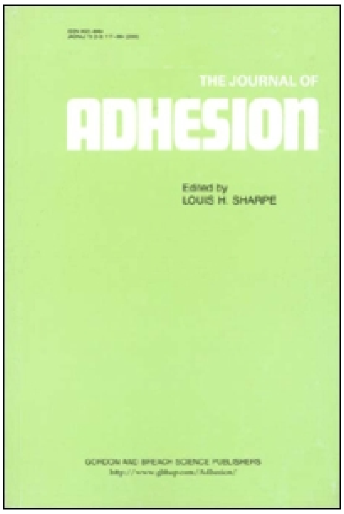

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Interphases Developed from Fiber Sizings and Their Chemical-Structural Relationship to Composite Compressive Performance*

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The relationship between interphase microstructure produced from fiber surface chemistry and the resulting composite structural properties is not well understood. This relationship is, however, key to predicting composite performance and to the understanding of how to assemble the constituents properly for best use of the unique properties of the fibers. In this study, a significant difference in laminate compressive performance is observed for both static and dynamic loading. Two different fiber sizings, an unreacted bisphenol-A-based epoxy and the thermoplastic, polyvinylpyrrolidone (PVP), are identified as the source of these observations. The fiber, matrix and processing remained the same in both systems. However, morphological differences in the interphase region were observed. The resulting mechanical properties indicated that the PVP sizing *improved static compressive strength by* 51% and *increased the fatigue life of notched cross ply laminates* (*cycled at* $R = -1$) *by at least two orders of magnitude* over the bisphenol-A-sized composites. The mechanism by which PVP brought about these changes is unclear and requires further study. However, these results also indicate that the selection of interphase characteristics requires additional information about the fiber-matrix bond than merely strength.

KEY WORDS Fiber sizing; fiber-matrix interphase; poly(n-vinylpyrrolidone); meso-indetation testing; microbuckling; composite compression strength; morphology; mechanical performance.

INTRODUCTION

Oxidative fiber surface treatments and applied sizings have been shown to alter the mechanical performance of various composite systems drastically. For example, Madhukar and Drzal[1-3] reported in some cases a 2- to 3-fold increase in lamina strengths through the application of commercial fiber surface alteration techniques.

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While oxidative fiber surface treatments offer improved composite strength over non-surface-treated systems, the improvements are limited to particular levels of applied treatment.[4] Moreover, there exists no *a priori* knowledge of appropriate surface-treatment levels and their effects on composite properties. Sizing or coating the fibers with a material, usually a polymer, presents a potentially more precise method of controlling/designing particular interphase properties into a composite. Here one can add a known volume of a third material with specific properties to bridge the fiber and matrix, thus ridding one of the unknowns of oxidative surface treatments.

Micromechanical predictions of laminate performance suggest that there is a preferred set of interphase conditions for desired laminate properties.[5-7] These predictions include a third constituent with properties unlike the fiber or matrix. A number of potential variables are available for the formation/design of an interphase from sizings. Among these are tensorial stiffness and strength, toughness, morphology, and thickness of the resulting interphase region. In addition, the potential for gradients of these mechanical properties to exist should not be ruled out.

However, many questions remain regarding the critical properties and dimensions of the interphase that are necessary to bring about the optimum laminate performance for all states of deformation (static and dynamic). There is also uncertainty concerning the extent of the interphase, and the resulting tensorial elastic and strength properties, formed when processing sized fibers within certain matrix systems. Thus, there are two main questions which one must answer:

- What are the elastic, inelastic and dimensional properties of a resulting interphase region?
- How do those local properties influence the various deformation states producing final failure of the composite?

Precise investigations have been made in an attempt to identify interphase properties and their relationship to composite strength. For instance, Madhukar and Drzal qualitatively demonstrated that a *strong* interface produces a composite with improved unidirectional compressive strength.[1] However, they also reported that different interfacial failure modes accompanied the different interface strengths.[8,9] These differences suggest that there are specific elastic and inelastic properties that control the local state of stress or strain, controlling the processes of fiber-matrix separation which ultimately determine what one calls **strength**. Thus, each interface condition investigated by Madhukar abd Drzal consists of a very specific set of elastic and inelastic properties which dictates where, how, and at what load level the fiber and matrix will separate. Therefore, it is not surprising to note that the different failure modes observed for the interface strength tests[8,9] also resulted in distinct and contrasting laminate compressive failure modes.[1]

The present study attempts to provide further insight into interphase properties obtained from fiber sizings and their resulting influence on composite performance. Emphasis, however, will be placed on compression performance. The materials employed were obtained from McDonnell Aircraft Co., through Dexter Hysol, under the Air Force program "Development of Ultralightweight Materials."[10] In that program, more than twenty systems were assembled which possessed state-of-the-art alterations to the interphase. The present study focuses on three such materials containing

Courtaulds's Apollo 45–850 carbon fiber in Dexter Hysol's thermoplastically-toughened epoxy, HC 9106-3. Following the nomenclature of Swain,[11] the systems of interest are designated 810**A**, 820**A** and 810 **O**. The "8" represents the nominal fiber strength of 850 ksi, and the next two digits, "10" or "20" denote the level of surface treatment, 100% and 200%, respectively. Details of the oxidative surface treatment levels are not known but are related to a standardized degree of application, designated 100%, and deemed *optimum* by the manufacturer. The trailing **A** and **O** signifies the type of sizing applied to the surface after oxidative treatment (identified later within this study). It is important to keep in mind that the only variable present in these studies is the fiber surface characteristics as modified through the surface treatments and sizings; the fiber, matrix and processing remained constant for all composites.

