ADHESION OF CARBON FIBERS TO VINYL ESTER MATRICES

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SUMMARY: In this study, chemical and physical factors governing adhesion were investigated to determine the underlying cause for inadequate fiber-matrix bonding between carbon fibers and vinyl ester polymers. Scanning tunneling microscopy of a family of fibers differing only in the level of surface treatment showed that surface roughness is minimized at the standard 100% treatment level and increases at treatment levels greater than 100%. A series of experiments where carbon fibers were exposed, individually or in combinations, to the vinyl ester initiator, accelerator, promoter, or catalyst found preferential adsorption of some of these constituents on the fiber surface, which could lead to an interphase having properties different than the polymer bulk properties. Two micromechanical test methods, microindentation and fiber fragmentation, were employed to quantify the level of adhesion between carbon fibers and vinyl ester matrix. Application of a fiber sizing was found to increase the level of adhesion and improve mechanical properties of carbon fiber-vinyl ester composites.

KEYWORDS: carbon fibers, vinyl ester, fiber-matrix adhesion, sizing, coating.

INTRODUCTION

The manufacture of heavy tow carbon fibers, having nominal filament counts of 50,000 to 250,000, has lead to price reductions, with carbon fiber price projections of $5 per pound by the year 2000 [1]. Because of their superior specific strength and stiffness, the low price carbon fibers could be economically competitive with glass fibers for use in markets previously deemed too expensive, including the automotive industry. Additional economic advantage would be enjoyed if carbon fibers could be substituted for glass fibers used in existing composite manufacturing methods, such as resin transfer molding with vinyl ester matrices. However, composites of carbon fibers in vinyl ester polymers possess unacceptably low mechanical properties due to low fiber-matrix adhesion. The objective of this study was to gain an understanding of factors controlling interfacial adhesion and to develop a fiber coating that would improve both fiber-matrix adhesion and mechanical properties of carbon fiber-vinyl ester composites.

Adhesion in fiber reinforced polymer composites is influenced by multiple chemical and physical factors. Successful commercial surface chemical treatments of carbon fibers remove the native defective fiber surface leaving a structurally sound surface for bonding. At the same time, the surface concentration of polar chemical groups is increased and the surface

micro topography is altered [2]. Surface analysis of carbon fibers by Xray Photoelectron Spectroscopy (XPS) has shown that the chemical species added are primarily oxygen (carboxylic acid, carbonyl and phenol) and nitrogen (amino) containing species [3]. Trace elements such as sodium, potassium, sulfur and silicon are also found on the surface but usually in concentrations of 1% or less [4]. In some cases alkali elements (e.g. sodium) in high concentrations ~3% have been shown to be detrimental to composite interfacial durability in high temperature oxygen and high moisture environments [5].

In epoxy based polymer composites, chemical bonding has been found to take place between the epoxy and amine groups of the matrix and oxygen and nitrogen species present on the fiber surface. It has been shown that as little as 3% chemical bonding accounts for a 25% increase in interfacial shear strength. The chemical groups increase the thermodynamic surface free energy and hence increase thermodynamic wetting. Commercial surface treatments create topographical variations with a depth of 5-15 nm and a periodicity of 100 nm. The increase in surface topography can likewise account for a 25% increase in interfacial shear strength independently of the enhancement resulting from chemical bonding [6].

It is conceivable that some or all of the physical and chemical mechanisms responsible for adhesion in carbon fiber-epoxy systems could be operating at the carbon fiber-vinyl ester interphase. The free radical polymerization of vinyl esters is carried out with the use of multiple constituents such as the reactive diluent styrene together with initiators, accelerators, promoters, and catalysts. Preferential adsorption of any of these components on the fiber surface would change the stoichiometry, reaction kinetics or crosslink structure, which could result in a polymeric network with unsuitable adhesion properties. The effect of surface topography and chemistry on fiber-matrix adhesion was investigated with a goal of developing a strategy to improve carbon fiber-vinyl ester adhesion in resin transfer molded composites.

MATERIALS

The carbon fibers selected for study were Panex 33 [1] obtained in the heavy tow form of 160K filaments from the Zoltek Corporation. A family of fibers was provided having a proprietary electrochemical surface treatment of 0%, 25%, 50%, 75%, 100% and 150% of standard amperage levels.

