FACTORS THAT AFFECT ADHESION AT THE FIBER-MATRIX INTERFACE IN COMPOSITES

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INTRODUCTION

The development of methods to assess adhesion (interfacial shear strength - IFSS) at a composite's fiber-matrix interface has been driven primarily by the recognition that the fiber-matrix interface or interphase has a profound affect on composite failure. Although several methods have been developed to assess fiber-matrix interface adhesion, the single fiber fragmentation test (SFFT) is preferred among researchers because the fiber loading is consistent with full-scale composite loading. In addition, the SFFT technique isolates the response of the fiber-matrix interface from competing factors, such as fiber-fiber interactions, void content, and perturbations to the residual stress field caused by adjacent fibers. Hence, this test offers a "pristine" view of the fiber-matrix interface stress-transfer process, and the opportunity to assess the factors that influence fiber-matrix interface adhesion, debonding, and failure modes.

In the SFFT technique, a single fiber is aligned along the axis of a dog bone cavity and embedded in a resin having an extension-to-failure that is typically 3 to 5 times higher than the fiber. The matrix is strained causing the fiber to break. The strain is increased until the resulting fiber fragments are too short for a sufficient load to be transmitted into them to cause additional failure. This point is termed saturation. The lengths of the fragments at this point reflect the adhesive character of the fiber-matrix interface. Since micro-mechanics models are used to extract an estimate of the IFSS from SFFT experimental data, the usefulness of the results are dependent on the accuracy of the micro-mechanics models. Because the current models use simplistic matrix assumptions, interpreting results from this test, except in the simplest cases, has been complicated. This problem has been addresssed recently by the development of a new micro-mechanics model[1] that accounts for the non-linear viscoelastic behavior of the polymer matrix. The impact of the new model on interpretation of data from the SFFT will be discussed.

In the development of the new micro-mechanics model, the fiber-matrix interface/interphase region for the test specimen was forced to be as simple as possible by embedding bare E-glass fibers in a polymeric matrix. In these systems, the interface/interphase region consisted primarily of a resin region whose cure behavior has been altered by thermodynamic interactions with the fiber surface[2] and perturbations to the resin cure reaction caused by specific chemical interactions (hydrogen bonding) with the fiber surface. In the manufacture of industrial "sized" glass fibers, the glass fiber is coated with "sizing" agents that (1) facilitate high-speed processing and (2) attempt to promote strength, stiffness, and durability in the final composite by "optimizing" compatibility with specific matrix resins. The sizing generally comprises a fraction of (0.2 to 2) % of the fiber mass and the coating as illustrated by Figure 1 is non-uniform.[3] Therefore, the interface/interphase region consists of a sizing layer whose structural integrity, chemical structure, and morphology depends on many processing parameters[4] and a region of resin matrix whose cure behavior has been altered by interactions with the sizing.

Although rapid characterization of sized fibers is essential for their efficient manufacture,[4] the observed changes in morphology and chemical structure at the fiber surface must be correlated with the key factors that control interface/interphase performance. The most critical factors are the cure behavior of the resin in the interface/interphase region, the fiber-matrix interface stress-transfer efficiency, and fiber-matrix interface failure modes associated with fiber fracture. Agarwal and Broutman[5] and others have noted that the interface is critical in maintaining the delicate balance between composite strength and fracture toughness. These researchers state that although an increase in interface strength improves a composite's transverse strength and promotes good environmental performance, a reduction in

interface strength may be required to improve fracture toughness (e.g., impact toughness)!

Even though the sized fiber morphology has been shown to be non-uniform, it is reasonable that systematic changes in processing parameters should produce, on average, morphology and chemistry changes that can be evaluated using interface testing to be critical or non-critical with respect to fiber-matrix interface performance. To this end, the concentration of the precipitating solution is varied in this report to effect changes in the thickness and morphology of the sizing deposited on E-glass fibers. The impact of these changes on fiber-matrix interface adhesion and debonding failure will be discussed. In addition, the results from these model systems will be compared with SFFT specimens made with a commercially prepared "model" sizing.

EXPERIMENTAL

The details of the experimental procedure can be found elsewhere.[6]

RESULTS AND DISCUSSION

Test Protocol Effects

Previous research has shown that fiber fragmentation in the SFFT occurs when the matrix is exhibiting non-linear viscoelastic behavior. As a result a new model was developed to account for this behavior[1] and the equation that is recommended for calculating the IFSS at the fiber – matrix interface is given below:

$$t_{\text{int erface}} = \frac{d_f\, b\{e,t\}}{4}\left(\frac{\sinh(b\{e,t\}l_c/2)}{\cosh(b\{e,t\}l_c/2)-1}\right)s_f\{l_c\} \qquad (1)$$

where

$$b\{e,t\} = \frac{2}{d_f}\left[\frac{E_m\{e,t\}}{(1+n_m)(E_f - E_m\{e,t\})\ln\left(2r_m/d_f\right)}\right]^{1/2}$$