The study of these materials originally commenced with the mechanical characterization of laminate strength and durability. It soon became apparent that distinct differences existed between the two fiber sizings stated above and the interphases which they formed within their composites. Thus, characterization of the fiber sizing composition was then conducted. However, we will first present the characterization of the sizings and their resulting interphases and then present details of the composite mechanical performance. Through this inquiry we attempt to make a connection between sizing composition, interphase formation, resulting interphase properties, potential interphase failure mechanisms and laminate performance. Although not all of this will be realized in this study, at the very least we seek to present further evidence of fiber-matrix interphases and their puzzling consequences on laminate properties.

EXPERIMENTAL

The as-received fibers (45–850 100% **A**, 45–850 100% **O** and 45–850 200% **A**) were stripped of their sizing with N-methyl pyrrolidone (NMP). The solutions of sizing and solvent were collected for analysis to determine their composition.

Films of the sizings were cast on KBr disks and dried at 60°C for 24 hours. Fourier transform infrared spectroscopy (FTIR) was performed on a Nicolet Model 800 in transmission mode in the mid-infrared. A liquid-nitrogen-cooled MCTA detector was used and 128 scans per file were taken. Proton NMR was also carried out on a Varian 400 MHz NMR for confirmation of FTIR results on the **O** sizing. The **O** sizing was analyzed from a D_2O solution of the extracted size.

The **A** and **O** sizings were also analyzed by X-ray photoelectron spectroscopy (XPS) on the fiber surface. A stand-alone film for the **O** sizing was formed by extraction with NMP and analyzed. The solution was dried at 60–70°C under vacuum for 4 hours. The XPS analysis was performed on a Perkin-Elmer PHI 5300 spectrometer with a Mg K_α achromatic X-ray source (1253.6 eV), at a 45° take-off angle. All binding energies were referenced to the hydrocarbon peak at 284.6 eV.

The T_g of the **O** sizing was characterized by a Perkin-Elmer DSC-4 differential scanning calorimeter. Sample pans were loaded with the stripped sizing and the solvent was removed by means of a vacuum oven. A slow cooling from 180°C was followed by a fast heating rate of 20°C/min. to exaggerate the transition.

Analysis of the interphase microstructural details was undertaken through scanning electron microscopy. Unidirectional specimens, sectioned 20° to the fiber direction, were mounted in metallographic epoxy and polished. An etchant typically used for PEEK matrix materials was found to be effective in removing the thermoplastic phase within semi-crystalline and crosslinked polymers.[12] A five-minute etching time was found to be most effective in revealing the typical microstructure.

Meso-indentation[13] and 90° flexure of unidirectional composites were employed to characterize the shear and transverse interphase properties, respectively. The transverse flex tests did not conform to the ASTM standard (specimen width of 12mm and the span-to-depth ratio, 6.7:1).[11] Quasi-static (IITRI) compression tests were performed on unidirectional specimens per ASTM D-3410 with untapered glass/epoxy tabs and a gage length of 15 mm (0.6 inches). The unidirectional specimens were all taken from a 152 mm (6 inches) square, 32-ply (nominally 3.8 mm thick) laminate, one for each interphase variation. Additional laminates were manufactured in the balanced cross-ply configuration $[0°/90°]_{8s}$ for durability testing. Long-term performance was assessed through fully reversed cyclic fatigue ($R = -1$ at 10Hz) of a center-holed configuration, at 75% of ultimate compression strength.[11] The 152 mm (6 inch) long fatigue specimens contained a 6.4 mm (0.25 inch) circular hole machined in the center of their 25.4 mm (1.00 inch) width.

