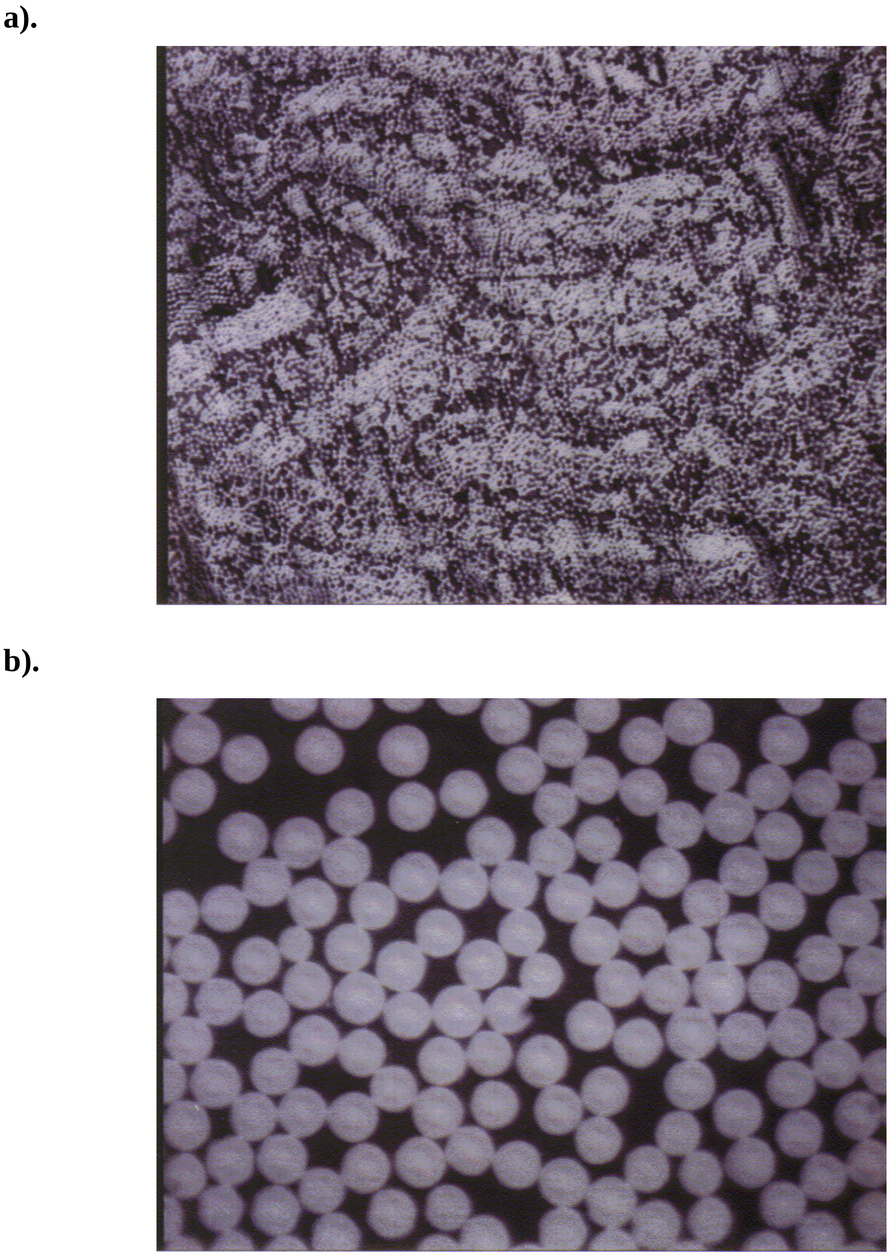

Figure 7 Optical micrographs of cross-sectioned and polished pultruded Hexcel AS-4 K-90 PVP sized carbon fiber/vinyl-ester composite. a). 10 X magnification b). 100 X magnification.

fraction to 65.6% or the theoretical fiber volume fraction of the G' sized composite utilizing equation (5). In addition, the differences in the inherent properties of the AS-4 and AS-4D fibers was taken into account utilizing the R factor in equation (5).

Tensile Properties

Static tensile strength, modulus, and strain-to-failure were determined for all sizing combinations (Figure 8, 9, and 10). The LSP composites displayed the highest tensile strength at a value of 2185 ± 38 MPa while the G' composite had the lowest value of 1673 ± 39 MPa (Note: 30% increase). All the thermoplastic sized fiber composites outperformed the standard G' by **at least 25%**. The HSP composite had the lowest tensile strength amongst the thermoplastic sizings at a value of 2083 ± 77 MPa which was a manifestation of the poor inter-tow consolidation and possibly voids.

The tensile modulus was determined for the G', HSP, and K-90 PVP composites (Figure 9). Due to a data acquisition problem encountered during the early portions of the tensile tests, no initial stress-strain data was obtained for the LSP sized composite system and only two sets of replicate initial stress-strain curves were obtained for the G', HSP, and K-90 PVP sizing systems. Because only two data points were available for the tensile modulus calculation, no standard deviation was determined. For the HSP and K-90 PVP sized composites, the modulus was nearly identical to that measured in the standard G' sizing. (HSP:121.7 GPa K-90 PVP: 125.2 GPa and G': 120.3 GPa). However, the significance of this variation cannot be assessed due to the limited modulus data.

The strain-to-failure was determined for all four composite systems (Figure 10). The strain-to-failure data were not normalized for variations in fiber volume fraction and/or differences in the inherent fiber strain-to-failure. Due to the inability to normalize this data, no conclusions about a sizing's affect on this property can be postulated.

