

Chapter 2

INTRODUCTION

Polymer composites consisting of continuous reinforcing fibers embedded in polymeric matrices are becoming increasingly important as structural components for the infrastructure and construction industries due to their improved corrosion resistance and high strength/weight ratios compared to traditional metallic materials^{2.1}. Carbon and glass reinforcing fibers with high moduli and strengths are typically used in these composites as the primary load bearing constituents. Rapidly processable polymer matrix resins include thermosetting materials such as epoxies, the so-called “vinyl esters” (e.g., dimethacrylate oligomers diluted with styrene), and “unsaturated polyesters” (polyester oligomers diluted with styrene). The matrices protect the brittle reinforcing fibers, bind them together, and transfer loads to the fibers in the vicinity of fiber breaks via fiber-matrix adhesion.

The fatigue performance of these composites was particularly sensitive to the morphology of the fiber-matrix interphase regions^{2.2-2.6}. This "interphase" can be defined as the region of finite mass between the fiber and matrix with properties different from either the fiber or the matrix.^{2.2} One method for controlling both fiber-matrix adhesion and the physical properties of the interphase region is to apply a sizing (i.e., a fiber coating from a polymer solution) to the surface of the fibers prior to impregnation with the matrix resin. The sizing may or may not interdiffuse with the matrix resin during the cure reaction. Interdiffusion results in a gradient in chemical composition as one moves outward from the fiber. Broyles et al.^{2.5} tested the durability and lifetime of vinyl ester matrix composites consisting of fibers sized with two dissimilar thermoplastics. The carboxylate modified poly(hydroxyether) sizing, a ductile engineering thermoplastic, showed a 20-fold increase in the notched fatigue life of the composite compared to the unsized case, while that sized with the brittle poly(vinylpyrrolidone) exhibited only a 6-fold increase. Relationships between the structure of these fiber-matrix interphase regions and the properties of the composites are not adequately understood. For example, the relative roles and importance of fiber-sizing adhesion, sizing-matrix adhesion, interphase morphology and interphase mechanical properties are not at all clear. This paper addresses the design and characterization of carbon fiber-vinyl ester interphase regions. Initial data defining the

relationships between interphase structure and composite performance are presented. One goal in this work is to use micro-mechanical properties measured in interphase regions in a continuum mechanics model to predict composite performance properties.

Interphase regions have been designed by tailoring tough ductile polymeric sizings to partially diffuse into a thermosetting matrix resin during cure to enhance sizing-matrix adhesion. The chemical and physical interactions between the fiber, sizing, and resin during composite fabrication result in an interphase region with a gradient in chemical composition and mechanical properties. It is anticipated that this mechanical gradient may be beneficial towards improving composite performance. It has also been observed that the carboxy modified poly(hydroxyether) sized fibers form a relatively stiff tow which can result in less fiber breakage and fuzzing during composite processing. Preliminary results suggest that these composites have decreased moisture uptake relative to similar composites prepared with a commercial epoxy sizing. It is anticipated that this will improve the moisture stability of the composite.

EXPERIMENTAL

Materials

The fibers were Hexcel AS-4 unsized but surface treated 12K tow. The vinyl ester matrix material was kindly donated by the Dow Chemical Company. This resin was 70 wt. % of a vinyl ester (dimethacrylate terminated) oligomer (M_n of ~ 700 g/mole) diluted with 30-34 wt. % styrene (figure 1). Benzoyl peroxide (Aldrich) was used as received as the initiator for the free radical cure reaction. The poly(hydroxyether) and the “carboxy modified poly(hydroxyether)” (PKHW-35) sizing materials were kindly donated by Phenoxy Associates, Rock Hill, SC (figure 2). The carboxylic acid modified material was a derivative of the original poly(hydroxyether) with a minor concentration of carboxylic acid groups grafted onto the backbone. This modification facilitated its dispersion in water. The carboxylic acid grafted poly(hydroxyether) was obtained as a 35 wt. % aqueous dispersion of $\sim 1\mu\text{m}$ average diameter particles which was diluted to 2 wt. % with water for sizing. The poly(hydroxyether ethanolamine) thermoplastic (figure 2) was prepared by chain extending an epoxy resin with ethanolamine and was also kindly supplied by the Dow Chemical Co. A 2 wt. % solution was prepared for the sizing process by heating 3 vol % acetic acid in water to $\sim 45^\circ\text{C}$ and dissolving the thermoplastic in this solution.

“Vinyl Ester Resins”

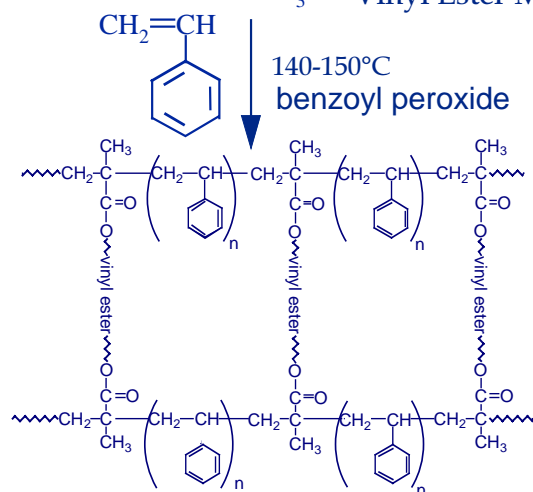
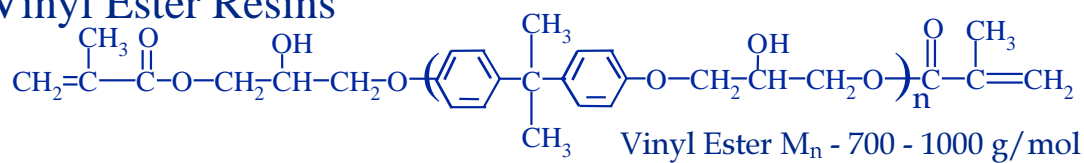


Figure 1: Dimethacrylate (“vinyl ester”) - styrene matrix components.

