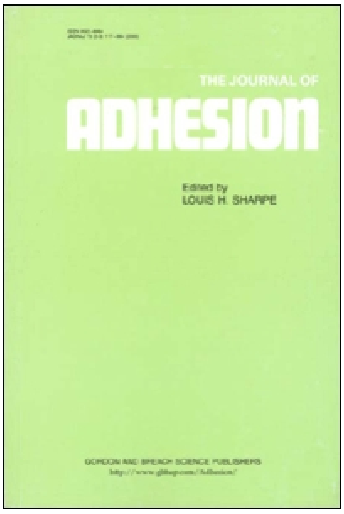

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Designed Interphase Regions in Carbon Fiber Reinforced Vinyl Ester Matrix Composites*

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Fiber-reinforced polymer matrix composites are finding increased use in structural applications where long-term mechanical and environmental durability are key issues. This has prompted impetus for fundamental studies to determine relationships between the structure of fiber/matrix "interphase" regions and composite durability in both our laboratories and those of others. This study describes initial interphase and composite properties for a series of carbon-fiber-reinforced vinyl ester matrix composites wherein the fiber sizing chemical structure has been varied within a series of ductile poly(hydroxyether)s. The mechanical properties of the sizings were similar. The primary difference between the systems studied was the amount of sizing-matrix interdiffusion and, hence, the microstructure of the interphase regions. A number of techniques were used to evaluate both the "macro and micro" properties of the composites as a function of interphase structure. These include atomic force microscopy and nano-indentation to map sizing/matrix interdiffusion compositional gradients and the resulting mechanical properties across bi-layer films comprised of the fiber "sizings" and vinyl ester matrices. Micro-debond tests were carried out by the Korean group to probe adhesion between the "sized" fibers and matrices. Fatigue cycling proved to be particularly useful in highlighting the influence of the tailored interphases on the durability of the carbon fiber/vinyl ester composites.

Composite fatigue properties of AS-4/vinyl ester composites having a tough, ductile polyhydroxyether thermoplastic in the "interphase" region were improved dramatically

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(relative to using unsized fibers) with < 1 wt.% of the sizing in the composite. The thermoplastic sizing dissolved in the thermoset at the cure temperature, but microphase separated into ~ 90 nm diameter inclusions during matrix curing. A gradient in chemical composition and morphology resulted, which moved outward from the fiber into the thermoset matrix. It is hypothesized that the unusually good fatigue resistance of composites from these materials can be at least partially attributed to this interphase gradient.

Keywords: Vinyl ester; carbon fiber; composite; interphase; adhesion; interfacial shear strength

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 with traditional metallic materials [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 is particularly sensitive to the morphology of the fiber-matrix interphase regions [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]. One method for controlling both fiber-matrix adhesion and the physical properties of the interphase region is to apply a sizing (*i.e.*, a polymeric fiber coating) 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.* [5] tested the durability and lifetime of vinyl ester matrix composites consisting of fibers sized with two dissimilar thermoplastics. A carboxylate modified poly(hydroxyether) sizing, a ductile engineering thermoplastic, yielded a 20-fold increase in the notched fatigue life of the composite compared with 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 micromechanical properties measured in interphase regions in a continuum mechanics model to predict composite performance.

Interphase regions have been designed by tailoring tough, ductile polymeric sizings to diffuse partially 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 12 K tow. The vinyl ester matrix material was kindly donated by the Dow Chemical Co. This resin was 70 wt.% of a vinyl ester (dimethacrylate terminated) oligomer with an M_n of 700 g/mole diluted with 30 – 34 wt.% styrene (Fig. 1). Benzoyl peroxide (Aldrich) was used as received as