Fracture Surface Investigation

SEM was used to investigate the tensile specimen's fracture surfaces (excluding HSP) (Figure 11, 12, and 13). The failed surfaces of the tensile specimens showed differences in terms of the qualitative level of fiber/matrix adhesion. However, in all

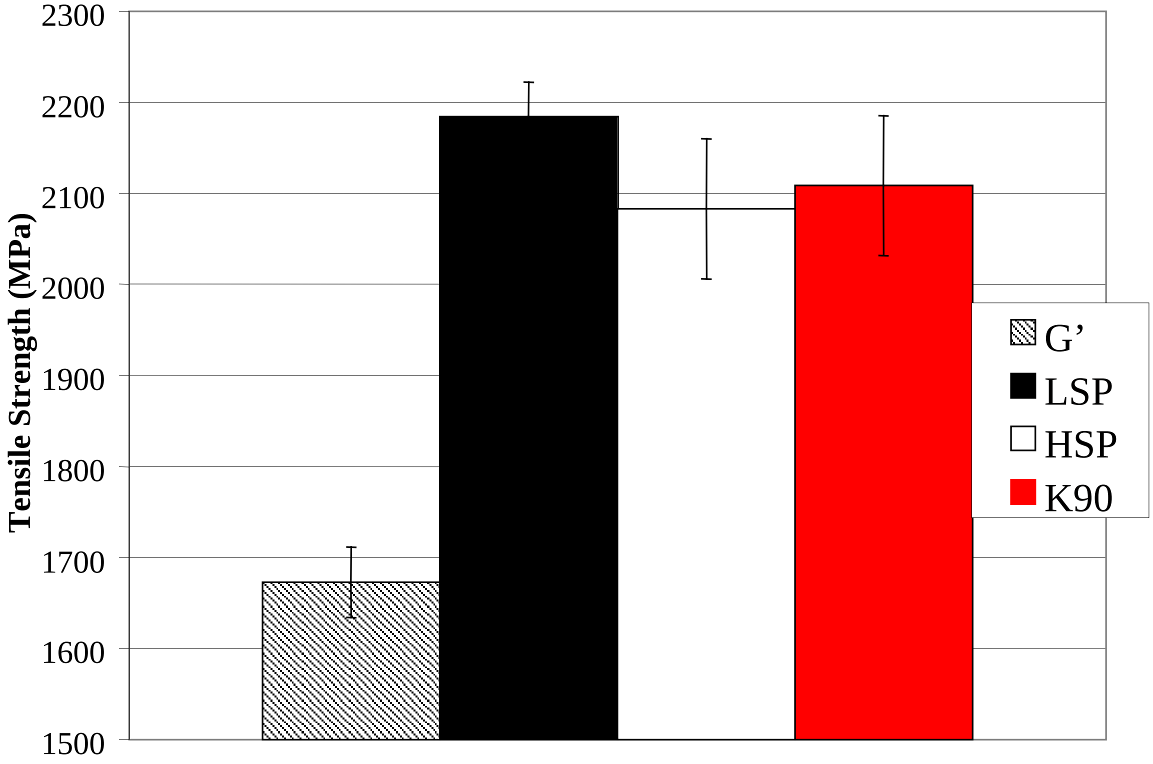

Figure 8 Static tensile strength of pultruded Hexcel carbon fiber/vinyl-ester composites with various sizing agents. Mechanical property results normalized from the theoretical fiber volume fraction to 65.6% or the theoretical fiber volume fraction of the G’ sized composite.

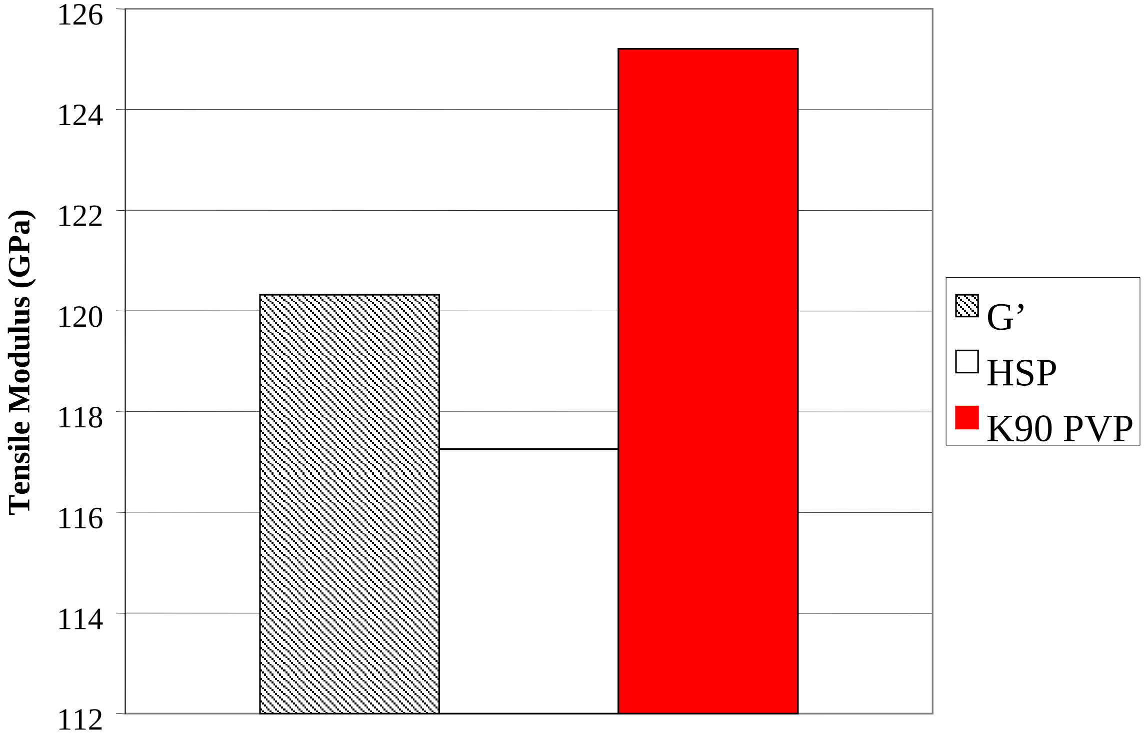

Figure 9 Static tensile modulus of pultruded Hexcel carbon fiber/vinyl-ester composites with various sizing agents. Mechanical property results normalized from the theoretical fiber volume fraction to 65.6% or the theoretical fiber volume fraction of the G’ sized composite. Normalization for differences in the inherent fiber properties included also.

