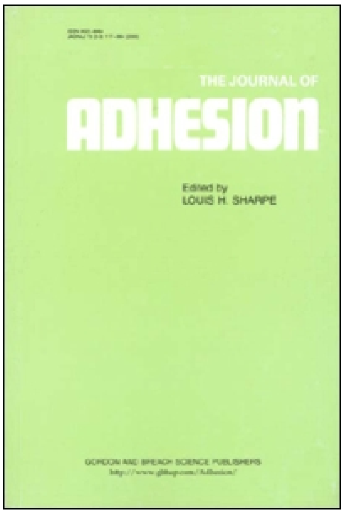

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Interface/Interphase Studies in Epoxy Matrix Composites

B. Okhuysen[a]; R. C. Cochran[a]; R. E. Allred[b]; R. Sposili[c]; T. M. Donnellan[c]
[a] Naval Air Warfare Center, Warminster, PA, USA [b] Adherent Technologies, Albuquerque, NM, USA [c] Grumman Corporate Research Center, Bethpage, NY, USA

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Interface/Interphase Studies in Epoxy Matrix Composites*

B. OKHUYSEN and R. C. COCHRAN
Naval Air Warfare Center, Warminster, PA 18974, USA

R. E. ALLRED
Adherent Technologies, 9621 Camino del Sol NE, Albuquerque, NM 87111, USA

R. SPOSILI and T. M. DONNELLAN**
Grumman Corporate Research Center, Bethpage, NY 11714-3580, USA

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The effect of surface treatments and fiber sizings on the stress transfer characteristics and composite properties of AS-4 carbon/epoxy materials has been determined. Fiber surface chemistry was systematically varied from acidic to basic with RF glow discharge plasmas of CO_2 and NH_3 and characterized with ESCA techniques. Sizings applied to some of the treated fibers consisted of diglycidyl ether of bisphenol-A(DGEBA). Single fiber tension tests were used to measure the interfacial shear strength of samples made with DGEBA/metaphenylene diamine resin. Short beam shear and transverse flexure tests were used to examine the composite properties of modified materials.

Results showed that the plasma treatments were effective in altering the surface chemistry of the fiber but that changes in surface chemistry had surprisingly little effect on the critical stress transfer length. Sizing had a more significant effect on the transfer length. The interlaminar shear strength of the composites were unaffected by the treatments. Transverse flexure tests were more sensitive to the changes in surface characteristics. The work indicates that the interface properties of AS-4 fibers are close to optimal but that improvements in composite performance are possible through interphase formation.

KEY WORDS interface; interphase; plasma surface treatment; fiber surface acidity; critical fiber length; adhesion; composite performance.

INTRODUCTION

The importance of interface control in composites is that it provides a means to alter the properties of systems with well-characterized constituents. It has been recognized for the past twenty-five years that the interface in composites can dramatically impact the performance of the material.[1] Work in interface science has concentrated

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**Corresponding author.

on the alteration of the fiber surface characteristics or on study of the effect of specific fiber coatings on composite properties. Fiber surface modifications that have been examined include physical roughening for mechanical interlocking and chemical modification of the fiber surface.[1-7] The chemical treatments have been preferred since they afford improvement without the potential for degradation of the fiber properties that is inherent in surface roughening.[2] Electrooxidative techniques have been developed and are conventionally used in treatment of carbon fiber surfaces. These treatments remove weak boundary layers from the surface and produce increased surface activity with formation of both acidic and basic moities.[8,9] Low-energy plasma processes have been developed that have demonstrated the potential to tailor the acidity of the surface characteristics for optimization of the adhesion between the fiber and a specific resin.[4,5,10-12] These plasma techniques have been shown to provide increased levels of surface activity with functionalization of basal plane sites in the fiber surface.

Work has also been performed in the characterization and modification of the interphase material that is present between the fiber and the resin in the composite. This interphase can form naturally either as a result of altered chemical reaction kinetics in the region adjacent to the fiber surface[13] or as a result of the interaction between the sizing applied to the fiber prior to processing and the resin.[14,15] Alternately, coatings that are designed to afford specific characteristics to the composite system, such as stiffness or toughness, have been purposely applied to the fiber.[16-18] These coating processes typically are applied to fibers that have already been exposed to some surface enhancement treatment.