The Derakane [7] family of vinyl ester resins was used in this study. Vinyl ester resins, as shown in Figure 1 for Derakane 470, typically contain styrene as a reactive diluent for viscosity management and inhibitors to retard polymerization during storage. Room

Figure 1. Structure of Vinyl Ester Monomer in Derakane 470.
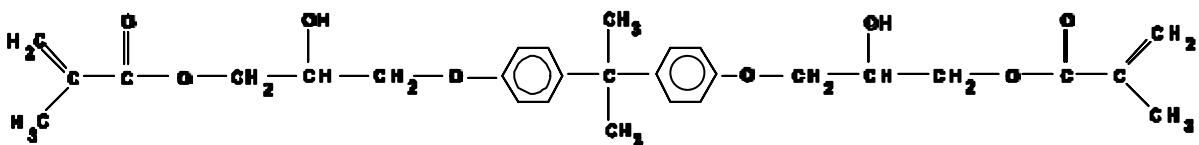
DERAKANE 470

temperature polymerization was carried out with the addition of peroxide catalyst benzoyl peroxide (BPO), methyl ethyl ketone peroxide (MEKP), or cumene hydroperoxide (CHP), along with the promoter cobalt naphthenate (CoNap), and the accelerator dimethyl aniline (DMA). Three different vinyl esters were used in this study. Derakane 411-C50, shown in Figure 1, is an epoxy based vinyl ester; 470-36 is an epoxy novolac based system; and 8084 is an elastomer modified system containing carboxy-terminated butadiene rubber end groups. The manufacturer's recommended formulation for room temperature polymerization to yield a gel time of approximately 20 minutes was used to process all samples.

EXPERIMENTAL

Fiber Surface Morphology. The structure of carbon fiber surfaces was evaluated by scanning tunneling microscopy, a technique that provides high magnification images of conductive materials. Changes in fiber surface roughness of the Panex 33 family of surface treated variants were imaged with a Nanoscope 3 [8] scanning tunneling microscope (STM) fitted with a platinum-iridium tip and operated in the constant current mode. The STM samples were prepared by securing taut fibers to the mounting stub with conductive adhesive. The instrument was operated at a nominal current of 1nA at a bias voltage of 200 mV. Surface roughness was determined using the software resident on the Nanoscope 3. A minimum of 5 images were collected and averaged for measurement of the surface roughness parameter R_a, the mean z values relative to the center plane, and Rq, the standard deviation of z (height) values, for each of the Panex 33fibers.

Fiber Surface Chemistry and Chemisorption Studies. X-ray photoelectron spectroscopy is a highly surface sensitive method that has been extensively used to probe the composition of the outermost 50-100D of carbon fiber surfaces. The effect of the anodic surface treatment of fiber surface chemistry was evaluated with a Physical Electronics PHI5400 X-ray photoelectron spectrometer fitted with a monochromatic aluminum x-ray source. The details of the curve fitting routine used to quantify the atomic concentration and peak shape analysis can be found elsewhere [9]. A baseline surface chemical composition for each of the Panex 33 surface treated variants was established.

In a unique set of experiments designed to evaluate adsorption of the vinyl ester monomer and its additives, sections of 100% surface treated Panex 33 fibers were immersed in solutions containing one of the components of the vinyl ester system. Each solution contained vinyl ester resin, peroxide initiator, promoter, or accelerator in phenyl ethyl ether at concentrations equivalent to yield a monolayer of fiber coverage. Subsequent experiments contained binary and tertiary solutions of two and three constituents per solution to construct a model more consistent with the chemical environment that exists during composite fabrication. Fibers were submersed in the solutions for 2 hours at room temperature. Afterwards the fibers were refluxed with acetone for 24 hours in a soxhlet extractor to remove excess material and dried for 3-4 hours at 120EC. In another set of exposures, the fibers were submersed for 2 hours at 90EC, a common RTM molding temperature. Following the acetone reflux and drying steps, the fibers were analyzed by x-ray photoelectron spectroscopy to determine any variation in fiber surface composition relative to the Panex 100% surface treated fiber. Any change in surface chemistry would indicate a reaction with one of the components of the vinyl ester system.

Fiber-Matrix Adhesion Measurements. Adhesion between carbon fibers and vinyl ester matrices was measured using two micromechanical test methods. The single fiber fragmentation test incorporates a single fiber in a microtensile coupon. Tensile loading causes the encapsulated fiber to fracture into successively shorter lengths, ultimately reaching the critical transfer length, l_c. The experimentally derived value of l_c is related to the interfacial shear strength (IFSS), τ, by a shear lag analysis [10] resulting in the relationship

$$\tau = \frac{\sigma_f d}{2 l_c} \qquad (1)$$

where σ_f is the fiber tensile strength and d is the fiber diameter.