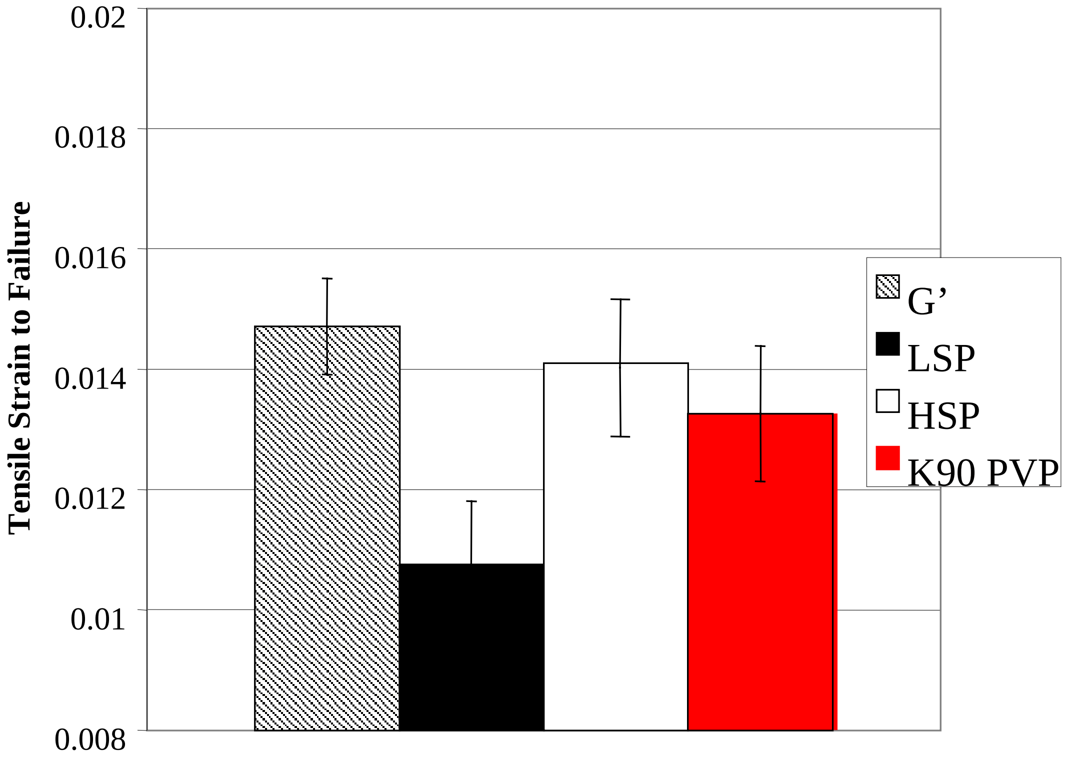

Figure 10 Static tensile strain to failure of pultruded Hexcel carbon fiber/vinyl-ester composites with various sizing agents. Strain-to-failure was not normalized for variations in fiber volume fraction and/or variations in fiber properties.

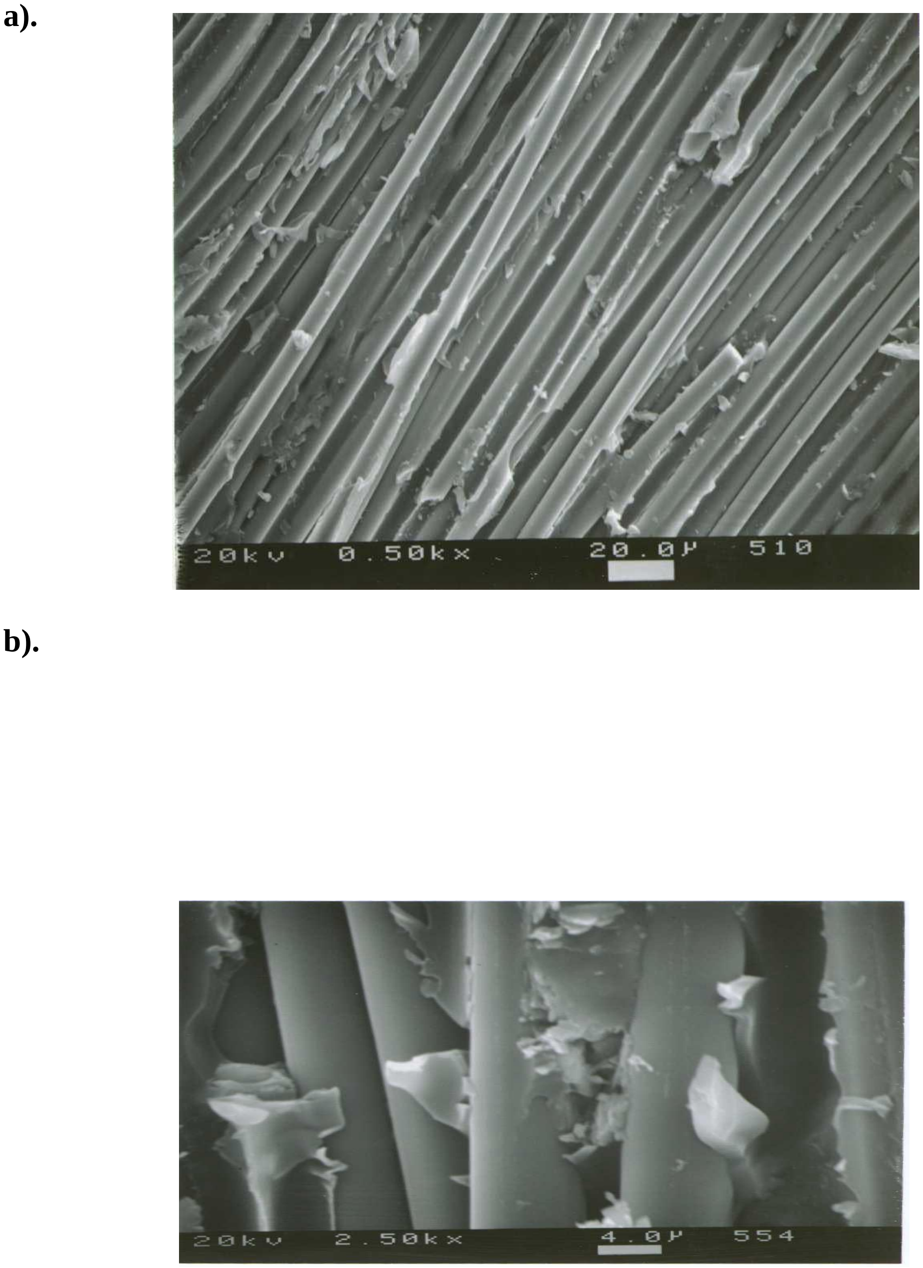

Figure 11 Optical micrographs of tensile fracture surface for pultruded Hexcel AS-4 G' sized carbon fiber/vinyl-ester composite. a). 500 X magnification b). 2,500 X magnification.