It has been found that each of these approaches can improve resin-fiber stress transfer and some correlations between surface modification and either single fiber or composite properties have been reported.[19-27] The agreement in the literature is not universal. The surface modifications sometimes fail to produce any marked change in the fiber-resin stress transfer characteristics. Similarly, improvements identified through single fiber testing occasionally do not translate directly into composite performance.[23,25] Explanations for these results are difficult because the surface treatments and sizing used are often proprietary and the specimen geometries and test procedures used vary. Also, it is possible that surface interactions and interphase formation characteristics are system-specific and process-specific. It would be useful to identify the improvements achievable in conventional carbon/epoxy materials through independent alteration of the surface chemistry and fiber coating in a well-defined and controlled materials system.

The work described here is a systematic study of the relative influence of surface modifications and sizings on the properties of epoxy matrix composites. The particular materials selected for study, AS-4 carbon and diglycidyl ether of bisphenol-A/metaphenylene diamine resin, have been well characterized. The objective was to identify critical characteristics that can be used in improvement of the properties of composite materials. Specifically, surface modifications made with plasma processes that can dramatically alter the surface chemistry of carbon fibers are described. The influence of these modifications on the interfacial shear strength and the composite performance of a carbon/epoxy system is studied. Further, the effect of interphase formation induced through sizings applied to the treated fiber surfaces on the composite properties is presented.

EXPERIMENTAL

Materials

As-oxidized, unsized Hercules AS-4 fibers were used in the study. Some of the surface-treated fibers, along with a control set, were sized with epoxy resin. These fibers were exposed to a 1% solution of diglycidyl ether of Bisphenol-A, DGEBA, (Dow DER 332®) in methyl ethyl ketone and then dried. The resin used was a molar mixture of Shell Epon 828® epoxy and m-phenylenediamine hardener from Aldrich (14.5 parts MPDA per 100 parts epoxy by weight). The crystalline MPDA was melted at 72°C while the epoxy was preheated to 72°C. The mixed resin was degassed between 70 and 74°C prior to cure.

Processes

Surface modifications The surface modifications examined were applied using low-energy plasma techniques. Both batch and continuous plasma processes were used in the study. Batch plasma treatments were conducted in a March Plasmod reactor with a 105 mm diameter by 150 mm length treatment chamber. The Plasmod is a capacitatively-coupled, radio-frequency system operating at 13.56 MHz. The unsized AS-4 fibers were held in the center of the reaction zone by winding them over a wood frame. Carbon dioxide and ammonia plasma gases were used to produce acidic and basic surface chemistries on the carbon fibers. The plasma treatments were conducted for 120 sec at 50 W and 800 mtorr. Following the plasma treatments, the samples were allowed to sit in the flowing source gas for 5 min before opening the reactor to the atmosphere.

Continuous plasma treatments were conducted using a prototype research reactor that consists of 3 separate, independently-controlled plasma chambers in series. The continuous plasma system is capacitively coupled and operates at 13.56 MHz. Plasma operating parameters for both systems were optimized based upon surface chemical characterization results in conjunction with the visible emission spectrum of the plasma. A 30 sec scrub in Ar plasma in the first plasma chamber was used to preclean the carbon fibers before the surface modification treatments. Ammonia treatments were conducted for 60 sec at 70 W under 2 torr pressure with a flow rate of 5 sccm^{-1}. Carbon dioxide treatments were conducted at 20 W under 1 torr pressure and a flow rate of 50 sccm for 60 sec.

Single fiber specimens Single fiber fragmentation experiments were used to assess the relative influence of interface and interphase on the interfacial shear strength. Unsized and sized fibers treated by the batch plasma processes were incorporated into epoxy tensile dogbone specimens. The specimens were processed at 75°C for 2 hours and 125°C for two hours. The cured specimens were carefully polished on both sides to aid in the observation of the embedded single fiber during testing.