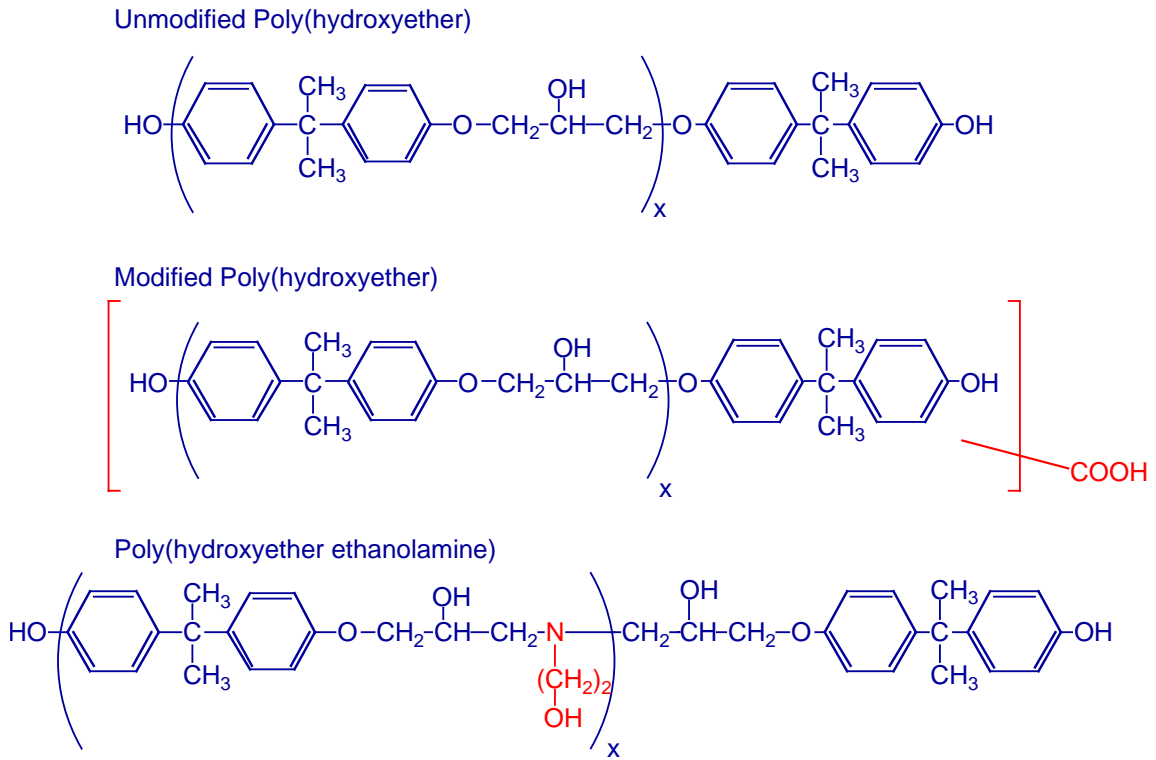


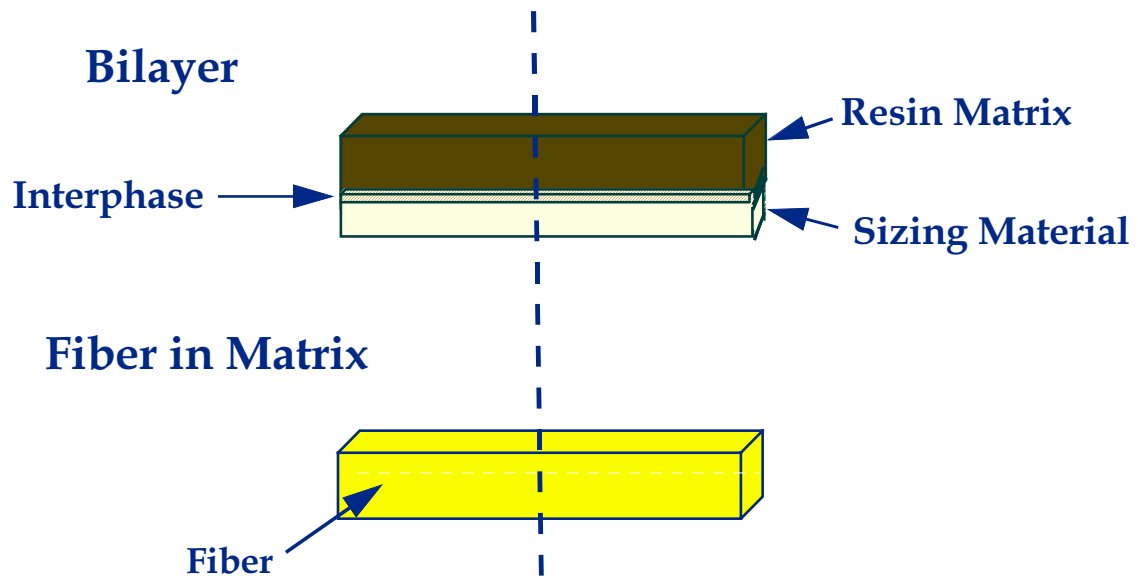
Figure 2: Thermoplastic sizing materials for carbon fiber reinforced vinyl ester matrix composites.

The fiber tow was sized on a custom made small scale sizing line^{2,6}, the tow was wound onto a drumwinder, and cut to 16.5 cm length plies. The plies were then dried at 150°C for 3 hours. The amount of carboxy modified poly(hydroxyether) sizing based on fiber weight was 1.12%. At 64% fiber volume in the composite panel, this corresponds to 0.8% by weight sizing based on the weight of the total composite. The amount of poly(hydroxyether ethanolamine) sizing based on fiber weight was 1.5 wt. %. At 60 volume % fiber in the panels, this corresponds to 0.7 wt. % sizing based on the total composite weight. The plies were stitched at 3.8-5 cm intervals to hold the fibers in place. The matrix resin was prepared for the cure reaction by dissolving 1.1 wt. % benzoyl peroxide in the vinyl ester resin at room temperature, then degassing under mild vacuum. No accelerator was used. Seven ply (crossply symmetrical about the center ply), 16.5 cm x 16.5 cm panels were cured using a resin infusion process on a Wabash (model 9112) vacuum hot press by heating from 25°C to 150°C over 30 min., holding at 150°C for 20 minutes, then cooling to approximately room temperature over a period of 1 hour under pressure.