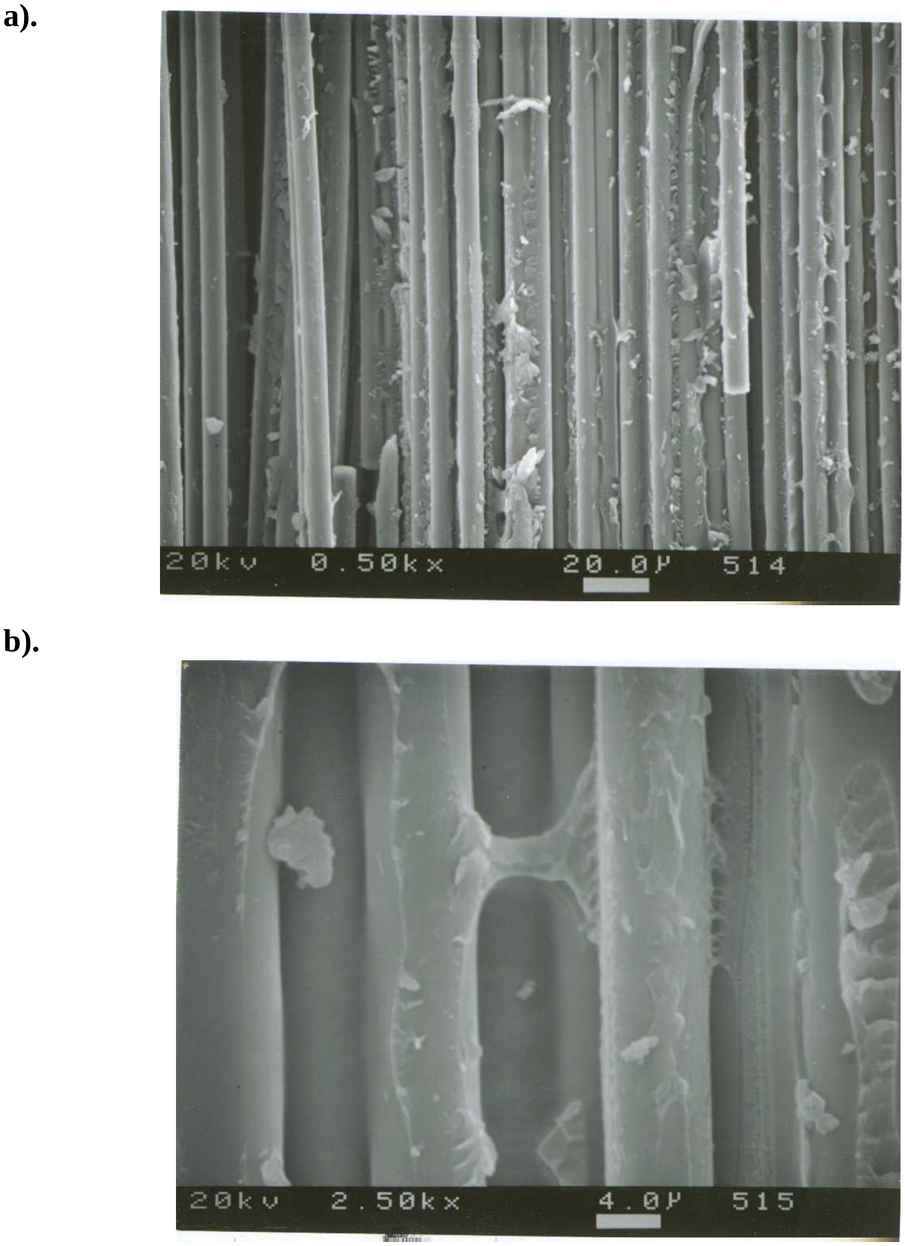

Figure 12 Optical micrographs of tensile fracture surface for pultruded Hexcel AS-4 low-spread Phenoxy™ (LSP) sized carbon fiber/vinyl-ester composite. a). 500 X magnification b). 2,500 X magnification.