Composite specimens Composites were produced with the fibers that were treated in the continuous plasma process. The carbon fibers were incorporated into prepregs with a Research Tool Corporation Model-30 hot-melt prepregger. For some of the prepregs, an epoxy sizing, consisting of a 1% solution of DGEBA (Dow DER 332) in methyl ethyl ketone (MEK), was applied to the carbon fibers during the prepreg operation. After each batch of prepreg was made, it was cut into 12″ × 12″ plies, sandwiched between sheets of Mylar®, sealed in polyethylene bags, and frozen. Frozen storage was necessary due to the high reactivity of the catalyzed epoxy resin. Sixteen-ply unidirectional laminates were produced in an autoclave. Standard vacuum-bagging procedures were used with a bleeder-to-prepreg-ply ratio of approximately 1:2. The cure cycle included two 2-hour holds at 75°C and 125°C, respectively, under a pressure of 85 psig (586 KPa). Laminate quality was examined by photomicroscopy and ultrasonic inspection. Image analysis of specimen microstructures was used to estimate the fiber volume fraction (V_f) of the laminates.

Procedures

Fiber surface analyses The continuous plasma treated AS-4 filaments were analyzed using wet chemical techniques and electron spectroscopy for chemical analysis (ESCA). Amine sites on the ammonia plasma treated fibers were determined using an ion-exchange procedure given in Ref. 28. Acid sites were measured on the carbon dioxide plasma treated fibers using the non-aqueous titration procedure discussed in Ref. 10.

ESCA analysis were run at Rocky Mountain Laboratories, Inc. (Golden, Colorado) using a Surface Sciences SSX-100 spectrometer with an Al Kα source. Survey spectra were taken to examine the as-received surface chemical stoichiometry. High-resolution spectra were taken of the C_{1s} peaks to determine possible surface bonding states. C_{1s} high-resolution peaks were averaged over 10–15 scans using a spot size of 600 μ^2 with a 1.0 eV flood gun. A Gaussian curve-fitting routine was used to resolve the high-resolution photopeaks into component peaks based on binding energy references from model compounds.[29] The spectra have not been charge referenced.

Single fiber tests The tests were performed using procedures previously published by Drzal.[2,3] Specimens were placed in a test frame mounted on the stage of a transmitted-light microscope. Tension was applied through discrete 0.05 inch elongation steps. Fiber breaks were most easily observed by cross-polarizing the light transmitted through the specimen and observing photoelastic stress effects around the fiber. After each step, the specimen was scanned under the microscope and new damage was recorded. When the fiber was fragmented to the point that no new damage occurred, the broken fiber was scanned and fiber fragments were measured using a filar eyepiece. The fiber diameter was also measured. These data yielded L_c/D ratios that were fit to a Weibull distribution.

Composite tests Short beam shear and transverse flexure tests were used to study treatment effects on composite performance. The short beam shear tests (SBS) were performed according to ASTM D-2344. The specimens for both tests measured 1.5 in. × .25 in. (3.8 cm × 0.64 cm). Specimens were cut on a diamond saw and milled to final tolerances with a carbide cutter. The span-to-depth ratio used for the short beam shear tests was 4:1 and that used for the 90° flexure test was 10:1. Tests were conducted on an MTS test machine with a three-point flexure fixture at a cross-head speed of 1.3 mm/min.

RESULTS AND DISCUSSION

Fiber Surface Treatments

The ESCA survey spectra show that the fiber surfaces are composed almost entirely of carbon, oxygen, and nitrogen with trace amounts of Ca, P, and Si. Waltersson has shown that Ca and Si are common impurities in carbon fibers from processing the PAN fiber precursor or from oxidative surface treatments.[30] Phosphorous was observed only on the as-received fibers and is likely a residue from the manufacturer's oxidative surface treatment. Surface composition results, normalized to 100% C, O, and N, are given in Table I. Results show that the as-received fiber contains 9% oxygen and under 3% nitrogen in the near surface. A factor of two higher oxygen content has been reported by Hammer and Drzal for AS-4 fibers.[3] This discrepancy is likely an indication that the manufacturer has changed their surface oxidation process over time. Nitrogen in the as-received fiber is also substantially lower than that reported in Ref. 3. Nitrogen in as-produced carbon fibers is residual from the PAN carbonization process and an indication of the degree of carbonization.[3]