One limitation of the single fiber fragmentation test is that the matrix failure strain must be sufficiently large to complete the fiber fracturing process. For carbon fibers, the matrix failure strain to successfully conduct the fragmentation test is typically 4-6%. Because many vinyl ester matrices do not possess adequate strain properties, the fragmentation test can not be used to measure the interfacial shear strength. An alternate method of measuring adhesion in these low strain systems is the indentation test. In this test, a section of composite is mounted and polished to an optically flat surface to expose the fiber end in cross section when viewed with reflected light microscopy. A hemispherical diamond microindentor is centered over a fiber and slowly lowered at a controlled rate to load the fiber end in compression, resulting in a circumferential disbond from the surrounding polymer. The load required to generate the disbond is used to calculate the interfacial shear strength (11). Because the microindentation test is not dependent on the strain properties of the polymer, this test was successfully employed to measure the interfacial shear strength of carbon fibers in the strain sensitive Derakane 470-C36 vinyl ester matrix.

The baseline interfacial shear strength was determined on the series of Panex 33 surface treated variations. The indentation test was then used as a screening tool to assess the changes in adhesion associated with fiber coatings. Coatings that demonstrated an increase of interfacial shear strength were then selected to produce unidirectional carbon fiber-vinyl ester composites manufactured by resin transfer molding. The resultant composites were evaluated using the iosipescu shear test.

RESULTS AND DISCUSSION

Fiber Surface Morphology. The graphitic structure of the family of Panex 33 fiber surface is clearly discernable in the representative scanning tunneling micrograph of Figure 2. Graphitic ribbons are oriented along the major fiber axis and can be seen to undulate and intersect each other. Fiber surface roughness was measured on the areas not influenced by the curvature of the fiber channels as illustrated in the box in the left micrograph of Figure 2. Surface roughness measurements are graphically presented in Figure 3. With increasing surface treatment a reduction of fiber surface roughness was produced, reaching a minimum near the standard 100% treatment level. At treatment levels greater than 100%, fiber surface roughness increased. One effect of the surface treatment is the removal of the structurally weak outer layer of graphite from the fiber. However, at surface treatment levels greater than the standard 100%, the fiber may become excessively etched and could yield defects that would cause a depression of fiber strength.
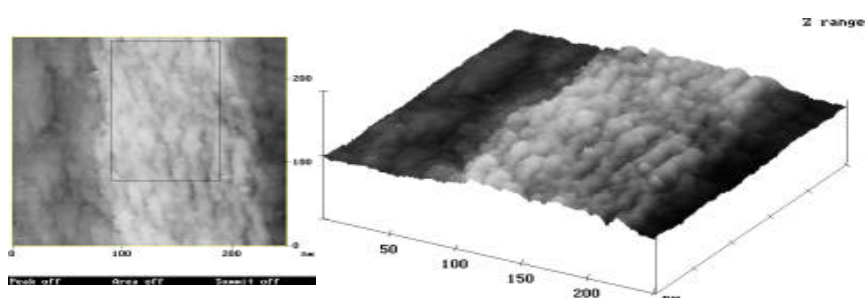
STM of Panex 33- 100%ST

Figure 2. Representative scanning tunneling micrograph of Panex 33-100% Surface Treatment. The box in left micrograph is area used for roughness measurement.

Fiber Surface Chemistry and Chemisorption Studies. The baseline atomic surface concentrations as determined by X-ray photoelectron spectroscopy of the Panex 33 fibers are reported in Table 1. One obvious effect of the surface treatment is an increase in the amount of atomic oxygen from 5.0 atomic percent for untreated fiber to 10.7 atomic percent at the 100% level of surface treatment, along with an increase in nitrogen from 3.5 to 6.4 atomic percent. In the case where the Panex 33 fibers were treated in solutions having only single components, evidence of reactions were found for three compounds, namely, Derakane 470, dimethyl aniline, and cobalt naphthenate. The vinyl ester treated fibers resulted in a surface with increased carbon/oxygen functionality, especially C-O groups. For the case of the dimethyl aniline treatment, a small decrease in C-O functionality was detected, yet the oxygen/carbon ration was found to be insignificantly changed from the 100% surface treated fiber. The fiber surface was found to be enriched with cobalt following exposure in the cobalt naphthenate solution. Because no significant changes in the C1s signal or the oxygen/carbon ratio were detected, it is suspected that the cobalt is strongly phyisorbed and does not chemically react with the fiber. In the binary series of adsorption experiments where

Table 1. Surface Atomic Concentration of PANEX 33 Surface Treated Variants.