Bilayer films of the poly(hydroxyether) sizing materials and the vinyl ester matrix were prepared to study sizing-matrix interactions (figure 3). These films were prepared in small silicone rubber molds. First, a thin film of the poly(hydroxyether) sizing material was cast and dried; the carboxy modified poly(hydroxyether) and the poly(hydroxyether ethanolamine) films were cast from the aqueous sizing solution/dispersion, while the poly(hydroxyether) film was cast from THF; then the vinyl ester (with benzoyl peroxide initiator) was poured into the mold on top of the sizing material. This was immediately placed in a preheated oven at 150°C for 30 minutes to cure. Single fiber model composites were made by suspending a single fiber that had been sized using the small scale sizing line in our laboratory in the same mold used for the bilayer samples, adding vinyl ester and curing under identical conditions. Modified poly(hydroxyether) specimens were cured at 150°C for one hour and three hours. 100-mg samples were then stirred in 5 ml of DMAc and the DMAc was decanted and added fresh 7 times. Samples were then dried at 50°C in nitrogen for three days and at 120°C in vacuum for 14 hours.

Composite characteristics

Fiber volume fractions of the composite panels used in these experiments were calculated by measuring their densities in air and in isopropyl alcohol. An ~ 4 gram sample of each



Cross section cut and microtomed (R.T or cryo)

Figure 3: Sample preparation of sizing-matrix bilayer cross-sections.

composite was weighed. The sample was then immersed in isopropyl alcohol and reweighed. The density of the composite was calculated using Archimedes' principle and equation 1

$$\rho_{\text{composite}} = W_{\text{air}} \rho_{\text{IPA}} / (W_{\text{air}} - W_{\text{IPA}}) \quad (1)$$

where $\rho_{\text{composite}}$ was the density of the composite, ρ_{IPA} was the density of isopropyl alcohol, W_{air} was the weight of the sample in air and W_{IPA} was the weight of the sample in isopropyl alcohol. The fiber volume fraction was then determined using the rule of mixtures where v was the fiber volume fraction calculated from equation 2,

$$v = (\rho_{\text{composite}} - \rho_{\text{resin}}) / (\rho_{\text{fiber}} - \rho_{\text{resin}}) \quad (2)$$

ρ_{fiber} was the density of the carbon fiber, and ρ_{resin} was the cured network density. The fiber volume fractions were estimated to be 0.60-0.62. The densities used for the fiber and resin were $\rho_{\text{fiber}} = 1.78 \text{ g/ml}^{2.8}$ and $\rho_{\text{resin}} = 1.18 \text{ g/ml}^{2.9}$.

As a quality control step, linear ultrasonic C-scans were conducted on all the composite materials. These tests were done using a Sonix HS1000 HiSPEED instrument. A 15 MHz, 32 mm 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 to the bottom surface of the specimens. These scans indicated a larger dissipation in the poly(hydroxyether ethanolamine) composite samples as compared to the poly(hydroxyether). This was postulated to be caused by poor interface adhesion in the former case as all the other material constituents were the same and no unusual porosity was observed in either of the composite systems.

Atomic Force Microscopy (AFM) and Nano-indentation

Bilayer samples were cut through the middle and microtomed smooth, and then the smoothed blocks were analyzed by AFM. The samples were initially trimmed with a razor blade to obtain a trapezoidal shape (~1 mm. in length) with the interface near the middle of the trapezoid. The samples were microtomed with a Reichert-Jung Ultracut E apparatus. All samples were cut with a diamond knife at room temperature. A Digital Instruments Dimension 3000 instrument using the Nanoscope IIIa controller was used to obtain the images. The images were collected in the Tapping Mode™ using etched silicon tapping tips with spring constants in

the 20-100 N/m range. The nano-mechanical properties of the bilayer samples were also studied using the AFM apparatus. Digital Instruments indentation software and a diamond tipped cantilever with a 325 N/m spring constant was used to produce a number of nanometer size indentations in the samples. Force-nanoindentation depth curves from these indentations were then corrected to remove tip deflection of the cantilever^{2,10}. The tip deflection was calibrated using a sapphire substrate as an infinitely stiff material; and then this component was removed from the data collected from the samples under study. The force-indentation depth curves were then used to calculate the elastic and plastic components of the indents^{2,11}. The plastic component was calculated by taking the initial slope of the unloading curve and extrapolating back to zero force. The elastic component was then calculated by subtracting the plastic depth from the total depth of the indent at maximum force.

Mechanical Testing: Quasi-static Compression and Fatigue Tests

Quasi-static compression tests were performed on an MTS test frame to assess composite strength. A loading rate of 200 pounds per second was applied. This loading cycle was programmed into the Microprofiler that controlled the machine once a test was begun. A 5.08 cm. test gauge length was used. The specimens were loaded into the grips at a grip pressure of 7 MPa and specimen alignment was ensured with a spirit level. Emory cloth (100 grit) was wrapped around the grip sections of the specimens to prevent slip. An MTS Model 632 extensometer with a gauge length of 2.54 cm and a maximum strain limit of 4% was used to monitor strain. Aluminum extensometer tabs were used to hold an extensometer and the signal from the extensometer was amplified using a 2310 Vishay Measurements Group amplifier.

Fatigue tests were conducted using a sinusoidal, fully reversed tension-compression ($R = -1$) mode at a frequency of 10 Hz. Specimens were 15.2 cm X 2.54 cm. A 6.4 mm diameter hole was drilled in the center of the specimens to create a notch prior to testing.

Micro-debond Analyses

Fibers, both sized and unsized, were used in micro-debond tests to determine the interfacial shear strength between the fibers and the matrices. Vinyl ester / carbon fiber samples for microdroplet micro-debond tests were prepared by applying a small droplet of the vinyl ester resin containing 1.1% benzoyl peroxide onto the carbon fiber that had been sized with each respective sizing (and also the unsized fiber). Then the droplets were cured at 130°C for 20 min

in nitrogen. Thermoplastic polymer / carbon fiber specimens were prepared by flowing a thin polymer droplet around the fiber above the polymer's glass transition. Droplets were debonded via an Instron 5567 instrument at a displacement rate of 0.3 mm/min. The debonding load was measured using a balance (Mettler B 2400) together with a personal computer to record load and deflection data. The interfacial shear strength was calculated from the debonding load, fiber diameter and embedded fiber length as the load required to debond the droplet per unit of fiber surface area covered by the droplet. At least 50 droplets were debonded for each material and the results were averaged.

X-ray Photoelectron Spectroscopy (XPS)

Fibers were analyzed using a Perkin Elmer PHI 5400 X-ray photoelectron spectrometer operating at 17.9 V with a sampling angle of 45°. Peak binding energy positions were referenced to carbon at 285 eV bond energy as 532.9, 102.1, and 400.3 eV for oxygen, silicon, and nitrogen respectively. The atomic concentration of each was analyzed based on peak areas.