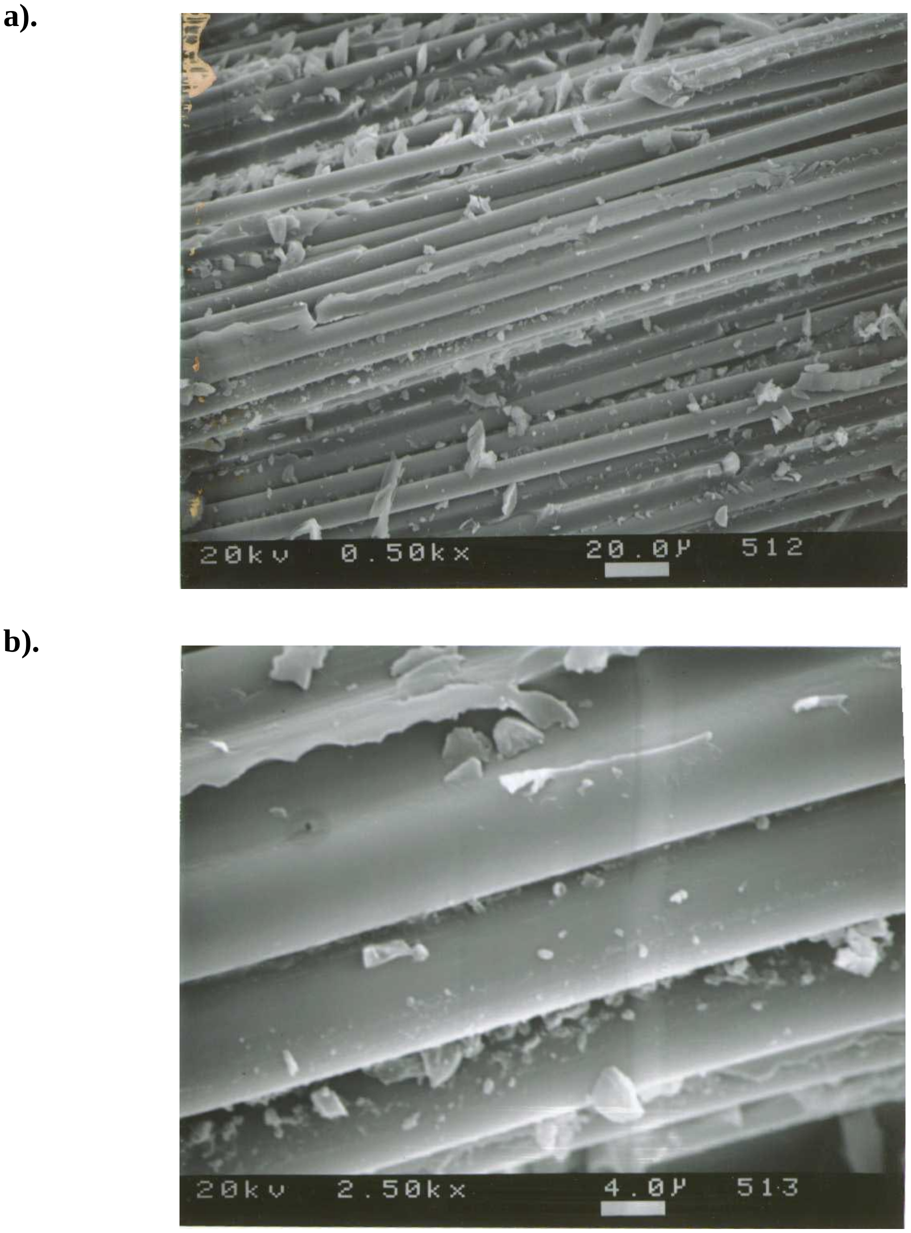

Figure 13 Optical micrographs of tensile fracture surface for pultruded Hexcel AS-4 K-90 PVP sized carbon fiber/vinyl-ester composite. a). 500 X magnification b). 2,500 X magnification.

cases, the failed fibers had extensive regions where matrix remained attached which was an indication of good fiber/matrix adhesion. The G' fracture surface showed the least amount of matrix attached to the fiber surface (Figure 11). The LSP displayed the largest extent of matrix covering the fiber surface (Figure 12). The K-90 PVP fracture surface displayed only slightly more matrix intact with the fiber surface as compared to the G' (Figure 13). From this data, it can be concluded that all three sizing systems had good fiber/matrix adhesion but LSP had the highest level of fiber/matrix adhesion. As was discussed in the introduction, on-axis static properties are not strong functions of fiber/matrix adhesion unless the fiber/matrix adhesion is poor. The fiber/matrix adhesion could not be classified as poor for any sizing system tested in these experiments. Therefore, the differences in static tensile strength discussed in the previous section cannot be entirely contributed to differences in fiber/matrix adhesion. In addition, if fiber/matrix adhesion were controlling the observed differences in static tensile strength, then the K-90 PVP system would have performed drastically different than the LSP system. As was presented earlier, the LSP and K-90 PVP systems had similar tensile strengths (2185 MPa and 2109 MPa). This suggests that mechanisms other than alterations in fiber/matrix adhesion expressed quantitatively by an ISS are affecting the tensile properties determined in these experiments. The other mechanisms include alterations in fiber processability (fiber protection, wettability, and alignment) and alterations in the interphase mechanical property profile.

Longitudinal Flexure Properties

The geometry and load placement of the longitudinal flexure test was such that the top of the specimen was exposed to compressive forces while the bottom was exposed to tensile forces while interlaminar shear was minimized. Therefore, this property can be considered on-axis and should not depend heavily on fiber/matrix adhesion as long as a minimum level of adhesion is present. The longitudinal flexure strengths for the thermoplastic sized composites were **at least 11%** higher than that for the standard G' sizing (Figure 14). The trend was consistent with the static tensile strength findings. The LSP sized composite again showed the highest strength at a value of 1274 ± 30 MPa