RESULTS AND DISCUSSION

Spectroscopy of the A & O Sizings

The infrared spectrum presented in Figure 1 is that of the **A** sizing as extracted from the 100% surface treated Apollo 45–850 fiber. The material was identified as an diglycidyl ether of bisphenol-A.[14] The spectrum of the **O** sizing, presented in Figure 2, was identified from matching spectra[15] as the thermoplastic poly (N-vinyl pyrrolidone) or

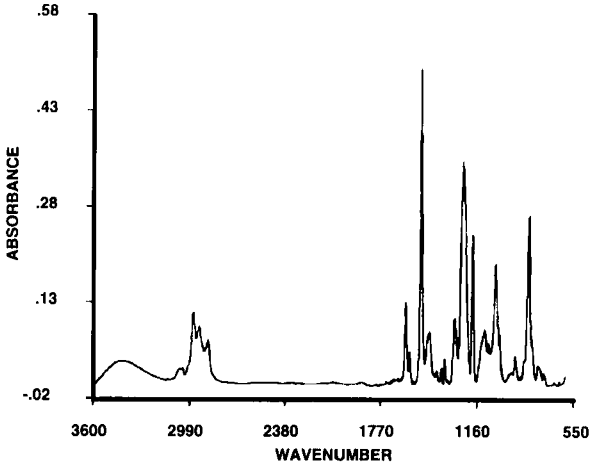


FIGURE 1 Infrared spectrum of the **A** sizing extracted with NMP.

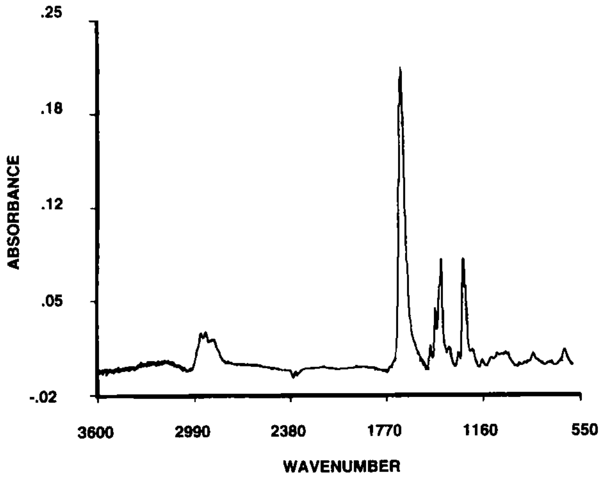


FIGURE 2 Infrared spectrum of the O sizing extracted with NMP.

PVP. The structure of poly (N-vinylpyrrolidone) is shown in Figure 3. DSC measurements of the sizing show a T_g of 110°C, consistent with a version of commercially-available PVP, named K-17 (BASF), possessing a viscosity average molecular weight of 9,200.[16]

Since the **O** sizing was extracted with N-methyl pyrrolidone (NMP), the solvent alone was run on KBr disks to determine its IR spectrum so as to ensure its complete removal prior to infrared analysis of sizing films. The infrared spectrum showed bands at 1110 and 985 cm^{-1}, which are characteristic of NMP.[17] These two bands are absent from the spectrum of the **O** sizing (Figure 2), thus confirming that the major portion of the NMP solvent was removed from the film.

Proton NMR also showed that the **O** size is comprised of poly (N-vinylpyrrolidone). Peaks were observed at δ2.17, δ1.9, δ3.15, δ3.5–3.65, and δ1.45–1.6 (δ in ppm from TMS) typical of free radical catalyzed material.

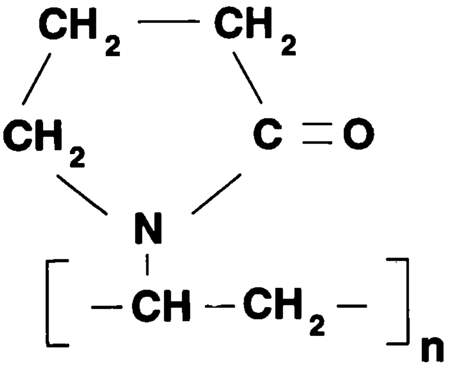


FIGURE 3 Structure of poly(n-vinylpyrrolidone).

X-ray Photoelectron Spectroscopy of the A & O Sizings

Table I shows the XPS atomic concentrations obtained for the 100% and 200% surface treated fibers with the **A** sizing present on the fiber surfaces, the 100% surface treated fibers with the **O** sizing on the fiber surface, and the extracted **O** sizing film. Virtually identical atomic concentrations were obtained for the 100% and 200% **A** sizings on the fiber surface. The small quantity of nitrogen detected in both the 100% and 200% samples most likely originates from the underlying fiber. Two main peaks corresponding to the hydrocarbon peak at 284.6 eV and a C—O peak at 286.2 eV were resolved from the primary peak. No high binding energy peaks corresponding to carbonyl species are observed, but a small broad shake-up satellite at 291.1 eV, indicative of aromaticity, is present. These observations are consistent with the infrared identification of this particular sizing as a bisphenol-A-based epoxy.