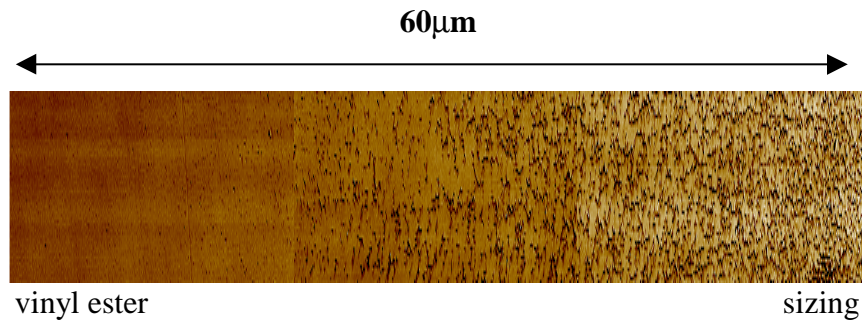
RESULTS AND DISCUSSION

The objective of the present study was to relate composite fatigue properties and interfacial shear strengths of a series of carbon fiber reinforced vinyl ester matrix composites to sizing and interphase structure. Carbon fibers derived from a poly(acrylonitrile) precursor were surface treated by the supplier (Hexcel), sized in our laboratories with a series of physically similar poly(hydroxyether) thermoplastics, and used as the reinforcing fibers with a vinyl ester-styrene matrix. It should be noted that the term "vinyl ester" refers to a family of matrix resins comprised of oligomeric poly(hydroxyether) backbones having methacrylate endgroups which are diluted with styrene monomer. The molecular weight of the vinyl ester prepolymer and the amount of styrene can be varied. For this study, the number average molecular weight of the dimethacrylate (vinyl ester) prepolymer was ~700 g/mole and this was diluted with 30 weight percent styrene. It is important that the constituents and concentrations of the particular resin composition are specified because the solubility of the sizings in the resin (and hence, the amount of sizing-resin interdiffusion) may differ as resin composition is varied within the "vinyl ester" family.

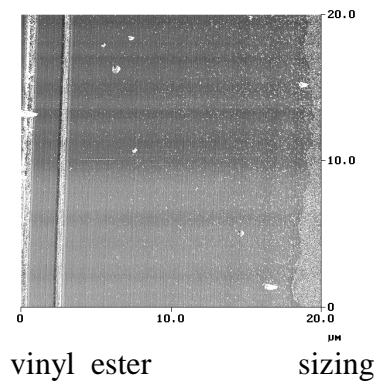
The surface chemistry of the carbon fiber would be expected to affect fiber-sizing adhesion. Thus, the atomic composition (counting all atoms except hydrogen) of the unsized carbon AS-4 fibers was characterized using X-ray photoelectron spectroscopy. These analyses indicated that the fiber surface was 80-85 atomic % carbon. Nitrogen and silicon were both found on the surface in ~1-3 atomic % along with a significant amount, 10-15 atomic %, of oxygen. The oxygen is believed to be bonded to carbon as ether linkages or hydroxyl groups because no higher binding energy shoulder on the oxygen peak representing doubly bonded oxygens was observed. It is assumed that the relatively high oxygen concentration originated from the proprietary surface treatment applied by the supplier.

The choices of sizing materials (figure 2) were based on the anticipated need for (1) limited (but finite) solubility in the matrix resin during cure, (2) tough, ductile mechanical properties in the interphase region, and (3) to have strongly hydrogen bonding groups (e.g., acidic hydroxyl groups) in the polymer chain to enhance fiber-sizing adhesion. The “limited solubility” characteristic between sizing and matrix resin was an attempt to control sizing-matrix interdiffusion to maintain an interphase region containing the ductile polymeric sizing, yet have sufficient interdiffusion to achieve good sizing-matrix adhesion. Both sizings (figure 2), the carboxy modified poly(hydroxyether) and the poly(hydroxyether ethanolamine), had similar chemical structures to the vinyl ester prepolymer component of the matrix resin but neither sizing was soluble in the matrix resin at room temperature.

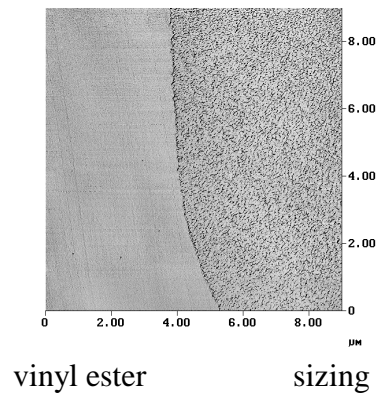
Interphase regions between the sizings and matrix were examined to try and relate the structure of these regions to composite fatigue performance. The interdiffusion and resultant morphology of interphase regions between each sizing material and the vinyl ester network were examined by constructing bilayer sizing material-matrix samples (figure 3), then microtoming cross-sections and studying them using atomic force microscopy (figure 4). The relative size of the interphase regions where visible interdiffusion between the sizings and the vinyl ester matrix occurred decreases in the order unmodified poly(hydroxyether) > carboxy modified poly(hydroxyether) > poly(hydroxyether ethanolamine) (no visible interdiffusion). The interdiffused sections of the interphase regions for the unmodified poly(hydroxyether) sizing consisted of a homogeneous dispersion of relatively spherical inclusions 80 - 90 nm in diameter of the poly(hydroxyether) material embedded in the vinyl ester continuous matrix. It is believed



(A)



(B)



(C)

Figure 4: Atomic force microscopy images (tapping mode, phase image) of sizing-matrix bilayer cross-sections illustrating relative interdiffusion of sizing with matrix: (A) Unmodified poly(hydroxyether), (B) Carboxy modified poly(hydroxyether) sizing, and (C) Poly(hydroxyether ethanolamine) sizing.

that this sizing partially dissolves in the matrix resin at the elevated cure temperature and phase segregates as the network forms (i.e., as high molecular weight is achieved).