	Panex 33 Carbon Fiber Surface Treatment Level						
Element	0 %	25%	50%	75%	100%	150%	155%
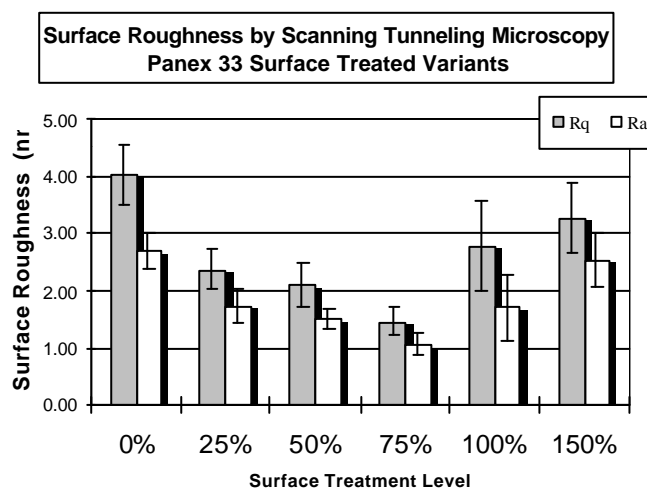
Figure 3. Surface roughness parameters R_q and R_a of Panex 33 Surface Treated variants.

	Surface Atomic Percent						
Carbon	91.0	89.2	85.9	87.4	80.8	81.8	82.9
Oxygen	5.0	6.4	7.3	6.0	10.7	9.9	8.4
Nitrogen	3.5	3.4	5.2	5.0	6.4	6.7	6.5
Sodium	0.3	0.3	0.8	0.6	1.2	0.9	0.8
Sulfur	0.2	0.3	0.2	0.2	0.3	0.1	0.4
Silicon	nd	nd	0.2	0.2	0.1	nd	nd
Chlorine	nd	0.1	0.2	0.2	0.2	0.2	0.2
Magnesium	nd	nd	0.3	0.4	0.4	0.3	0.7

nd= not detected

two components were in placed in solution, the fiber surface was found to be enriched with cobalt after treatment in solutions containing cobalt naphthenate. The CoNap+MEKP solution resulted in nearly a doubling of the O1s/C1s ratio, likely due to some type of reaction or complexation between the cobalt compound and the peroxide. Changes in fiber functionality were detected in the tertiary solutions that contained cobalt naphthenate and are again associated with changes in COOR, COOH functionality and a decrease in C=O groups.

Table 2. Surface atomic percent Panex 33 fibers following chemisorption treatment.

	Panex 33-100%ST Fiber Surface Atomic Percent					
Treatment	C	O	N	Na	Co	MINOR[*]
As Rec'd	80.8	10.7	6.4	1.2		1.3
Derakane 470	78.9	14.7	4.6	1.4		2.3
Methacrylic acid	82.2	11.1	4.1	1.6		1.1
DMA	80.4	11.8	3.7	1.0		3.1
Styrene	82.7	9.6	5.3	1.9		0.5
BPO	83.0	9.6	5.6	0.9		0.9
CHP	80.6	10.8	5.8	1.5		1.4
CONap	80.3	10.4	4.8	1.1		0.8
CHP+CoNap	79.5	11.9	4.5	1.3	1.8	1.3
MEKP+CoNap	67.0	20.0	3.8	1.0	7.6	0.7
CHP+CoNap+DMA	60.8	23.7	3.2	1.0	8.4	3.3
MEKP+CoNap+DMA	61.5	23.5	3.5	1.2	8.4	2.6

*Na, S, Si, Cl, Mg

The changes in carbon functionality along with a shift in the low binding energy component of the O1s peakshape suggests that the cobalt is strongly adsorbed as a cobalt oxide. Table 2 and Table 3 presents the fiber surface functional groups following exposure to the single, binary, and tertiary solutions. No dependence on exposure temperature was observed for the set of adsorption experiments conducted at 90°C. In is reasonable to conclude that the adsorption of these vinyl ester constituents on the fiber surface can have an effect of the vinyl ester polymerization in the region near the carbon fiber surface and that this mechanism may be responsible for the low levels of fiber-matrix adhesion found in these systems.

Table 3. Surface functionality of Panex 33 fibers following chemisorption treatment.