E_m, E_f are the matrix and fiber moduli, respectively
ν_m is the matrix Poisson's ratio
ε is the global applied strain
t is the time
d_f is the fiber diameter
r_m is the radius of matrix parameter
l_c is the critical transfer length at saturation
$\sigma_f\{l_c\}$ is the strength of the fiber at l_c

This equation implies that IFSS values obtained from the SFFT can depend on the testing rate, through the non-linear viscoelastic behavior of the matrix. Tests at different average test rates (i.e., testing protocols) revealed that the behavior expected by increasing the time between strain increments (i.e., longer fragments with increased viscoelastic relaxation) was obscured by the impact of stress concentrations at the end of the generated fiber fragments.[7] Finite element analysis by Carrara and McGarry[8] and Laser Raman spectroscopy experiments by Galiotis[9] have indicated that stress concentrations at fragment ends can promote failure of the fiber-matrix interface at the molecular level. The onset of failure was shown by Galiotis to increase the fiber length required to transfer the shear stress into a fiber fragment. In the SFFT testing protocol, this has the net effect of increasing the size of the fragments at saturation and reducing the derived interface strength.

Research results by Holmes[7] indicate that the magnitude of the stress concentration at a fiber end is dependent on the viscoelastic relaxation behavior of the matrix. Thus increasing the viscoelastic relaxation time (i.e., time between strain increments) lowers the magnitude of the stress concentrations at the fiber ends. This has the effect of minimizing the onset of failure at the molecular level in the fiber-matrix interface. Data on bare E-glass SFFT test specimens made from epoxy and polyisocyanurate are shown in Tables 1 and 2. In both cases shorter fragments, and hence, a higher interface strength are obtained with the slow test protocol. The sensitivity of the interface strength to testing protocol reflects the strain rate sensitivity of the fiber-matrix interface and may influence the impact strength of a full-scale composite. The test results given in Tables 1 and 2 also imply that the onset of failure at the fiber-matrix interface depends on the strength and density of the chemical bonds at the fiber-matrix interface. Hence, interfacial shear strength values depend on testing rate, the molecular architecture of the resin, and the type and density of bonds at the fiber-matrix interface.

Interface/Interphase Processing Effects

The darkened (debond) regions associated with the fiber breaks in two specimens are shown in Figures 2 to 4. In Figure 2, the E-glass fiber was coated with a solution containing a mass fraction of 0.1 % of the hydrolyzed coupling agent γ-aminopropyl trimethoxysilane (γ-APTMS). In the darkened region, the fiber-matrix interface has absorbed by debonding, the energy generated by the fracture of the glass fiber. In fibrous composites this failure mode is preferred since the damage is isolated to the broken fiber. In Figures 3 and 4, the E-glass fiber was coated with a solution containing a mass fraction of 0.5 % of the same coupling agent. In these figures, matrix cracks perpendicular to the fiber axis are formed, in addition to the debond regions, when the fiber fractures. Since the degree of debonding will be limited in a stronger interface, the formation of matrix cracks in the specimen

coated with 0.5 % solution of the silane coupling agent suggests that this interface is stronger.

The matrix crack in Figure 3 was formed at 2.8 % strain with an initial crack length of 6 μm. Therefore, the matrix crack grew approximately 5 μm with an increase in strain of 0.4 %. In Figure 4, a matrix crack was formed at 3.2 % strain and has a length of 21 μm. Matrix crack formation in full-scale composites can reduce strength and stiffness and eventually precipitates composite failure. Consistent with the behavior noted in full-scale composites, many of the 0.5 % SFFT specimens failed before the test was completed. Similar tests performed on industrially coated γ-APTMS samples, resulted in the formation of matrix cracks and broken specimens. The industrial specimens were coated from a bath containing a 0.5 % solution of γ-APTMS. Preliminary data indicates that the coating thickness in the specimen coated by the 0.5 % solution is two times thicker than specimens coated from the 0.1 % solution. These results suggest that the morphology of the coupling agent layer, and possibly the degree of bonding associated with the thicker coating may influence fiber-matrix interface performance.