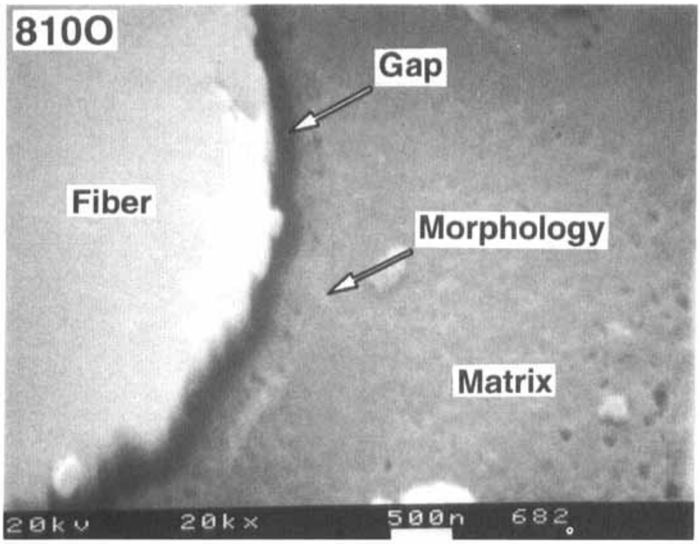
A large amount of nitrogen was found in the **O** sizing on the fiber surface. In order to confirm that the fiber itself was not the source of the nitrogen, an analysis was performed on the extracted **O**-sizing film. This experiment revealed that the nitrogen originated in the sizing material. It was also observed that the atomic concentration of the **O**-sizing film is very similar to the theoretical atomic concentration of poly (vinylpyrrolidone) of 75% carbon, 12.5% oxygen and 12.5% nitrogen. The main components which were fitted to the main photopeak envelope are a hydrocarbon peak at 284.6 eV, a C—O or C—N peak at 286.0 eV and a carbonyl peak at 287.4 eV. Again, these observations are consistent with the identification of the **O** sizing as polyvinylpyrrolidone.

Investigation of Microstructural Detail by Microscopy

As a direct comparison, 810**A** and 810**O** were etched and inspected by SEM. Under identical etching conditions the epoxy-sized fibers (Figure 4) did not reveal as distinct an interphase region as that observed in the PVP-sized composite (Figure 4). The epoxysized composite shows an irregular interface region between fiber and matrix. Particular regions about the epoxy sized fiber possess irregular gaps between fiber and matrix. On other portions of the **A**-sized fiber perimeter, matrix material is observed in direct apposition to the fiber. For many of the regions observed, the PVP interphase extended into the matrix approximately 10% of the fiber diameter, or ~0.5 μm. Although this size was readily observed around many of the fibers, it was not always uniform in thickness for each fiber. In some cases, the interphase region observed is

TABLE I
XPS atomic concentrations for the sizings of the Apollo 45-850 carbon fiber

	C (%)	O (%)	N (%)
100% **A** on fiber	85.3	14.0	0.07
200% **A** on fiber	85.2	13.1	1.7
O on fiber	82.0	9.8	8.2
O extracted w/NMP	79.0	13.4	7.6



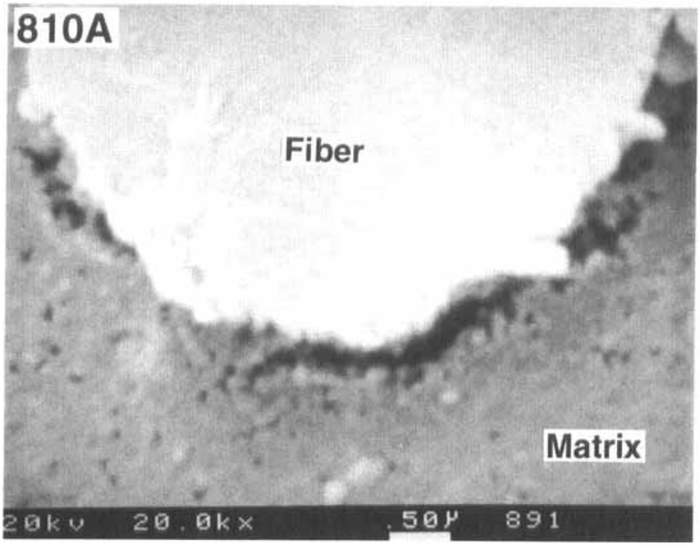


FIGURE 4 Scanning electron micrograph of the poly(n-vinylpyrrolidone) (O size) and the epoxy (A size) induced interphases, enhanced by a permanganic etchant.

somewhat smaller. In contrast to the epoxy interphase, the PVP-influenced interphase possesses two distinct regions. The first, closest to the fiber, appears as a gap next to the fiber measuring approximately 0.2 μm. Model studies suggest that at high weight percents of PVP K-17 in a bisphenol-A-based epoxy, the PVP may phase separate.[18] This could explain the presence of the gap (the etchant readily removes linear polymeric