The small size of the inclusions may be related to the fact that full cure takes place within about 3-5 minutes under the conditions used and the rapid reaction kinetics inhibit the growth of the poly(hydroxyether) domains. With the addition of carboxylate groups, the sizing material becomes reactive. When the composite panels investigated in this project were prepared, the plies were “pre-dried” for three hours prior to panel fabrication. Gelation studies on the carboxy modified poly(hydroxyether) sizing material suggest that during the 3 hour ply drying process, this sizing crosslinks. Studies showed that after one hour at 150°C, there was a 44% gel fraction and after three hour hours, there was a 65% gel fraction. This light crosslinking probably limited the mobility of this sizing as panels are prepared, and thus a significant fraction of sizing material was maintained in the interphase region. The interphase morphology using this carboxy-modified sizing was comprised of ductile inclusions of sizing distributed in the crosslinked matrix network. It is reasoned that this interphase composition and morphology may be related to the enhanced composite properties.

The poly(hydroxyether) becomes miscible at elevated temperatures while the poly(hydroxyether ethanolamine), which has an amine group in every repeat unit, does not. The carboxylate modified poly(hydroxyether) is lightly crosslinked during the drying of the sized fiber. The breadth of the interdiffused region decreases in the order unmodified poly(hydroxyether) < carboxy modified poly(hydroxyether) < poly(hydroxyether ethanolamine). An ~30 μm wide compositional gradient was evident in the unmodified poly(hydroxyether)/vinyl ester bilayer as compared to the much smaller gradient region for the carboxy modified poly(hydroxyether), and no interdiffusion was evident for the more polar poly(hydroxyether ethanolamine) sizing/vinyl ester bilayer. As will be described later in this manuscript, the fatigue properties of composites from these materials are far superior for the carboxy modified poly(hydroxyether) sizing case. Thus, the enhanced composite fatigue results may indeed be dependent on having a sizing with limited, but finite, miscibility with the matrix resin during cure.

Interphase Property Variations

One longer-term objective of our work is to measure material property variations across the interphase regions, then to relate these interphase characteristics to failure mechanisms in the composites. A goal is to develop a life prediction model that includes interphase properties (particularly gradients in properties across this region). One property of particular interest is the variation of yield strength across the interphase region. Information about yield strength within the interphase region can assist in establishing failure criteria for assessing the onset of damage via maximum shear stress failure criteria. The portion of this project described in this paper represents the initial stages of work where interphase profiles for sizing-matrix bilayers (no fibers present yet) have been probed and plastic deformation as a function of position is reported.

A nano-indentation technique using the AFM apparatus was used to profile the compositions in the interphase regions for the vinyl ester - poly(hydroxyether) bilayers and first attempts have been made at separating the plastic and elastic components of the deformations^{2,11}. An example of this is depicted in figure 5, which shows a number of indentations across an interphase region. Force-indentation depth curves for each point across the interphase regions were derived from these measurements by programming the apparatus to indent until a set force was reached, retract, then to repeat the same process 750 nm removed. This spacing ensured that each successive indent was well removed from the stress field of the preceding indent. Figure 6 depicts examples of force-distance curves from indentations across a carboxy modified poly(hydroxyether) sizing-vinyl ester matrix sample. The force-distance curves for the poly(hydroxyether ethanolamine) were similar to those for the carboxy modified poly(hydroxyether). This was expected because of their similar chemical structures. As each position was indented, the force increased with depth due to a combination of plastic and elastic deformation; then the force decreased as the tip was retracted. The hysteresis between the indentation and retraction curves was attributed to plastic deformation (taking into consideration a scaling factor 'A' in equation 3 dependent on AFM tip geometry). The plastic component was calculated by extrapolating the initial slope of the unloading curve back to zero force (h_i) and using the following expression^{2,12&2.13};

$$h_p = h_{\max} - A (h_{\max} - h_i) \quad (3)$$

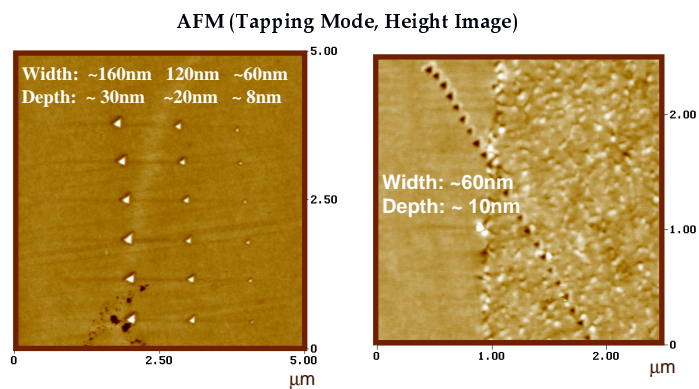


Figure 5: Atomic force microscopy image (tapping mode, height image) of indentations across an interphase region of a vinyl ester - carboxy modified poly(hydroxyether) bilayer.

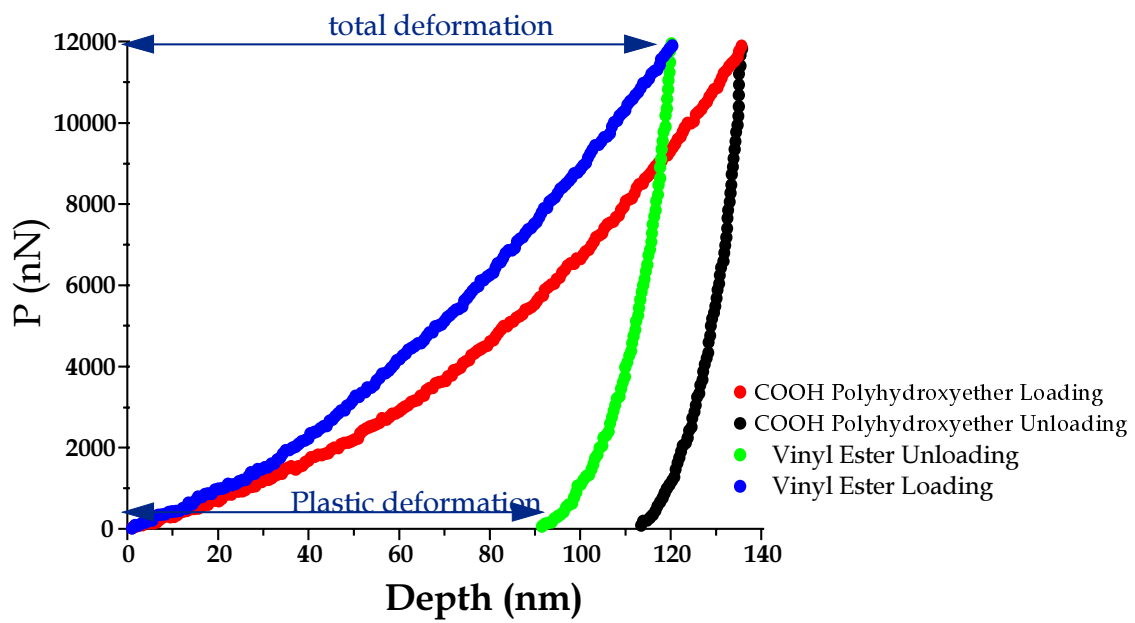


Figure 6: Force curves for a) Vinyl ester matrix and b) Carboxy modified poly(hydroxyether).

where h_p was the plastic depth, h_{max} the maximum depth, h_i the intercept depth and the constant A was a function of the shape of the indenter tip (0.75 for a pyramidal indenter). Then the plastic depth was subtracted from the total depth at maximum force to obtain the elastic component. The results reported herein are considered as “initial results” of an ongoing study.