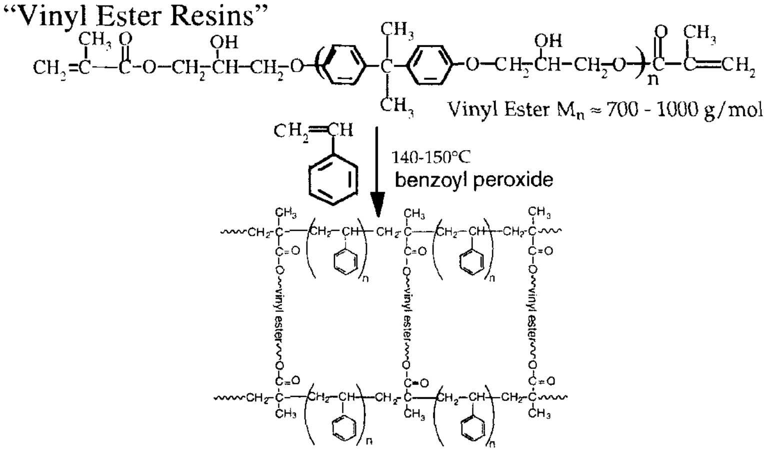
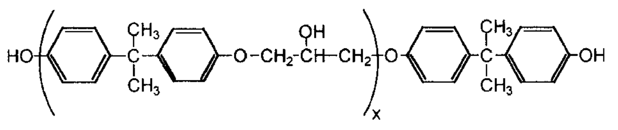


FIGURE 1 Dimethacrylate ("vinyl ester") – styrene matrix components.

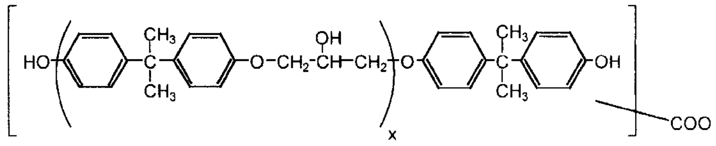
the initiator for the free radical cure reaction. The poly(hydroxyether) and the "carboxy modified poly(hydroxyether)" (PKHW-35) sizing materials were kindly donated by Phenoxy Associates, Rock Hill, SC (Fig. 2). The carboxylic acid modified material was a derivative of the original poly(hydroxyether) 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 1 μm average diameter particles which was diluted to 2 wt.% with water for sizing. The poly(hydroxyether ethanolamine) thermoplastic (Fig. 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 45°C and dissolving the thermoplastic in this solution.

The fiber tow was sized on a custom-made, small-scale sizing line [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

Unmodified Poly(hydroxyether)



Modified Poly(hydroxyether)



Poly(hydroxyether ethanolamine)

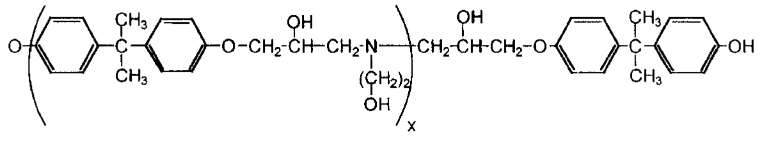
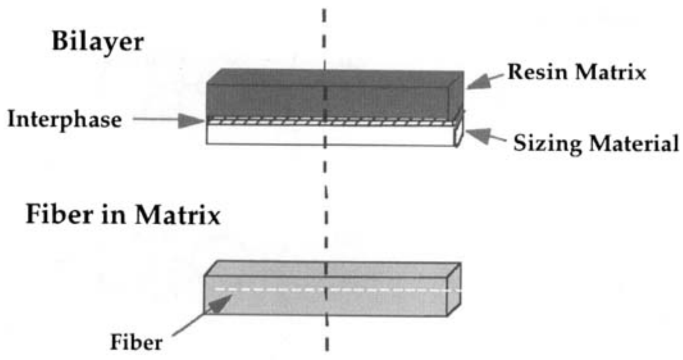


FIGURE 2 Thermoplastic sizing materials for carbon fiber reinforced vinyl ester matrix composites.

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 × 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 (Fig. 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



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

FIGURE 3 Sample preparation of sizing-matrix bilayer cross-sections.

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. Carboxy-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. A 4-gram sample of each composite was weighed in air, then immersed in isopropyl alcohol and reweighed. The density of the composite was calculated using Archimedes' principle and Eq. (1)

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

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 ν was the fiber volume fraction calculated from Eq. (2)

$$\nu = (\rho_{\text{composite}} - \rho_{\text{resin}})/(\rho_{\text{fiber}} - \rho_{\text{resin}}) \tag{2}$$

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 $\rho_{\text{fiber}} = 1.78\,\text{g/ml}$ (8) and $\rho_{\text{resin}} = 1.18\,\text{g/ml}$ [9].