Batch plasma treatment with CO_2 resulted in a substantial increase in surface oxygen content, and an increase in surface nitrogen as well. Wesson and Allred have shown that such increases in surface oxygen content are accompanied by increases in acidity and chemisorptive capacity.[10,11] They also report an increase in surface nitrogen after acidic plasma treatments.[10] Nitrogen may become incorporated into the fiber structure through air leaks or impurities. Continuous plasma treatment with CO_2 produced less oxygen content on the fiber surface than the batch treatment and did not result in additional nitrogen being incorporated into the fiber surface. The high resolution C_{1s} spectra show that the additional oxygen on CO_2-plasma-treated AS-4 surfaces is in the form of carboxyl and ester moieties. The non-aqueous titration results showed that the continuous CO_2 treatment produced 1.1 acid sites/nm.[2]

TABLE I
Surface chemical composition of AS-4 carbon fibers

Treatment	% Carbon	% Oxygen	% Nitrogen
As-received	88.2	9.1	2.7
Carbon dioxide plasma[a]	81.7	14.6	3.7
Carbon dioxide plasma[b]	86.4	11.4	2.2
Ammonia plasma[a]	86.9	9.2	3.9
Ammonia plasma[b]	84.5	10.4	5.2

[a]Batch treated.
[b]Continuous treated.

The treatments with ammonia plasma increased nitrogen content by a significant amount (Table I). Jones has shown that surface nitrogen from ammonia plasma treatment of carbon is in the form of amine (NH_2) groups occupying edge sites in the fiber surface.[31] The ammonia-treated fibers also show a high surface oxygen content. Oxygen can be incorporated into the fiber surface during the plasma treatment process from air leaks in the system or from desorption from the quartz reactor walls. Oxygen can also react with residual free radicals on the fiber surface upon exposure to air.

ESCA results reveal that the three fiber types constitute a gradient in surface chemistry from basic (ammonia treated) to mildly acidic (as-received) to strongly acidic (carbon dioxide treated). The three fiber treatments studied provide a good means for the evaluation of the effect of systematic alterations in surface acidity on interfacial shear strength.

Single Fiber Test Results

Estimates of the critical transfer length/diameter ratio (L_c/d), which is inversely proportional to the interfacial shear strength, are shown in Table II. Surprisingly, the differences in critical length were not large for the set of surfaces studied. The scatter in the results is consistent with that found in earlier studies[19] and it precludes quantitative interpretation of the results. However, the trends in L_c/d data provide some insight into the effects of the surface modifications studied on stress transfer. The value found for the unsized, untreated fibers agrees well with published results[20] even though the surface chemistries of the fibers appeared to be significantly different. This indicates that the as-oxidized fiber surface may have near optimum surface functionality for AS-4 type fibers. The increased surface activity in the plasma-modified fibers improves the transfer of stress from the resin to the fiber. It is interesting to note that there was no difference in the degree of improvement achieved through the acidic and basic treatments. Thus, in these experiments, the fact that the surface character was dramatically different was not as important as the increase in surface functionality in the improvement of shear strength. The results imply that either the increase in bond density is similar in both cases or perhaps that the principal effect of the treatments was a microroughening of the surface which improved mechanical interlocking.

Increased surface roughness has been listed as a contributing factor to the improved performance in surface-treated samples.[32] The plasma surface treatments

TABLE II
Single fiber fragmentation test results

Fiber surface condition	$L_c/d \pm$ std. dev.
Untreated, unsized	53.9 ± 16.1
Acid treated, unsized	48.3 ± 13.2
Base treated, unsized	48.2 ± 13.7
Untreated, sized	33.9 ± 9.3
Acid treated, sized	43.9 ± 13.1
Base treated, sized	35.1 ± 9.6

used in this study did not affect the physical surface characteristics of the fiber. Figure 1 compares the surfaces of the treated fibers with that of the as-received fiber. There is no surface etching or pitting observable on the treated fibers. Changes in the performance of the treated fiber materials are, therefore, not related to any increased roughening of the surface.

Comparison of the fragmentation test results obtained from the unsized and sized fibers showed that the presence of the sizing on the fiber was more significant than the surface character of the fiber. The largest change in shear strength was obtained with the as-received fiber. Indeed, the effect of surface treatment prior to the application of the sizing was an increase in L_c/d and, thus, a decrease in shear strength. Further, the relative effects of the acidic and basic treatments are no longer the same. The explanation for these results is not clear. There is the possibility that the modifications to the fiber surfaces influenced the structure and properties of the interphase subsequently formed and, in these cases, the structural changes led to reduced shear strength. From an experimental standpoint, there is also the possibility that, although all of the fibers were sized at the same time in the same solution, the thickness of the coating on the fiber surface could have been different based on the fiber surface chemistry. Fowkes and Mostafa[33] found significant differences in adsorption characteristics of polymer solutions as a function of substrate surface acidity. Additional work is required to identify the mechanism responsible for the results obtained.