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Table 1

Theoretical Calculations of IFSS
Bare E-glass/Epoxy

Variables & Outputs	FTP[a]	ITP[b]	STP[c]
l_c, μm	484	507	434
Fiber Strength, GPa	1.41	1.59	1.53
Elastic Modulus, GPa	3.06	3.06	3.06
Cox Model, MPa	**72 ± 6**	**79 ± 7**	**95 ± 9**
Secant Modulus, GPa	1.67	1.71	1.69
NIST Model, MPa	**64 ± 6**	**64 ± 4**	**77 ± 8**
Kelly-Tyson, MPa	**23 ± 4**	**22 ± 2**	**26 ± 3**

(a) FTP denotes Fast Test Protocol
(b) ITP denotes Intermediate Test Protocol
(c) STP denotes Slow Test Protocol

Table 2

Theoretical Calculations of IFSS
Bare E-glass/Polyisocyanurate

Variables & Outputs	FTP	ITP	STP
l_c, μm	416	421	395
Fiber Strength, GPa	1.53	1.76	1.50
Elastic Modulus, GPa	3.06	3.06	3.06
Cox Model, MPa	**100 ± 7**	**111 ± 7**	**104 ± 8**
Secant Modulus, GPa	1.89	1.78	1.79
NIST Model, MPa	**84 ± 9**	**87 ± 9**	**90 ± 9**
Kelly-Tyson, MPa	**29 ± 6**	**30 ± 5**	**31 ± 6**

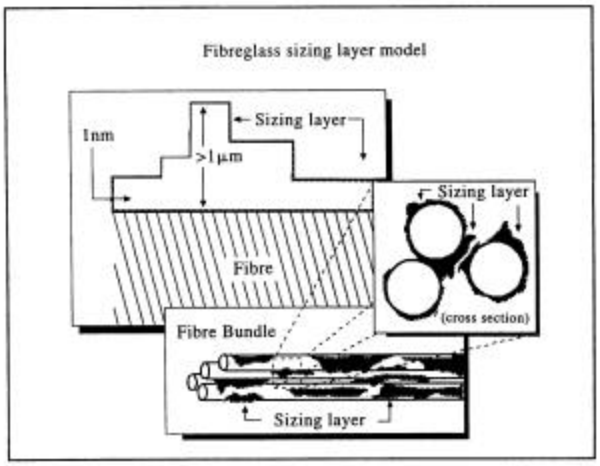

Figure 1. Commercial Glass Fiber Sizing Layer Model (adapted from Wu *et al.*[3])

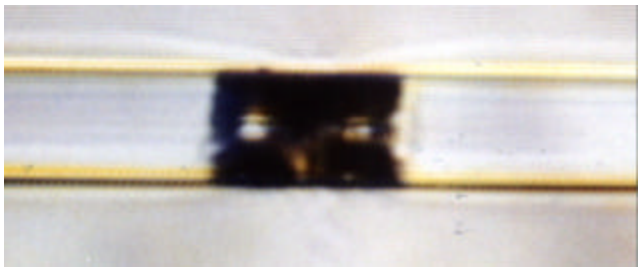

Figure 2. Debond Region Associated with Fiber Fracture of E-glass Fiber Coated from 0.1 % Solution of g-APTMS Embedded in DGEBA/m-PDA Epoxy Resin

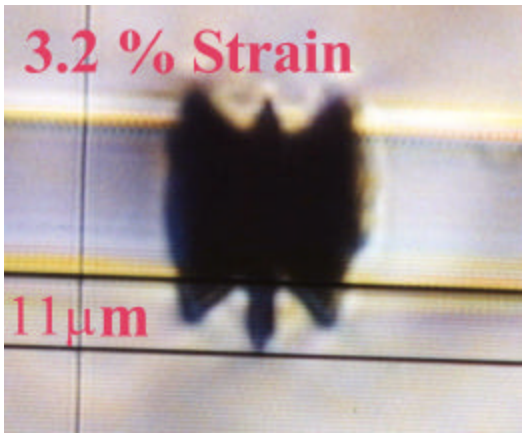

Figure 3. Debond Region Associated with Fiber Fracture of E-glass Fiber Coated from 0.5 % Solution of g-APTMS Embedded in DGEBA/m-PDA Epoxy Resin (Type 1 Matrix Crack).

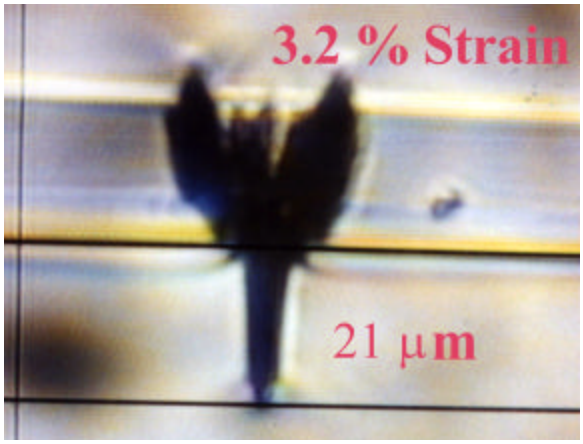

Figure 4. Debond Region Associated with Fiber Fracture of E-glass Fiber Coated from 0.5 % Solution of g-APTMS Embedded in DGEBA/m-PDA Epoxy Resin (Type 2 Matrix Crack).