It was noticed that for all indents that there was a “pile-up” or accumulation of material around the top of the indentation (figure 6). The degree of “pile-up” varied across the interphase region with the thermoplastic sizing materials showing a larger amount than the thermoset. This phenomenon was attributed to material actually being moved out of the hole during indentation. It was reasoned that this might affect the absolute values of the depths since attempts have been made to differentiate the elastic and plastic components of the indentation responses. However, it is not expected to change the general trends for each component across the interphases. The issue of the “pile up” is presently being studied and will be addressed in future work^{2.14&2.15}.

As expected, the data indicated that the depth of the indent was greater for the thermoplastic carboxy modified poly(hydroxyether) and that it also had a larger degree of plastic deformation relative to the thermoset vinyl ester. The plastic and elastic components of the indentations made across the interphase region of the carboxy modified poly(hydroxyether)/vinyl ester bilayer are depicted in Figure 7. The dotted lines in Figure 7 represent average values (for at least 10 indentations) for indentation in the vinyl ester and modified polyhydroxyether, while the solid lines represent 2 standard deviations from these average values. The indents increased in depth from the vinyl ester to the carboxy modified poly(hydroxyether) side of the bilayer, and the depth of the plastic component of the indents also increased. The data also indicated a gradient across the interphase extending 10-15 μ m from the vinyl ester to the interface and 5 μ m into the carboxy modified poly(hydroxyether) side of the bilayer. The zero point on the graphs was arbitrarily set as the point where the thermoset-thermoplastic interface was observed. This gradient characterized using nano-indentation on the vinyl ester side of the interphase corresponds well with the AFM image of this system. The process of interphase formation probably consists of the uncured vinyl ester resin swelling the carboxy modified poly(hydroxyether) and then for the latter to diffuse out into the vinyl ester material^{2.7}. Following this course, it is expected that the gradient in properties extends into the carboxy modified poly(hydroxyether) side of the interphase region as seen in the nano-mechanical data.

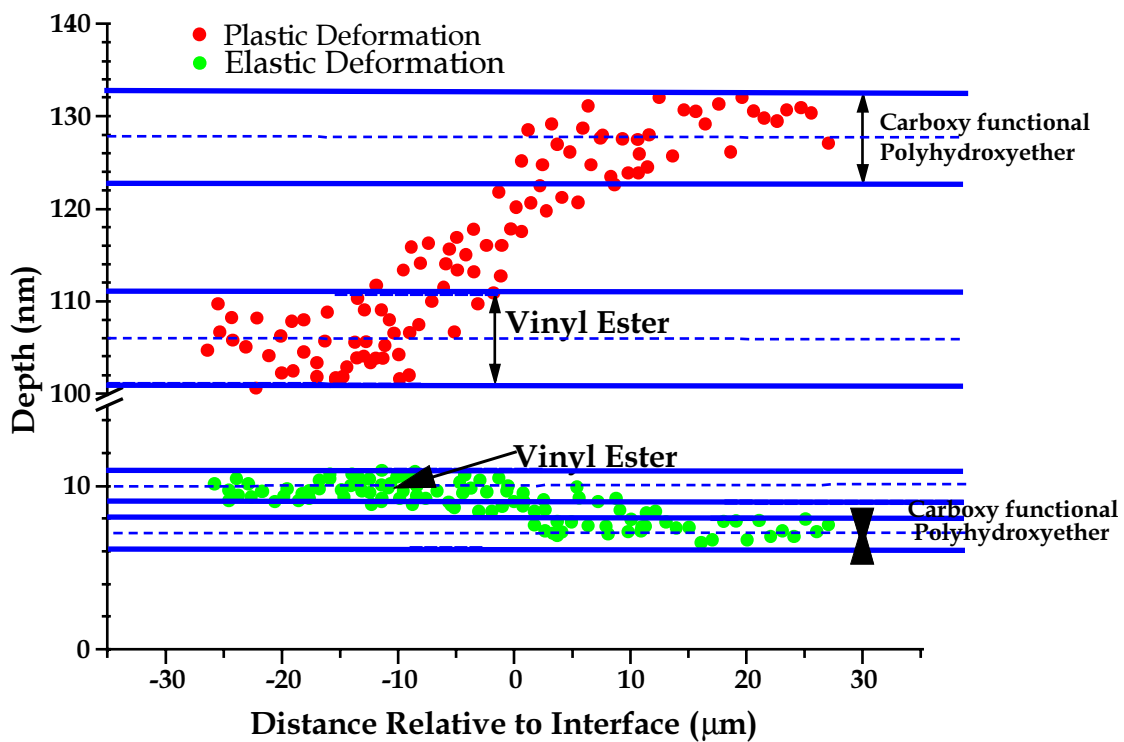


Figure 7: (Plastic and Elastic components of the indents produced across an interphase region of a vinyl ester - carboxy modified poly(hydroxyether) bilayer. Dotted lines represent the average depth of indents (solid boundary lines represent 2 standard deviations) in vinyl ester and carboxy modified poly(hydroxyether) respectively.