Also, there was a difference in the mode of failure between the sized and unsized samples. The unsized materials all exhibited an interface failure mode as shown in Figure 2. The sized fibers all had matrix cracks at the fiber breaks. Drzal has ascribed this difference to the fracture properties of the material that forms in the interphase in sized materials. Differences in failure mode may be responsible for some of the variations in mechanical properties observed in sized fiber and unsized-fiber-based composites.[23,24]

Composite Test Results

The results of the SBS and transverse flexure testing are given in Table III. All of the materials examined exhibited primarily interlaminar failure modes in the SBS tests and tension surface failure in the 90° flexure tests. There was some variability in the location of the fracture in the flexure tests. This variability may be due to the notch sensitivity of the resin-dominant flexure specimens. The agreement between the composite and single fiber results was mixed. The critical length data for the treated unsized fibers is consistent with the SBS and flexure strength data obtained on the composites. There was very little difference between the SBS and 90° flexure strength of the acid- and base-treated samples. However, the slight improvement in surface activity indicated by the decrease in L_c/d achieved by the plasma treatments did not affect the SBS fracture process. Similarly, sizing the fibers, which had a more significant effect on L_c/d, was not reflected in any improvement in the SBS strength. These data showed that the improvements obtained from the surface treatments did not translate into the SBS test. An explanation for the results is that the composite property studied did not require the improvement in surface activity