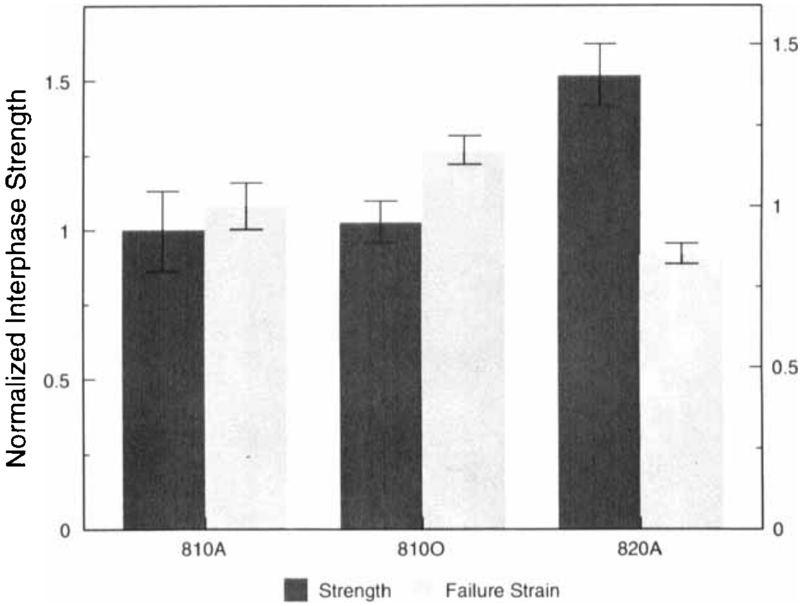


FIGURE 5 Meso-indentation results (normalized to 810A); error bars represent coefficient of variation.

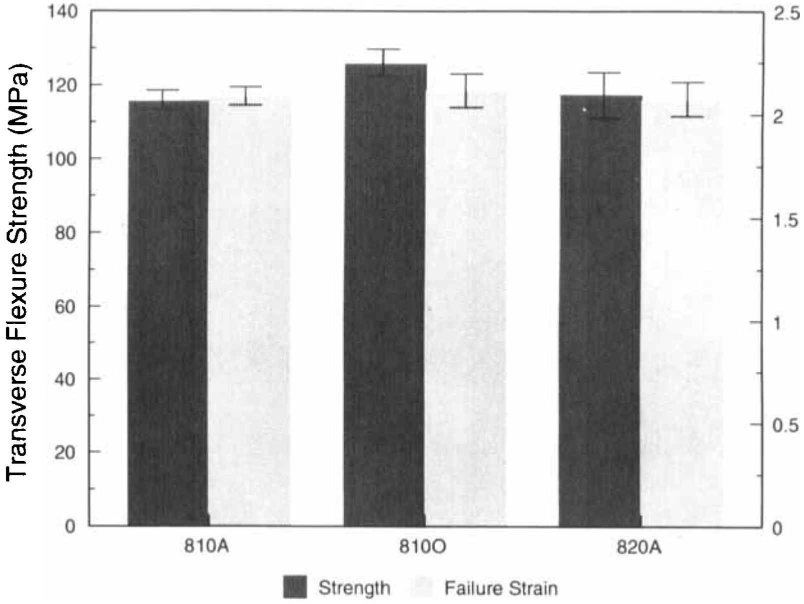


FIGURE 6 90° flexure; error bars represent standard deviation.

material). The second region extends beyond the gap with a morphology distinct from that of the surrounding matrix. This zone appears to be approximately 0.3 μm in thickness.

The formation of the PVP interphase might be explained through the simple process of diffusion. The maximum processing temperature of these composites was 177°C and, as previously stated, the T_g of the PVP size is approximately 110°C. Hence, the PVP is well into its rubbery regime and potentially able to disperse into the epoxy. This is not to neglect any other driving forces producing interaction of the two polymers. Simulated diffusion of PVP K-17 with a simple epoxy exists even at maximum cure temperatures of 120°C.[18]

Structural Characterization of the Interphase

The meso-indentation test has been shown to be a sensitive means of interrogating the fiber-matrix interphase quality.[19] The maximum mean hardness pressure (MMHP) (the applied indenter pressure at which interfacial failure occurs) provides a determination of interface strength through a compressive loading scheme. Meso-indentation strain to failure, termed the representative strain, provides an assessment of the interphase strain to failure in shear.[20] The results (normalized to the results of 810A) of the meso-indentation tests are shown in Figure 5. Statistically, there is no significant difference in interphase strength between the 810A and 810O systems. However, the representative failure strain of the 810O is ~ 15% greater than its A-sized counterpart. This suggests a more ductile interphase in the O-sized material.[14] The 820A system shows a 51% increase (over 810A) in interphase strength but with an even lower representative failure strain, indicating an embrittlement of the interphase with the additional level of surface treatment.

The 90° flexure test yields an assessment of the transverse strength of the interphase.[19] Case *et al.*, have also shown that the transverse strength of a composite system is affected by local (interphase) elastic properties.[5] Thus, one might consider that this test supplies interphase strength characterization as well as information on how the interphase influences the cohesive failure of the matrix. The 810O is only ~9% greater in transverse strength than its A-sized counterpart and not statistically different (Figure 6). The strains to failure of all systems are within 2% of each other. The strength results appear to be at least consistent with the meso-indentation test for the 810A and 810O.