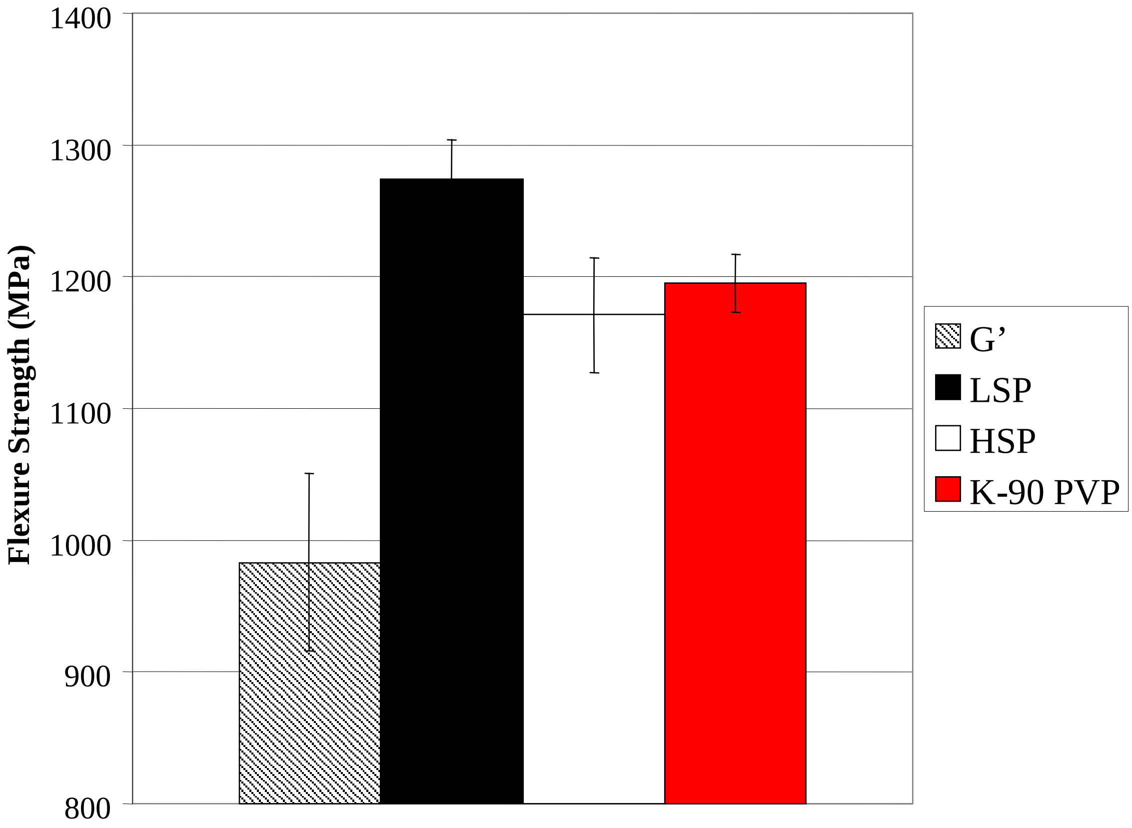

Figure 14 Static longitudinal flexure strength of pultruded Hexcel carbon fiber/vinyl-ester composites with various sizing agents. Mechanical property results normalized from the theoretical fiber volume fraction to 65.6% or the theoretical fiber volume fraction of the G’ sized composite.

compared to the 983 ± 67 MPa with the G’ (Note: a 30% increase) (Figure 14). The HSP and the K-90 PVP sized composite showed statistically equivalent longitudinal flexure strengths at a value of approximately 1180 MPa.

The modulus was found to be statistically equivalent between all four composite systems (Figure 15) with values ranging from 102.3 ± 3.4 GPa to 106.9 ± 1.1 GPa.

Short Beam Shear Properties

The geometry and load placement of the short beam shear test was conducted such that interlaminar shear was maximized at the specimen mid-section while minimizing tensile and compressive loads on the bottom and top respectively. Due to the shearing nature of the forces, the short beam shear (SBS) strength will be very sensitive to alterations in ISS and hence fiber/matrix adhesion. SBS testing showed that the thermoplastic sized composites outperformed the G’ by **at least 30%** (Figure 16) which was a slightly larger improvement than the on-axis mechanical properties discussed previously. The HSP and K-90 PVP sized composites had statistically equivalent SBS strengths at values around 60 MPa compared to the 43.0 ± 1.4 MPa observed with the G’. The LSP sized composite was again the best overall performer with a short beam shear strength of 66.1 ± 0.7 MPa. This represented a 10% increase over the K-90 PVP which was an indication of the higher ISS and improved fiber/matrix adhesion observed in the LSP system as compared to the K-90 PVP.

Compression Properties

The compressive strength and modulus for the LSP, K-90 PVP and G’ composites were determined (Figures 17 and 18). The compressive strength of the thermoplastic sized composites was at least **31%** greater than that of the G’ (≈ 990 MPa compared to 747 ± 110 MPa) (Figure 17). There were no statistical differences between the static compressive strengths of the LSP and K-90 PVP composites. These results were consistent with the static tensile strength. As was discussed in the introduction, the static compressive strength is only a weak function of fiber/matrix adhesion. Even though the fiber/matrix adhesion was hypothesized to be greater for the LSP sized composite compared to the K-90 PVP, the static compressive strength is relatively insensitive to

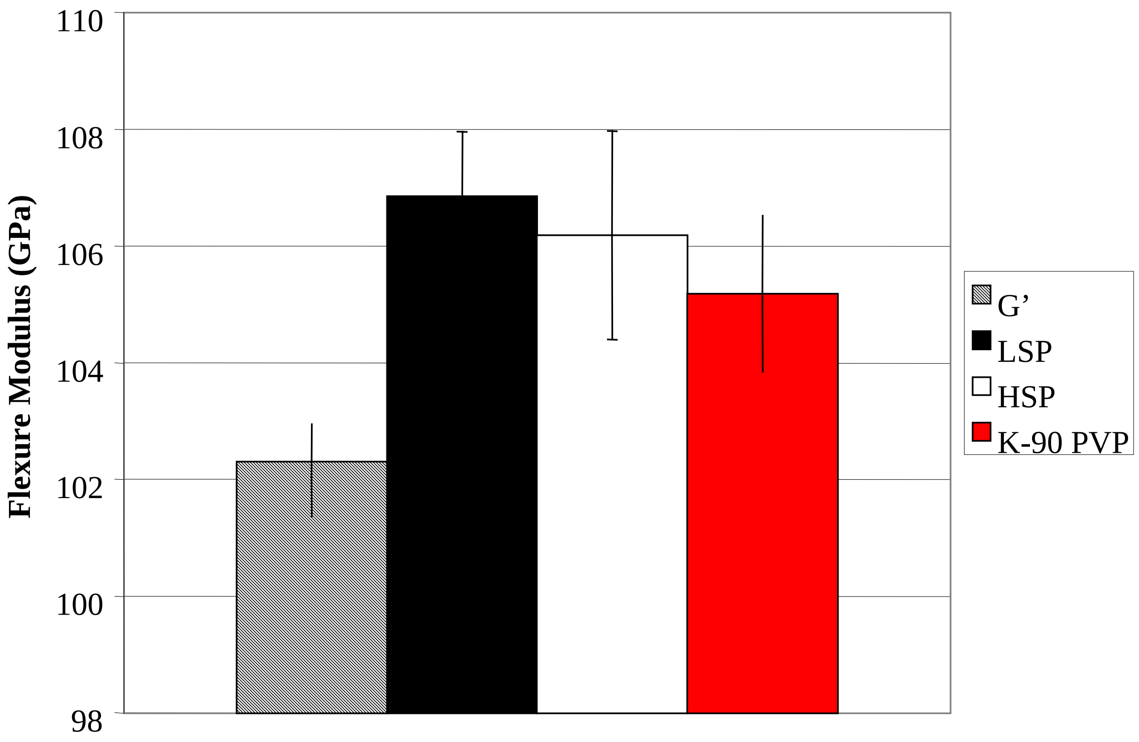

Figure 15 Static longitudinal flexure modulus of pultruded Hexcel carbon fiber/vinyl-ester composites with various sizing agents. Mechanical property results normalized from the theoretical fiber volume fraction to 65.6% or the theoretical fiber volume fraction of the G’ sized composite. Normalization for differences in the inherent fiber properties included also.