As a quality control precaution, 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 were analyzed using the FlexSCAN-C software provided with the instrument. The scans were gated both to the mid-plane 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 with those with the carboxy-modified poly(hydroxyether) sizing. 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, 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 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$^{\text{TM}}$ 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 [10]. The tip deflection was calibrated using a sapphire substrate as an infinitely stiff material; 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 [11]. The plastic component was calculated by taking the initial slope of the unloading curve and extrapolating 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 conducted on an MTS test frame to assess composite strength. A loading rate of 200 pounds per second (~91 kg/sec) 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. Emery cloth (100 grit) was wrapped around the grip sections of the specimens to prevent slip. An MTS Model 632 extensiometer with a gauge length of 2.54 cm and a maximum strain limit of 4% was used to monitor strain. Aluminum extensiometer tabs were used to hold an extensiometer and the signal from the extensiometer 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 × 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 micro-debond tests were prepared by applying a small droplet of the vinyl ester resin containing 1.1 wt.% 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 temperature. 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 BB 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 weights of the vinyl ester prepolymers 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 (Fig. 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 (Fig. 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 morphologies of interphase regions between each sizing and the vinyl ester network were examined by constructing bilayer sizing material-matrix samples (Fig. 3), then microtoming cross-sections and studying them using atomic force microscopy (Fig. 4). The relative size of the interphase regions where visible interdiffusion between the sizings and the vinyl ester matrix occurred decreased in the order: unmodified poly(hydroxyether) > carboxy modified poly(hydroxyether) > poly(hydroxyether ethanolamine) (no visible interdiffusion). The interdiffused sections of the interphase region 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 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 growth of the poly(hydroxyether) domains. With the addition of carboxylate groups, the sizing material becomes reactive. When the

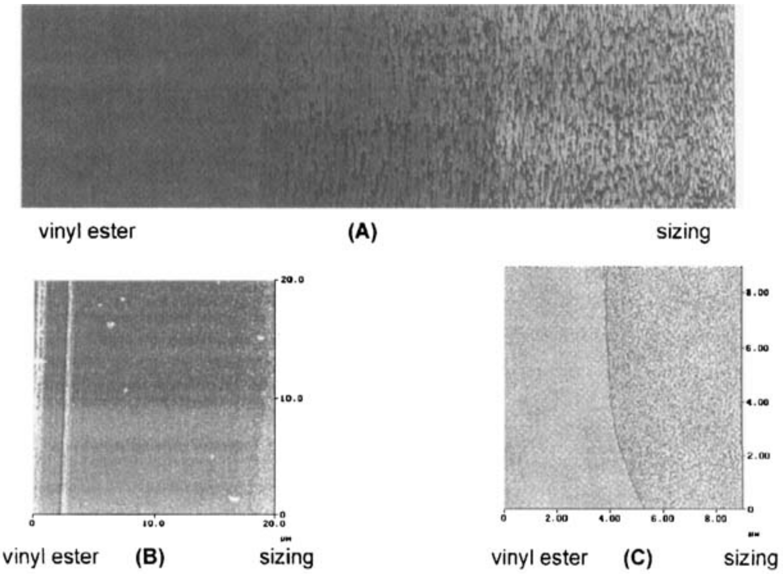


FIGURE 4 Atomic force microscopy images (tapping mode, phase image) of sizing-matrix bilayer cross-sections illustrating relative interdiffusion of sizing with matrix: (A) Unmodified poly(hydroxyether), (B) Carboxy-modified poly(hydroxyether) sizing, and (C) poly(hydroxyether ethanolamine) sizing.

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 hours, there was a 65% gel fraction. This light crosslinking probably limited the mobility of this sizing as panels were prepared and, thus, a significant fraction of sizing material was maintained in the interphase region. The interphase morphology using this carboxy-modified poly(hydroxyether) 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). A 30-μm-wide compositional gradient was evident in the unmodified poly(hydroxyether)/vinyl ester bilayer as compared with 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, interdiffusion 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, because 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 deformations as a function of position are reported.