Static Compressive Performance

All compression failures were within the gage section. The failure modes of all systems appeared to be consistent with the phenomenon of microbuckling. Transverse shear failures initiating at the free edge of the specimen combined with longitudinal splitting were observed for all specimens. However, it appeared that 810O possessed a greater number of longitudinal splits than 810A.The general nature of the failures observed were consistent with those observed by Odom and Adams[21] for identical test and specimen conditions and are, therefore, considered representative. Scanning electron microscopy of the failed surfaces revealed material (sizing and/or epoxy) clinging to the fibers of the 810O system (Figure 7). This did not appear to be the case for the 810A composite where the striations of the fiber are visible.

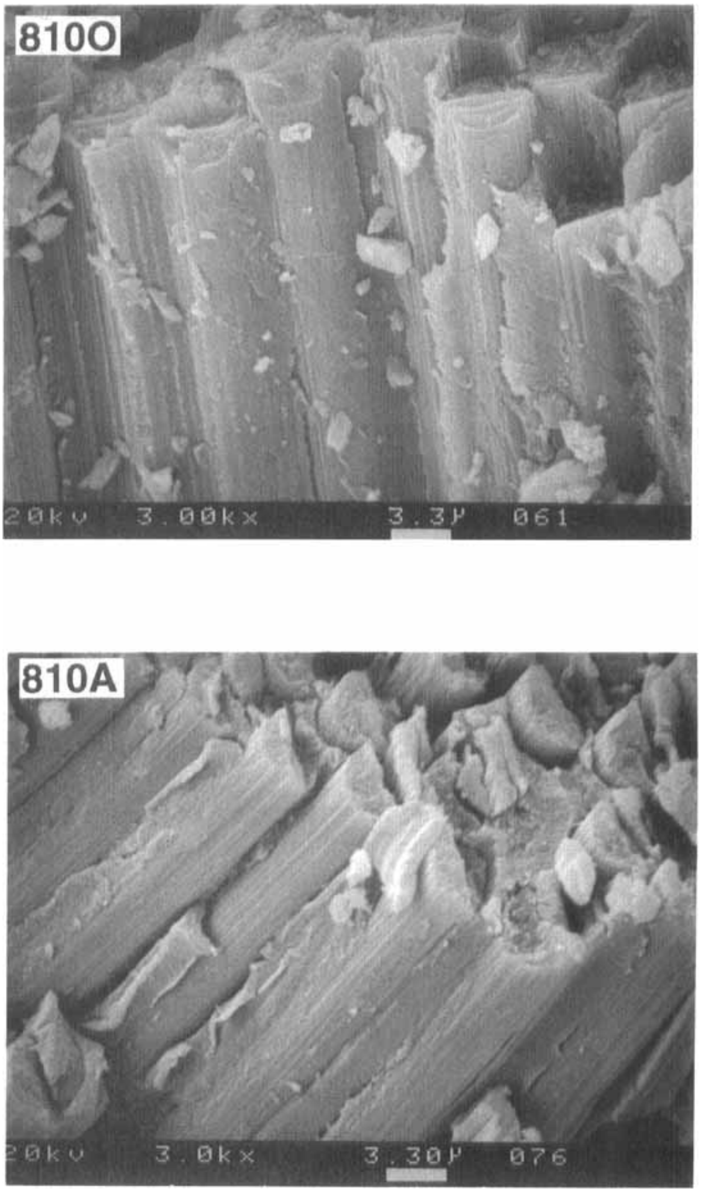


FIGURE 7 Scanning electron micrographs of failed 810**O** and 810**A** IITRI compression samples.

Both the strength and failure strain of the 810**O** were the greatest of the three systems (Figure 8). With only the change in sizing (from the 810**A**), the 810**O** exhibits a 51% greater strength and a 62% greater failure strain. The additional surface treatment of the 820**A** also yields a statistically-significant increase in compression strength over the 810**A**.[22] Compared with composites with either surface treatment level and the **A** sizing, the failure strain of the 810**O** is significantly greater than for the other systems.