TREATMENT	$C_{graphitic}$	C-OH	C=O	COOH	$\pi \div \pi^*$	plasmon
As Received	80.1	7.3	3.3	5.3	2.1	1.9

CHP	77.5	8.3	3.3	5.2	2.5	3.1
CoNap	78.0	7.2	3.6	4.9	2.4	3.9
BPO	79.4	7.6	4.3	3.3	3.2	2.2
DMA	85.5	4.8	0.9	3.2	2.1	3.6
MEKP	80.1	7.3	2.7	6.2	1.7	1.9
Styrene	79.7	7.5	3.3	5.0	2.4	2.2
Methacrylic Acid	80.2	6.7	3.0	5.4	2.1	2.6
Derakane 470	71.8	12.8	4.5	5.8	1.7	3.3
CHP+CoNap	79.4	7.6	2.8	5.1	2.0	3.0
BPO+DMA	78.6	8.1	2.7	5.2	2.4	3.1
MEKP+CoNap	77.7	7.5	1.9	8.5	1.5	2.8
MEKP+CoNap+DMA	84.7	4.0	1.9	6.3	1.6	1.4
CHP+CoNap+DMA	79.9	8.6	1.0	6.7	1.7	1.9

Fiber-Matrix Adhesion Measurements. Surface treatment of the Panex fibers produced higher levels of adhesion compared to the untreated fiber as determined by both the fragmentation test and the indentation test. As show in Figure 4, the Panex 33-100% IFSS is greater than the IFSS of the untreated Panex 33-0% for the 8084 and the 411-C50 vinyl ester systems. As further proof of the low level of adhesion of carbon fibers to vinyl ester, the IFSS of the 100% surface treated fiber in the vinyl ester polymer produced less than half of the IFSS when the same fiber was tested in an amine cured epoxy matrix. This is not due to the fiber itself, since equal levels of interfacial shear strength were found for Panex 33-100% and AS4 fiber in the amine cured epoxy matrix.
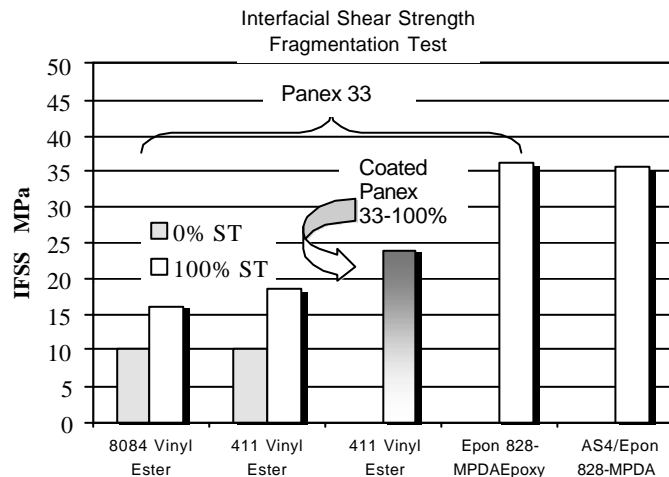

Figure 4. Interfacial Shear Strength Results for Carbon Fibers in both 411-C50 and Amine cured Epoxy Showing Effect of Surface Treatment

The indentation test was used to measure the IFSS of the Panex 33 family of surface treated fibers in the more brittle and strain sensitive 470-36 system. The interfacial shear strength showed nearly a 20 percent improvement in IFSS from 0% to 25% surface treatment level. Thereafter, increasing the level of surface treatment resulted in only marginal increases in IFSS, attaining a maximum value at the 100% standard surface treatment as shown in Figure 5. It should be noted that matrix toughness contributes to overall composite properties and some of the reduction here may be also due to the brittleness of the 470-36 matrix itself.