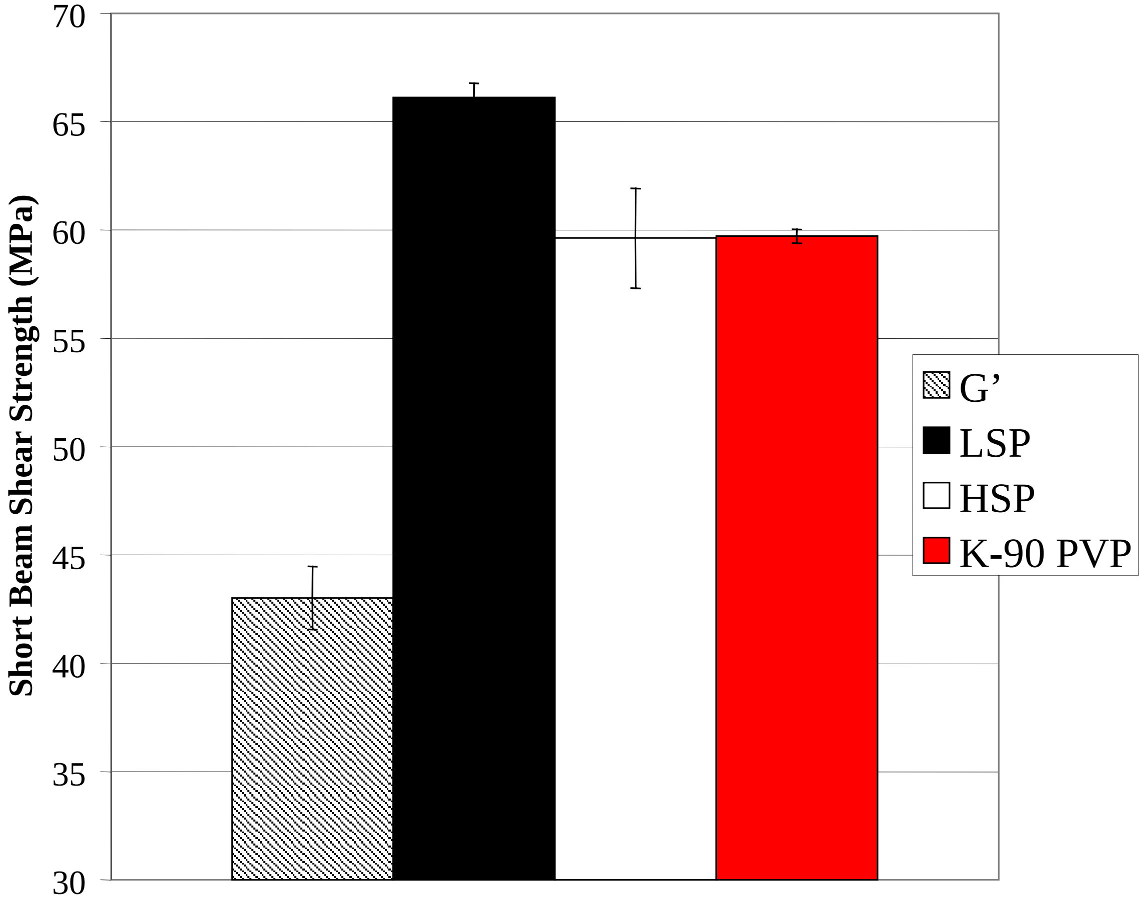

Figure 16 Short beam shear (SBS) strength of pultruded Hexcel carbon fiber/vinyl-ester composites with various sizing agents. Mechanical property results normalized from the theoretical fiber volume fraction to 65.6% or the theoretical fiber volume fraction of the G’ sized composite.

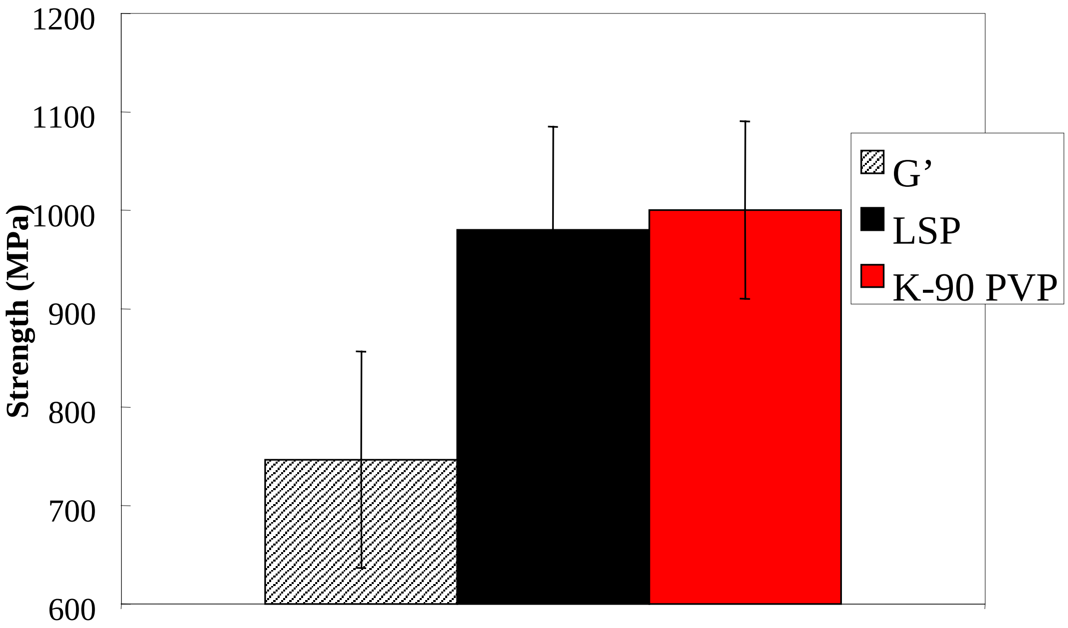

Figure 17 Compression strength of pultruded Hexcel carbon fiber/vinyl-ester composites with various sizing agents. Mechanical property results normalized from the theoretical fiber volume fraction to 65.6% or the theoretical fiber volume fraction of the G’ sized composite.