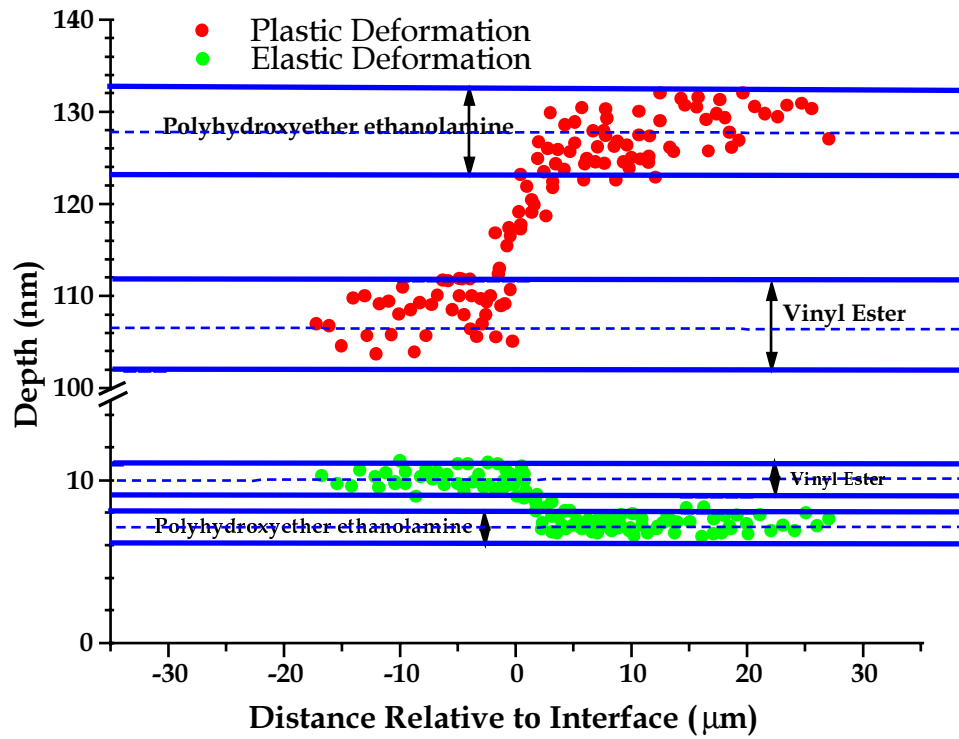


Figure 8: (Plastic and O elastic components of the indents produced across an interphase region of a vinyl ester - poly(hydroxyether-ethanolamine) bilayer. Dotted lines represent the average depth of indents in vinyl ester and poly(hydroxyether-ethanolamine) respectively. Solid boundary lines represent 2 standard deviations.

We have not yet been successful in observing compositional interphase gradients in the actual composites. Figure 9 illustrates an atomic force image of a polished composite cross-section with 0.8 weight % of the carboxy modified poly(hydroxyether) sizing. Although the image suggests a high quality composite and the interphase appears intact, no sizing layer is visible. By contrast, atomic force images of single fiber “model” composites (figure 10) do show a difference in the fiber-matrix interaction for an unsized and carboxy modified poly(hydroxyether) sized single fiber. The exact nature of this difference is not fully understood and is at present under further study.

Interfacial Shear Strength

Interfacial shear strengths (IFSS) on “model” single fiber composites were measured using a microdroplet debond method. The average IFSS of the control carbon fiber/vinyl ester samples prepared with unsized carbon fibers was 28 MPa (Table 1) whereas the values almost doubled for the carbon fibers coated with the poly(hydroxyether) and carboxy modified poly(hydroxyether) engineering thermoplastics.

Table 1: Interfacial shear strengths measured via a microdroplet micro-debond method from (A) a bead of sizing and (B) a bead of resin.

Thermoplastic	(A) IFSS (MPa) (thermoplastic bead/unsized fiber)	(B) IFSS (MPa) (vinyl ester bead/sized fiber)
No sizing	----	28+8
Poly(hydroxyether)	55.2+6.7	45.2+8.3
Modified Poly(hydroxyether)	---	44.4+7.3
Poly(hydroxyether ethanolamine)	53.2+7.4	22

This is consistent with good adhesion between these sizings and the vinyl ester matrix promoted by interdiffusion of these layers during cure (observed using AFM). The interfacial shear

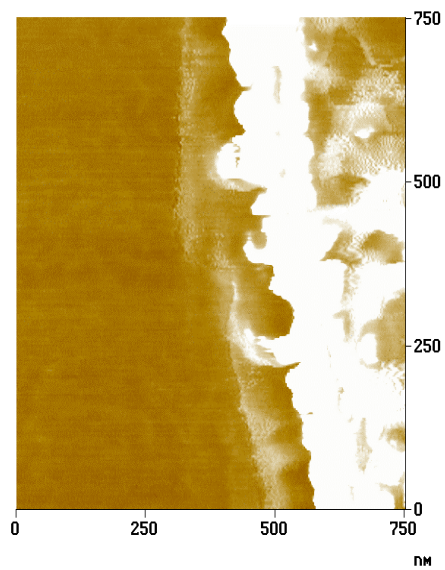


Figure 9: Atomic force microscopy image of a composite cross-section where the sizing material is the carboxy modified poly(hydroxyether).

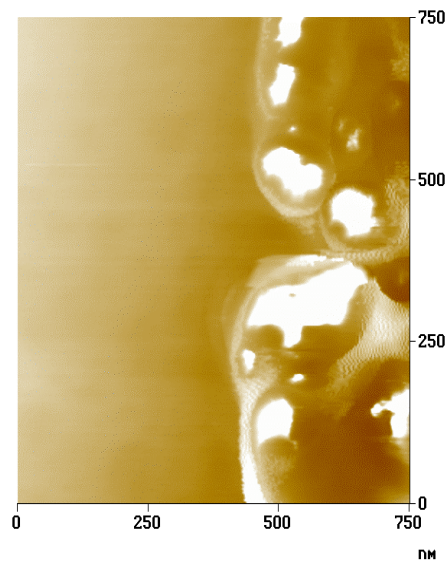


Figure 10: Atomic force microscopy image of a single fiber composite cross-section where the fiber was unsized.

strengths found for debonding droplets of the thermoplastic sizings from the carbon fiber were significantly higher than for debonding the vinyl ester from unsized fiber. It is hypothesized that acidic protons from the hydroxyl and carboxyl groups on the sizing backbones can interact with heteroatoms on the fiber surface and contribute to this enhanced adhesion. Further investigations of these adhesion mechanistic aspects are warranted and will be the subject of a future publication. The lightly crosslinked carboxy modified poly(hydroxyether) was less soluble in the resin than the unmodified poly(hydroxyether). The interdiffused interphase region observed by AFM was narrower, and it also yielded the largest IFSS. This suggests a necessity to control interdiffusion in the composites to ensure that a substantial amount of sizing indeed remains at the interface. In contrast to the encouraging results obtained with the carboxy modified poly(hydroxyether) sized fibers with the vinyl ester droplets, the samples prepared from the fibers sized with the poly(hydroxyether ethanolamine) and vinyl ester droplets provided almost the same IFSS as the control samples with the unsized fibers. This suggested poor adhesion, probably between the vinyl ester network and the poly(hydroxyether ethanolamine) sizing layer. Consistent with this result, the AFM micrographs indicated little to no interdiffusion between this polar sizing and the vinyl ester thermoset. More studies will be required to elucidate the mode of failure and thus, the adhesion mechanism.