A nano-indentation technique employing 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 [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

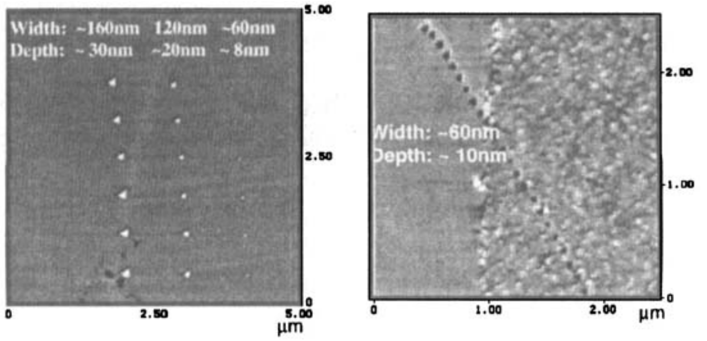

AFM (Tapping Mode, Height Image)

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.

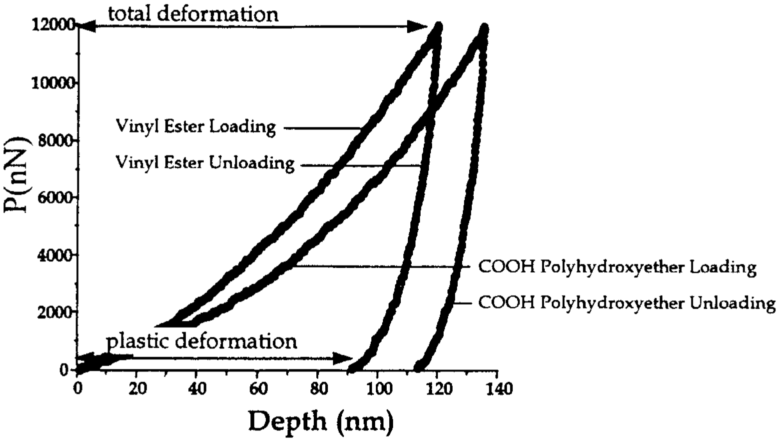


FIGURE 6 Force curves for (a) Vinyl ester matrix and (b) Carboxy-modified poly(hydroxyether).

was expected because of the chemical similarity of these two materials. 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. Hysteresis between the indention and retraction curves was attributed to plastic deformation (taking into consideration a scaling factor (ε in Eq. (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 [12, 13];

$$h_p = h_{\max} - \varepsilon(h_{\max} - h_i) \tag{3}$$

where h_p was the plastic depth, $h_{\max}$ the maximum depth, h_i the intercept depth and the constant ε was a function of the shape of the indenter tip (0.75 for a 3-sided 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 there was a "pile-up" of material around the top of the indentations (Fig. 6). The degree of "pile-up" varied across the interphase regions with the thermoplastic sizing materials showing a larger amount than the thermoset matrices. 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 were 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 [14, 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

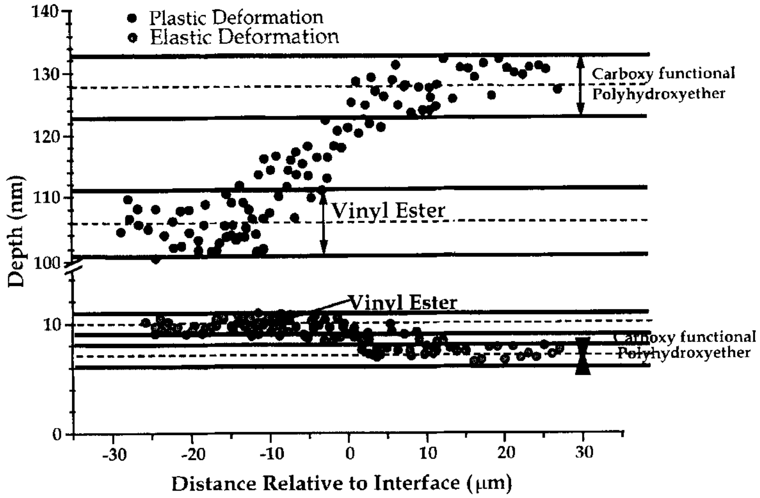


FIGURE 7 • Plastic and • Elastic components of the indents produced across an interphase region of a vinyl ester-carboxy-modified poly(hydroxyether) bilayer. Dotted lines represent the average depth of indents (solid boundary lines represent 2 standard deviations) in vinyl ester and carboxy-modified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