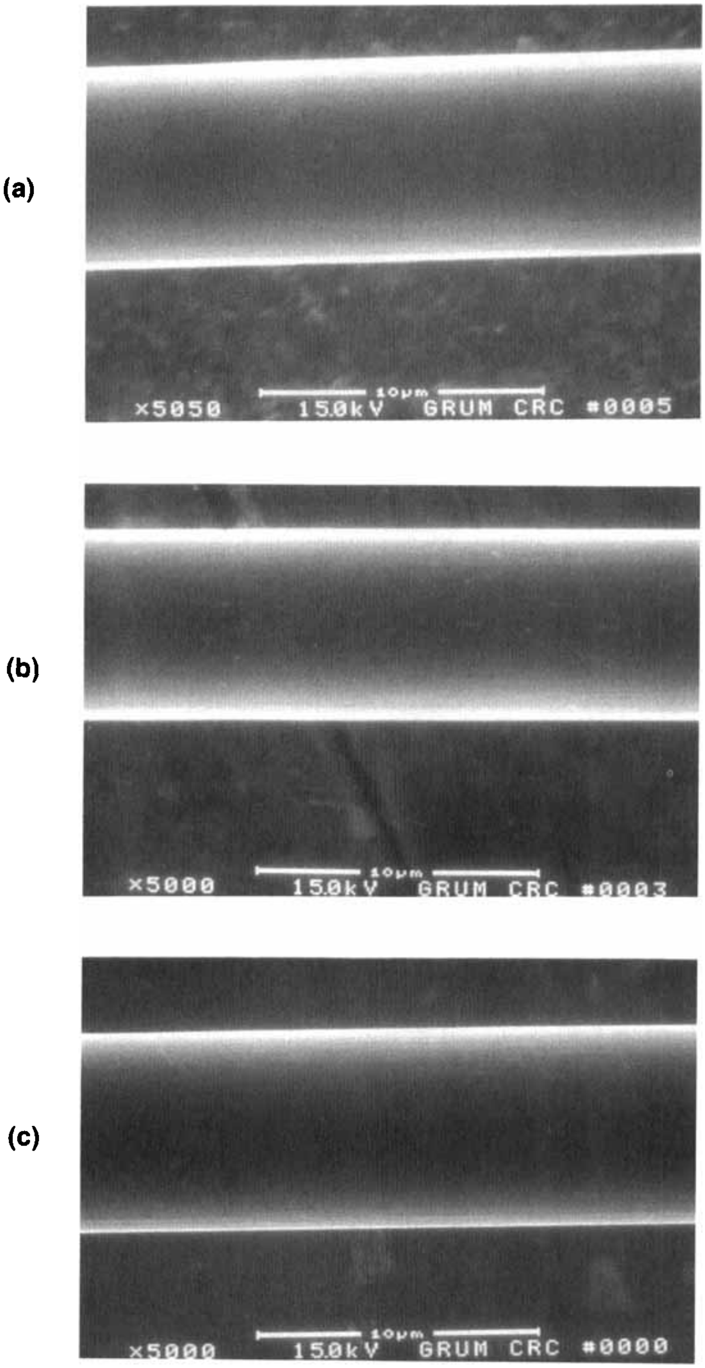

FIGURE 1 Surface characteristics of the fibers used in the study: (a) as-received AS-4 fiber; (b) base-treated fiber; and (c) acid-treated fiber.

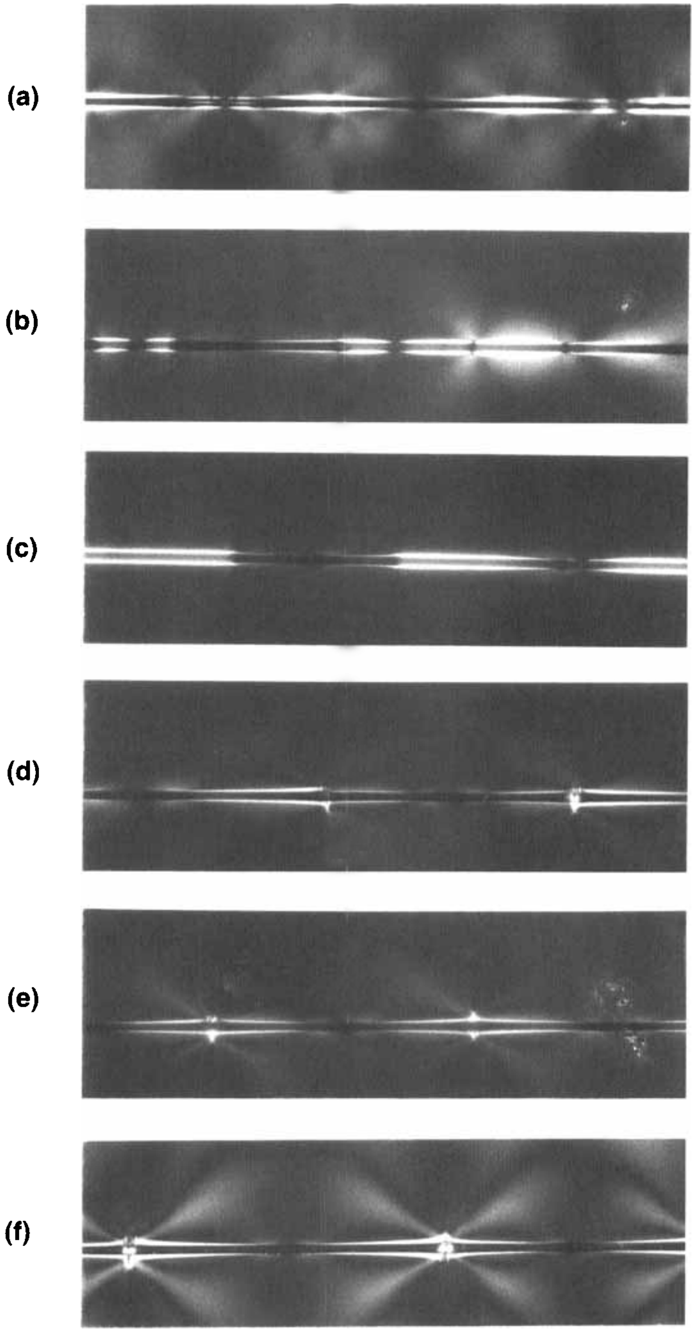

FIGURE 2 Optical micrographs of the fracture process in the single fiber specimens: a–c show the similarity in the interface fracture features of unsized fibers in the as-received, base-treated, and acid-treated condition; d–f show that sized samples of these fibers all exhibited a matrix-cracking failure mode.