Composite Characterization

Composite panels $(0^\circ/90^\circ)_{7S}$ were prepared with each of the two sizings and fully reversed ($R = -1$) notched fatigue tests were used to compare the as-processed fatigue lives as a function of the amount of sizing-matrix interdiffusion. Composite fatigue performance had previously been identified as being particularly sensitive to changes in the fiber-matrix interface^{2,4}. Improved fatigue performance is noted by a decrease in the slope of the S-N curve and increases in the stress level that defines the fatigue limit, i.e. the stress level at which the material survives 10^6 cycles (Figure 11). Significantly, by placing only 0.8 wt. % of the carboxy modified poly(hydroxyether) at the interface, a 50% increase in fatigue limit resulted as compared to the unsized material. By comparison, the poly(hydroxyether ethanolamine) interphase increased the fatigue performance of the composite relative to the unsized case, but

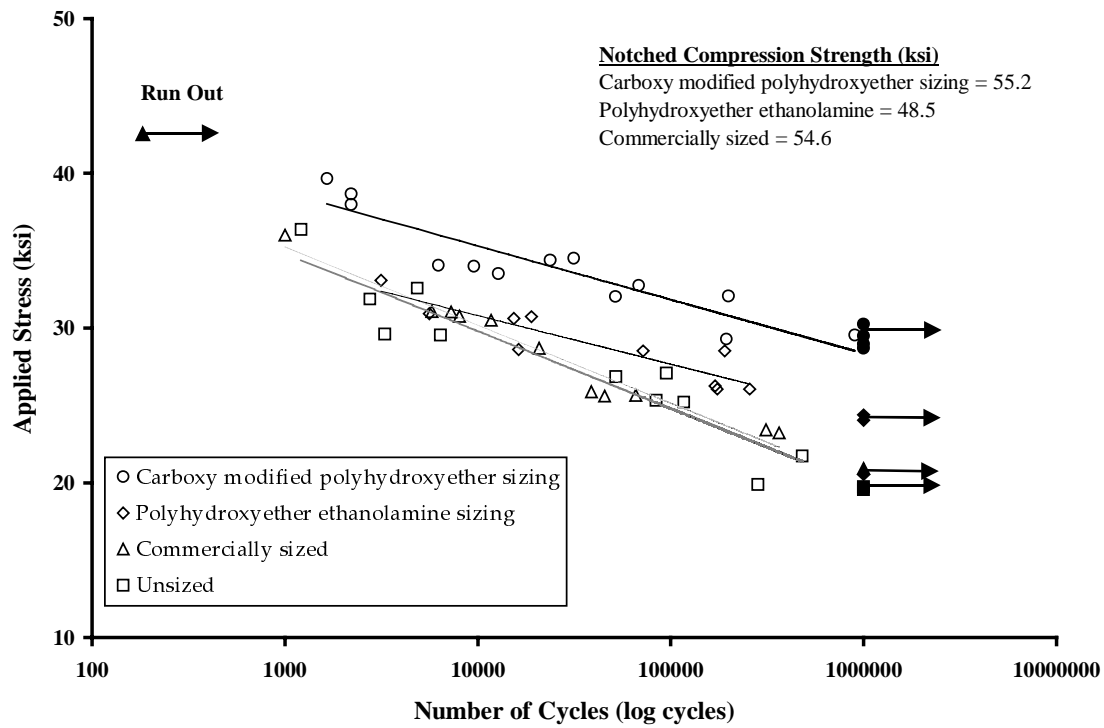


Figure 11: Fatigue durability of carbon fiber reinforced vinyl ester matrix composites as a function of sizing chemical structure.

did not lead to similar levels of durability enhancement. Fatigue limits for both sets of sized fiber composites relative to the unsized case were measured even though fiber-matrix adhesion for the poly(hydroxyether ethanolamine) materials was low. The slopes of the S-N curves were reduced for both sized systems relative to the unsized case. However, one can clearly see that at low cycle fatigue, the composite with the poly(hydroxyether ethanolamine) sizing did not outperform the unsized case. This could be associated with strength issues where the interface is so poor that it cannot prevent microbuckling at the stress concentration. However, at lower stress levels, the weak interface facilitated the growth of splits at the notch, the effect of the stress concentration was reduced, and therefore the stress levels in the material were not high enough to precipitate compression failure.

CONCLUSIONS

Interphase regions have been designed for carbon fiber reinforced vinyl ester matrix composites with a series of tough, ductile, thermoplastic sizings that interdiffuse into the matrix to varying degrees. Adhesion between the matrix and fiber was improved from 28 MPa in the unsized case to 45.2 and 44.4 MPa in the unmodified and modified poly(hydroxyether) cases respectively. Consistent with the adhesion data, atomic force microscopy showed interdiffused interphase regions with poly(hydroxyether) inclusions for both of these systems. By contrast, the interfacial shear strength was not improved by sizing the fiber with poly(hydroxyether ethanolamine), a sizing which did not interdiffuse with the matrix during cure. The relative amounts of sizing-matrix interdiffusion could also be qualitatively correlated to composite fatigue properties. Addition of <1 wt % poly(hydroxyether ethanolamine) to the composite improved fatigue durability (the stress limit where the samples endured a million cycles) from ~20 ksi in the unsized case to ~25 ksi. However, with as little as 0.8% by weight of the carboxy modified poly(hydroxyether) sizing in the composite, the fatigue limit for applied stress was improved by about 50% over the unsized fiber case, to ~32 ksi. Compilation of this adhesion, AFM imaging, and composite fatigue data suggests that tough ductile sizings designed for both fiber adhesion and matrix interdiffusion can significantly improve selected mechanical properties of these composites. Possibilities for extending the environmental durability of these composites via such interphase improvements will be the subject of future work in this area.