increased. The data also indicated a gradient across the interphase extending 10–15 μm from the vinyl ester to the interface and 5 μm into the carboxy-modified poly(hydroxyether) side of the bilayer. The zero point on the graphs was arbitrarily set as the point where the themoset-thermoplastic interface was observed. The 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 consisted 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 [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. In contrast to the 15–20 μm interphase observed in the carboxy-modified poly(hydroxyether)–vinyl ester bilayer, the interphase region for the poly(hydroxyether ethanolamine) and the nano-mechanical data (Fig. 8) show a sharper interphase with a breadth of only 1–2 μm. This was consistent with our qualitative observation

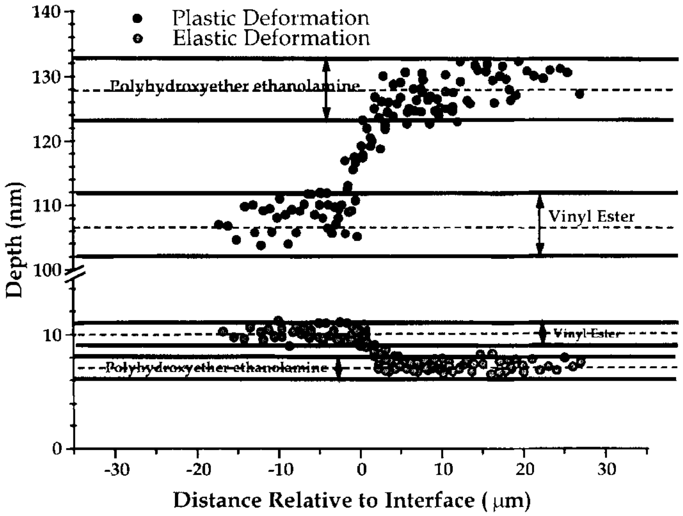


FIGURE 8 • Plastic and • Elastic components of the indents produced across an interphase region of a vinyl ester–poly(hydroxyether-ethanolamine) bilayer. Dotted lines represent the average depth of indents in vinyl ester and poly(hydroxyether-ethanolamine) respectively. Solid boundary lines represent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

that very poor adhesion existed between these two materials in the bilayers.

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 (Fig. 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.

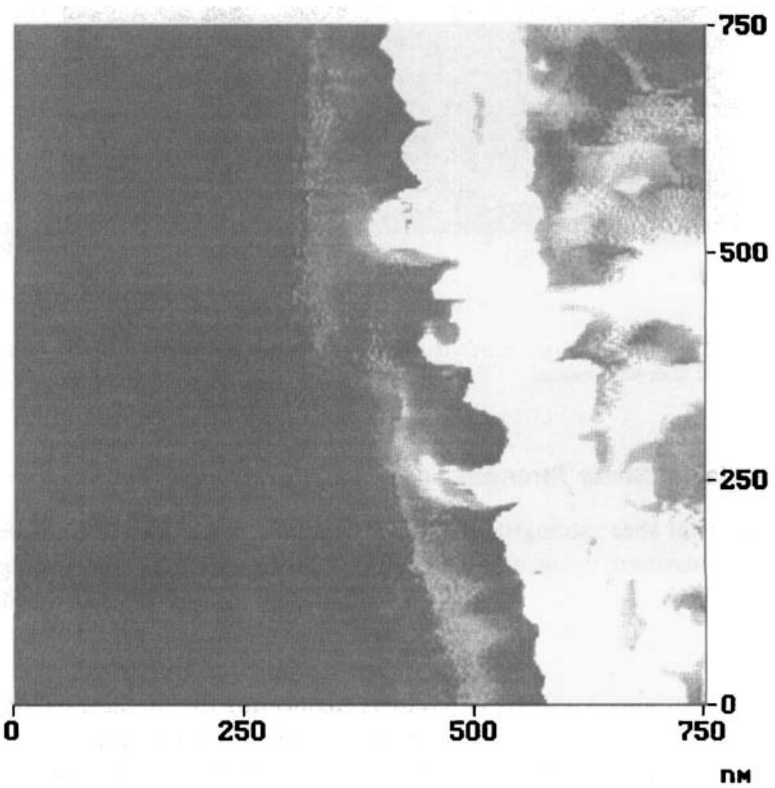


FIGURE 9 Atomic force microscopy image of a composite cross-section where the sizing material is the carboxy-modified poly(hydroxyether).