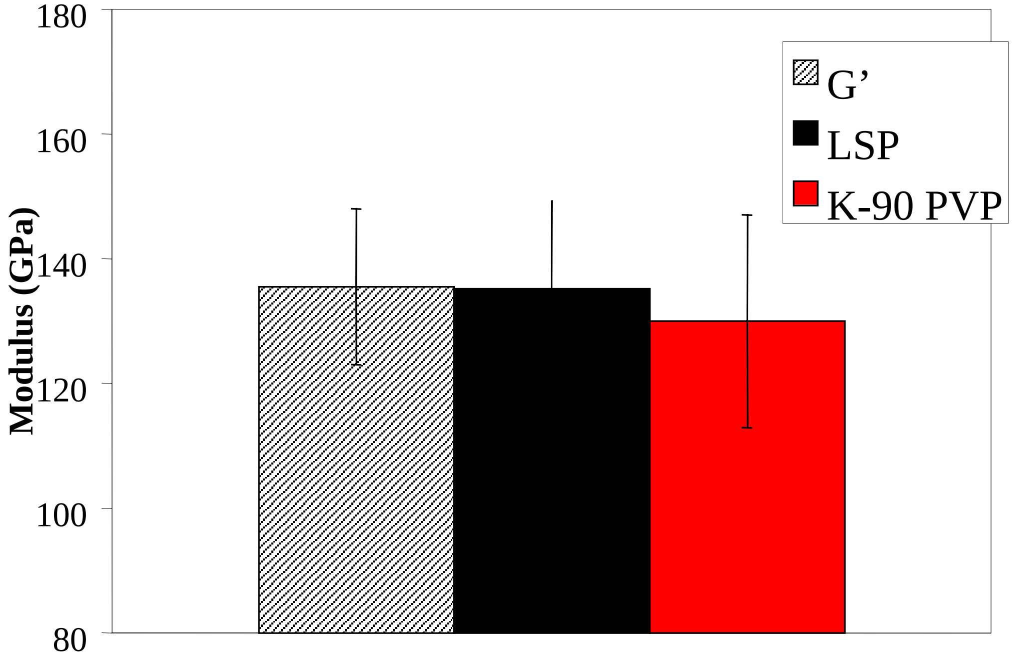

Figure 18 Compression modulus of pultruded Hexcel carbon fiber/vinyl-ester composites with various sizing agents. Mechanical property results normalized from the theoretical fiber volume fraction to 65.6% or the theoretical fiber volume fraction of the G’ sized composite. Normalization for differences in the inherent fiber properties included also.

these variations. The processability enhancements achieved with the thermoplastic sizing materials are the dominant factors in determining the static compressive performance. As was discussed in the introduction, a key parameter in optimizing composite compressive performance is the degree of fiber alignment. If the degree of alignment is perfect with the compressive loading axis, then the failure will be delayed and the compressive strength elevated to its maximum value. However, if misalignment or kink-bands are present, then failure will proceed at a lower load value. As was discussed earlier in the pultrusion section, the stiff nature of the thermoplastic sizing materials ensured better fiber protection and alignment. Due to its soft-pliable nature, the G' composite had numerous kink-bands. These kink-bands lead to a lower static compressive strength for the G' materials.

The compressive modulus was determined (Figure 18). The compressive modulus was found to be statistically equivalent for all the sizing materials tested (≈ 122 GPa).

CONCLUSIONS

In summary, the thermoplastic sizing materials offered numerous processing related advantages over the traditionally utilized G' or oligomeric epoxy sizings.

1. The high T_g thermoplastic sizings produced a stiff carbon fiber that was less susceptible to damage during the pre-wet-out portions of the pultrusion process.
2. The spread/tape-like thermoplastic sized fibers minimized damage in the dip bath entrance and also minimized wet-out time due to a reduction in wet-out distance.
3. The thermoplastic sizings optimized for interaction with the vinyl-ester matrix lowered the contact angle between the fiber and the matrix thus reducing the time required for tow wet-out. In addition, the lowered contact angle will allow for improved fiber/matrix adhesion in the final composite.
4. The high T_g thermoplastic sizing materials swelled and then relaxed with the vinyl-ester matrix thus making them rubbery at the resin dip bath exit. This allowed the fibers to be more easily compacted and compressed in the pultrusion die.

These processability improvements translated into a composite with improved surface finish and better fiber alignment. In addition, the mechanical performance of the final composite was greatly affected by variations in the composite’s sizing agent.

1. All of the thermoplastic sized composites outperformed the standard G’ sizing by **at least 25%** in static tensile strength.
2. All of the thermoplastic sized composites outperformed the standard G’ sizing by **at least 11%** in longitudinal flexure strength.
3. All of the thermoplastic sized composites outperformed the standard G’ sizing by **at least 30%** in short beam shear strength.
4. All of the thermoplastic sized composites outperformed the standard G’ sizing by **at least 31%** in compressive strength.
5. The tensile, longitudinal flexure, and compressive moduli were found to be unaffected by variations in the sizing.

These mechanical performance enhancements were achieved by altering a 1 to 3 wt% feature on the surface of the carbon fiber reinforcement. This corresponds to a material that occupied less than 2 wt% in the final composite. Because these thermoplastic sizing materials were commercially available materials and because such a low amount of them was needed to greatly improve mechanical properties, these sizing materials would make excellent replacements for the standard G’ or oligomeric epoxies that are presently being utilized in pultrusion of carbon/vinyl-ester composites.