As a result of the chemisorption investigation, it can be concluded that the constituents of the vinyl ester polymer can be chemisorbed or strongly physisorbed to the fiber surface. One
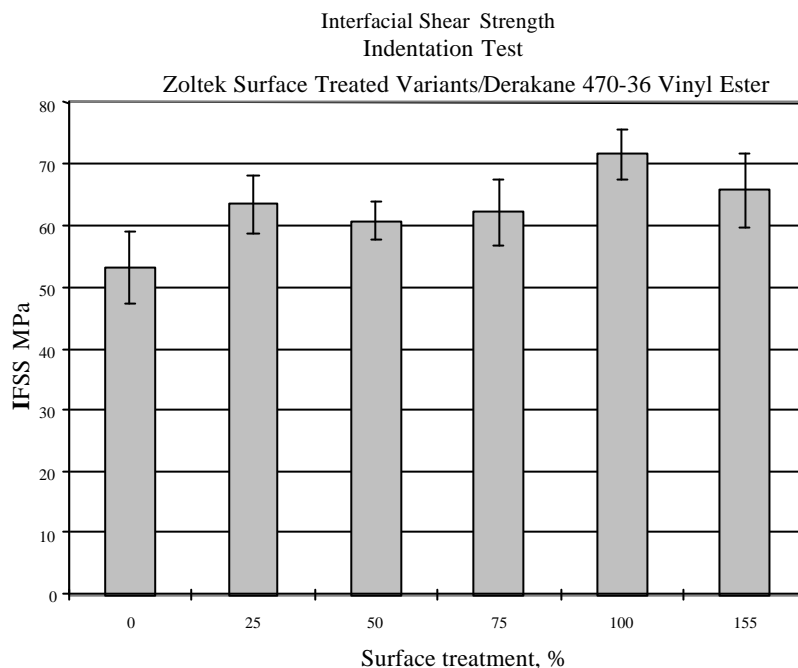

Figure 5. *Interfacial shear strength by indentation test.*

strategy to improve adhesion is to interfacially engineer the interphase through the use of a carbon fiber coating that will provide beneficial chemical and physical interaction with the vinyl ester monomer and its additives. In this way, the carbon fiber surface could be isolated from the free radical polymerization of the matrix and thereby produce a more uniform and desirable interphase which would improve adhesion.

An epoxy-amine coating was formulated to produce a balance between carbon fiber adhesion and compatibility with the vinyl ester matrix. Application of this coating to the carbon fiber was found to have favorable effects on promoting the IFFS of Panex 33 fiber in a vinyl ester matrix.

Unidirectional composite panels of the epoxy-amine coated Panex 33 fiber in vinyl ester matrix were manufactured using resin transfer molding. The coated Panex 33-150% surface treated fiber exhibited nearly a 100% increase in interfacial shear strength compared to the baseline, uncoated analog as shown in Figure 6. Composite flexural strength and shear strength also improved but not to the extent of the fiber-matrix adhesion. The benefits to the composite may be slightly obscured by the matrix properties. It should also be noted that the interaction between the epoxy-amine coating and the vinyl ester has to be optimized for compatibility and thickness and therefore further improvements in composite properties are to be expected.
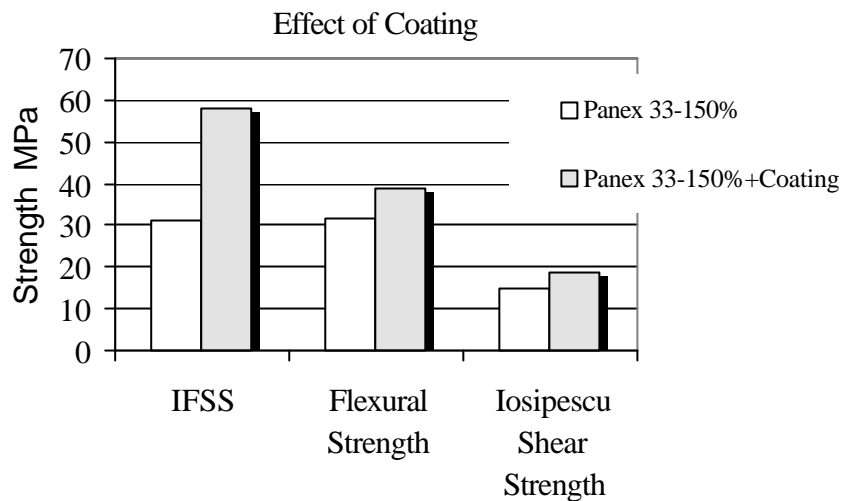
Figure 6. Effect of fiber coating on interfacial shear strength and composite mechanical properties.

CONCLUSIONS

Micromechanical test methods showed that the interfacial shear strength of carbon fibers is much lower in vinyl ester polymers than in epoxies. Adhesion of carbon fibers to vinyl ester matrices is not as high as to epoxy matrices because of the strong affinity of the vinyl ester constituents to the carbon fiber surface. This may be a result of preferential chemisorption and phsisorption of vinyl ester monomer and its additives on the fiber surface. The use of fiber coatings to interfacially engineer the interphase offers a potential avenue for improving adhesion. An epoxy based coating was shown to beneficial in promoting the interfacial shear strength and the mechanical properties of carbon fiber-vinyl ester composites.

ACKNOWLEDGEMENTS

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