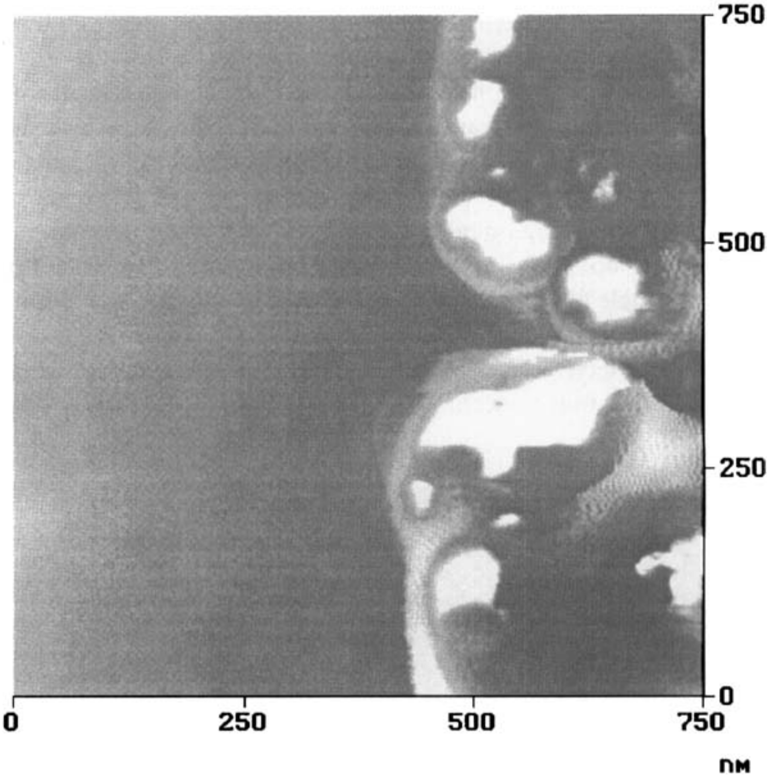


FIGURE 10 Atomic force microscopy image of a single-fiber composite cross-section where the fiber was unsized.

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 (Tab. I), whereas the values almost doubled for the fibers coated with the poly(hydroxyether) and carboxy-modified poly(hydroxyether) engineering thermoplastics. 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 strengths found for debonding droplets of the thermoplastic sizings from the carbon fiber

TABLE I 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

were significantly higher than for debonding the vinyl ester from the 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 mechanistic aspects of the adhesion 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 [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. 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 with the unsized material (Fig. 11). By comparison, the poly(hydroxyether ethanolamine) interphase increased the fatigue performance of the composite relative to the unsized case, but 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 was so poor that it could not prevent microbuckling at the stress concentrations. However, at lower stress levels, the weak interface facilitated the growth of splits at the notch and effects of the stress concentration were reduced and, therefore, the stress levels in the material were not high enough to precipitate compression failure.

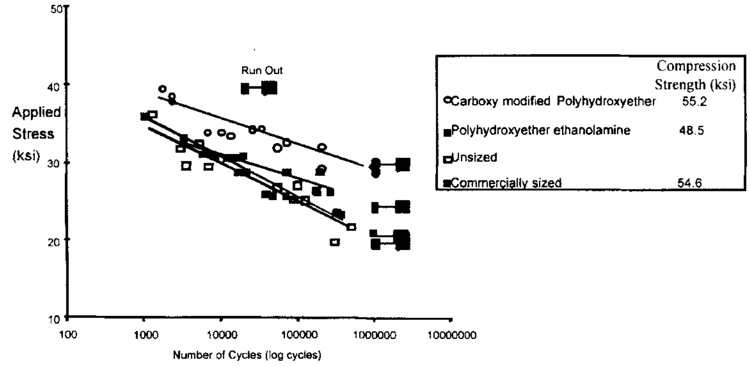


FIGURE 11 Fatigue durability of carbon fiber reinforced vinyl ester matrix composites as a function of sizing chemical structure.

SUMMARY

Interphase regions were 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 these 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.

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