The compressive axial moduli of the three systems was also altered by surface treatment and sizing: 810**A**, 810**O** and 820**A** possessed an E_{11} of 162.0, 148.9 and 174.4 GPa (23.5, 21.6, & 25.3 Msi), respectively. A drop in modulus has also been observed for other laminate configurations (both fiber dominated and matrix dominated) when comparing composites of 100% surface treatment, **A** sized to those with **O** sizing.[11] This may indicate the relative local change in the interphase properties, suggesting that the **O** sizing produces a more compliant interphase. However, if we consider micromechanical approaches for predicting fiber direction modulus from constituent properties (such as rule-of-mixtures), it is difficult to obtain the drop in modulus observed; 8% reduction from 810**A** to 810**O** and 15% reduction from 820**A** to 810**O**. Inferring that this drop in E_{11} is due to interphase compliance is also puzzling when considering micromechanical predictions of compression strength. Greater compliance at the interphase has been shown *analytically* not to improve compression strength.[6]

Dynamic/Long Term Performance

The quasi-static notched (gross-section) compressive strength of the cross ply laminates used for the fatigue study were all very similar: 291.6, 295.0 and 290.8 MPa (42.29, 42.78 and 42.17 ksi) for 810**A**, 810**O** and 820**A**, respectively. However, when each of these systems was fatigued (R = −1) at 75% of their ultimate static cross ply compressive

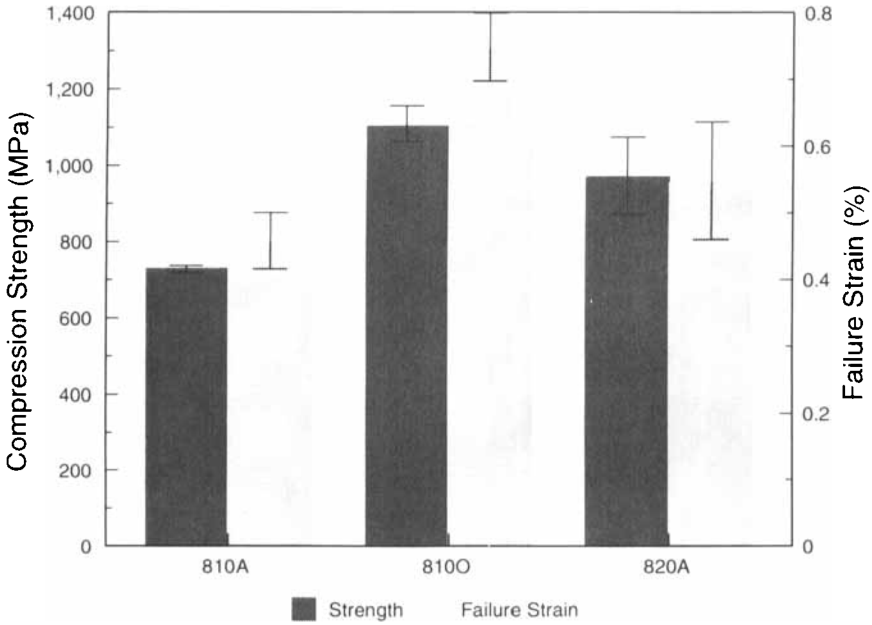


FIGURE 8 IITRI compression; error bars represent range of data.

strength, vastly different fatigue lives were observed. Two orders of magnitude difference in life was observed with only the change in sizing of the 810 system (Figure 9). Neither one of the 810**O** specimens failed after 10^6 cycles. Longitudinal splits emanated from the edges of the hole, yet no evidence of fiber buckling was observed at the edge of the hole where stress concentrations are highest (Figure 10). The 810**A** and 820**A**, on the other hand, did exhibit buckling of the fibers causing failure of these specimens in compression (Figure 10). The additional surface treatment of the 820**A** system also allowed for a slight increase in life over the 100% surface treatment but not to the extent of the laminates with **O**-sized fibers. Again, resistance to fiber buckling is observed and the onset of compressive failure of the 810**O** is delayed during cyclic loading. One should take away from this evidence that *high* static interface strength may not translate to *improved* long term performance. Thus, one must begin to consider other interphasal mechanisms and identify their contribution to improved compressive performance.

Assimilation of Mechanical and Sizing Identification Studies

It is apparent that the PVP sizing provides improved conditions (over the **A** sizing) at the interphase for static and dynamic compressive loading conditions. It is possible that the PVP induced interphase possesses a slightly lower modulus and greater ductility compared with an epoxy interphase. In contrast, Madhukar and Drzal[1] have shown