TABLE III
Composite properties

Fiber condition	V_f (%)	SBS strength MPa (ksi)	Flexural strength MPa (ksi)
Untreated, unsized	.53	78.2 (11.2)	61.2 (8.7)
Acid treated, unsized	.64	78.2 (11.2)	44.7 (6.4)
Base treated, unsized	.61	77.0 (11.1)	44.0 (6.3)
Untreated, sized	.60	80.1 (11.5)	53.8 (7.7)
Acid treated, sized	.64	78.2 (11.2)	49.6 (7.1)
Base treated, sized	.65	66.4 (9.5)	38.4 (5.5)

afforded by the plasma surface treatments. The single fiber test results indicated that the as-received fiber surface had a good level of adhesion between the fiber and the resin. The treated fibers also had good adhesion. The oxidative treatment of the as-received AS-4 fiber was sufficient to drive the critical shear failure process from the fiber surface and into the resin. Thus, the additional improvement in surface bonding had no effect on the critical fracture mode of the material. Similar results have been obtained by Madhukar and Drzal.[23,24] These workers report a movement in the locus of failure from the interface to the resin in composites that was related to the surface characteristics of the fiber used.

Other workers have observed more significant influences of surface treatment on the transverse tensile and flexure strength of composites.[5,23] In general, the work performed here supports this finding. The data from the unsized, treated set of samples were consistent with those from the single fiber and the SBS testing performed. There was no difference in the properties of the materials. Also, the sized samples indicated that for the untreated and acid-treated fibers, there was an improvement in the transverse flexure strength consistent with the single-fiber tests. However, direct correlation between the single fiber and 90° composite flexure test results is not possible. The highest composite flexure strengths were obtained in the untreated samples, although the single fiber data indicated that these samples should have had relatively low performance. One complicating factor in interpretation of these tests is the variation in the fiber volume fraction in the laminates produced for study. Both the SBS strength and the transverse flexure strength are sensitive to the fiber volume fraction[34,35] and any comparative study must consider V_f effects on observed results. In this study, process modifications were employed as needed to produce laminates with similar V_f. As indicated in Table III, the untreated fiber composites consistently gave laminates that were lower in V_f than those of the treated materials. Other laminates of the untreated material were produced that had 48 to 50 percent V_f. These materials had higher flexural strengths than those shown in Table III. The "good" performance of the untreated materials is actually a result of the low V_f of the laminates studied. Also, the base-treated, sized-fiber materials consistently had the lowest properties of those studied. It is possible that the interphase material formed in this case had properties that were significantly different from those formed in the as-received and acid-treated fiber cases. Closer examination of these laminates showed that the void content of the material was marginally higher than that of the other materials examined. This combined with the higher V_f of the laminates may be responsible for the results obtained. Also, even though care was taken, the treated fibers could have been contaminated by exposure to the environment prior to the prepreg step. Additional work on these materials is needed to resolve this inconsistency.

The results of the composite tests performed indicate that the as-received, oxidized fiber surface is nearly ideal for typical carbon/epoxy systems. The benefit in surface functionality derived from additional treatments did not translate into any improvement in the resin-dominant composite mechanical properties studied here. These results are naturally dependent on the effectiveness of the electrooxidative process in functionalization of the fiber surface. Higher modulus fibers that are difficult to functionalize due to their structure may benefit more from the plasma treatments described here. Further, the sizing examined had an effect on the resin-dominant properties studied. The potential for composite modification through alteration and control of the characteristics of the sizing used in the system is real. The improvements that can be obtained through interphase modification will be limited by factors that control the fracture process of the composite.

CONCLUSIONS

The effect of surface treatments and fiber coatings on the stress transfer characteristics and composite properties of AS-4 carbon/epoxy materials has been determined. The results of the study have shown that the plasma treatments were effective in altering the surface chemistry of AS-4 fibers. A range of surface fiber acidities were produced. However, the changes in surface chemistry had surprisingly little effect on the critical stress transfer length examined using single fiber fragmentation tests. Sizing had a more significant effect on the transfer length but not on the interlaminar shear strength of the composites. Transverse flexure tests were more sensitive to the changes in surface characteristics. The work indicates that the interface properties of AS-4 fibers are close to optimal but that improvements in composite performance are possible through interphase formation.

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