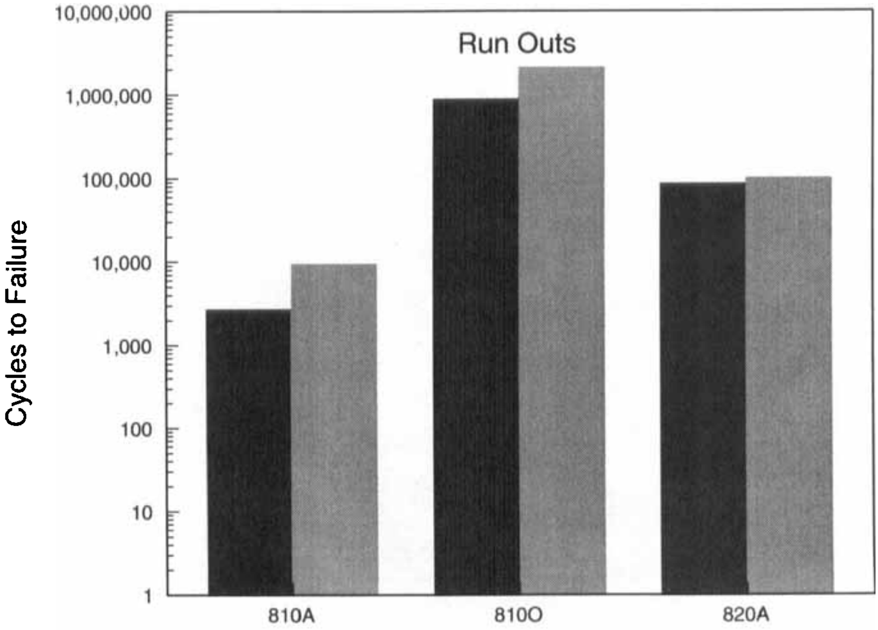


FIGURE 9 R = −1 fatigue of notched cross ply material at 75% of the ultimate compression strength of the gross cross section. Each bar represents a test, *i.e.*, two for each specimen.

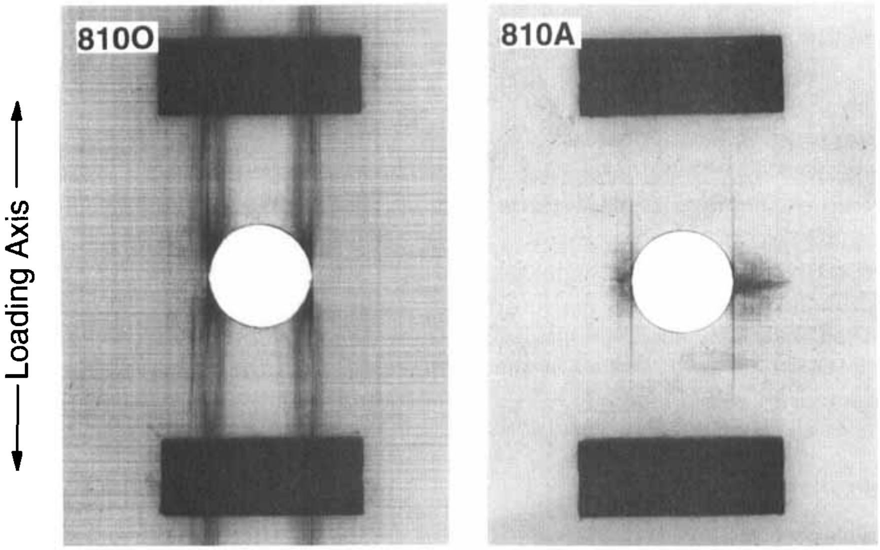


FIGURE 10 X-ray radiographs of the notched cross-ply fatigue specimens: 810O after 2.1 million cycles and 810A after 3000 cycles.

that the unreacted epoxy sizing of the AS-4C/Epon 828/mPDA system produced a brittle, high modulus interphase which, in turn, led to improved compressive strength over surface-treated and non-surface-treated fiber composites.[1,2] It is clear that these two interphase conditions are dissimilar and suggest that little is truly known about the interphase properties and their effect on compressive micromechanics. Likewise, there may be no unique combination of interphasal properties, including or excluding strength and stiffness, which lead to improved compressive performance. The PVP produces a distinctly different interphase region compared with its counterpart, an unreacted epoxy size. Obviously, the linear nature of the PVP distinguishes it from the epoxy by its inability to form a network. Yet, the PVP appears to interact with the epoxy as other thermoplastics do when added to epoxies as tougheners; they phase separate and form morphologies which are more, and sometimes less, damage tolerant. Thus, it may be possible that a morphological change was induced in a large enough volume to affect fiber-matrix damage mechanisms.

However, one leaves this reasoning with the question: What chemical properties of the PVP lead to this interaction with the fiber and matrix? The distinctive quality of the PVP is its polar nature (see Figure 3). The manufacturer of PVP cites the ability of the polymer to hydrogen bond as its primary mechanism of interaction for its many adhesion-related applications.[23] In particular, it is not unreasonable to consider specific interactions as a means of adhesion of the PVP to the fiber. Fractography of failed composite samples supports this claim (see Figure 7); PVP-sized fiber composites are routinely observed with polymer attached to the fiber surface.[11,24] For the matrix, one can not be certain as to whether the polar nature of PVP plays a role in the particular morphology formed either through direct reaction with the epoxy or chain entanglement with the network.

CONCLUSIONS

The presence of the thermoplastic poly (N-vinylpyrrolidone) (**O**) sizing enhances the compressive performance of the Apollo fiber/HC 9106-3 toughened epoxy composites over the bisphenol-A-based epoxy (**A**) sizing. The PVP sizing produces interphase morphology distinct from, and of greater extent than, that of the epoxy size. It is believed that these morphological differences establish a more ductile response in compression for as illustrated by the increased failure strains observed in interphase characterization and laminate tests.

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