USING SELF-ASSEMBLED MONOLAYER TECHNOLOGY TO PROBE THE FIBER-MATRIX INTERFACE

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INTRODUCTION

Adhesion at the fiber-matrix interface of composite specimens is often ascribed to the following factors: (1) mechanical interlocking, (2) physicochemical interactions, (3) chemical interactions, and (4) mechanical deformation of the fiber-matrix interphase region.[1,2] As noted by Drzal,[2] the interphase region is a complicated three-dimensional construction consisting of the bulk adherend, adherend surface layer, adsorbed material, polymer surface layer, and bulk adhesive. Drzal found that early models of adhesion were ineffective since they oversimplified the composition and nature of the fiber-matrix interface.

It is known from the research of Ishida, that resin can penetrate into the silane coupling agent layer and form an interpenetrating network of resin and coupling agent. This network may provide a basis for adhesion at the fiber-matrix interface through mechanical interlocking. The orientation of coupling agents such as γ-aminopropyl trialkoxy silane on the fiber surface and its impact on covalent bonding to the host matrix has also been questioned. In addition, the effect of adsorbed silane coupling agents on the matrix network structure has been investigated.[3]

Silane coupling-agents deposited by self-assembled monolayer (SAM) technology have no current industrial relevance. However, recent technology developments [4] in the deposition of functionalized SAM monolayers may provide an approach for reducing the complexity of the three-dimensional functionalized silane layer side of the interphase region in glass-fiber reinforced composites. With this approach, the efficacy that the various factors have on adhesion at the fiber matrix interface can be systematically investigated. In 1987, Nardin and Ward [5] appear to be the first to perform a quantitative study of this type. In their research, they focused on the adhesion of a low-viscosity epoxy resin (Ciba Geigy XD 972) to polyethylene fibers. These authors concluded that fiber-matrix adhesion as measured by the fiber-matrix interface strength was an additive sum of the first three factors delineated by Sharpe and Drzal.

$$\tau_{\mathrm{int}\,erphase} = \tau_M + \tau_{PCI} + \tau_{CB} \qquad (1)$$

where

$\tau_{\mathrm{int}\,erphase}$ denotes the total fiber-matrix adhesion as measured by the interphase strength.

τ_M denotes the adhesion at the fiber-matrix interphase due to mechanical interlocking.

τ_{PCI} denotes the adhesion at the fiber-matrix interphase due to physicochemical interactions.

τ_{CB} denotes the adhesion at the fiber-matrix interphase due to chemical bonding.

From their research, each term contributed equally to the adhesion of epoxy resin to polyethylene fibers. Using this equation as a starting point, this research will focus on determining the impact of the first three factors on the adhesion of diglycidyl ether of bisphenol-A (DGEBA) cured with meta-phenylene diamine (m-PDA) to E-glass fibers.

EXPERIMENTAL

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

RESULTS AND DISCUSSION

From the single fiber fragmentation test (SFFT) the average number of fiber breaks in a given length of test specimen reflects the strength of the fiber-matrix interface. An increase in the number of breaks indicates an increase in the fiber-matrix interface strength. In Figure 1, the number of fiber breaks in the complete gauge section of a test specimen versus the amine concentration in the depositing solution is shown for two types of interfaces. The S-shaped solid line represents data from E-glass fibers coated using the aqueous deposition process (industrial-

type interface). The dotted straight line represents data from E-glass fiber coated using the SAM deposition process.

For the aqueous deposition process, molar mixtures of propyltrimethoxysilane (PTMS) and γ-aminopropyl-trimethoxy silane (γ-APTMS) were used to vary the concentration of amine on the fiber surface. Of particular interest on the S-shaped curve is the average number of fiber breaks (44 ± 6) at zero percent covalent bonding (100 % PTMS). This number of breaks indicates that the shear stress transfer process at the fiber-matrix interface is facilitated by a significant interaction between the matrix and fiber. Since covalent bonding is ì formallyî eliminated because of the non-bonding nature of the silane coupling agent, this interaction, according to the Sharpe and Drzal formalism and the Nardin and Ward model, must involve physicochemical interactions and/or mechanical interlocking.

In the Nardin and Ward model, physicochemical interactions between a polymer and a surface are expressed mathematically by the following expression:

$$\tau_{PCI} = \alpha(\gamma_S - \gamma_C) \qquad (2)$$

where

γ_S denotes the surface free energy of the treated fiber.

γ_C denotes the critical surface tension of the fiber.

α is a numerical constant obtained from plotting τ_{PCI} versus γ_S.

Since SAM technology admits the formation of thin films of coupling agents were the alkyl chains register, these intephases should be more resistant to penetration by epoxy resin and curing agent. Hence, mechanical interlocking should be minimized in these interfaces. Therefore, the impact of physicochemical interactions on the adhesion process can be assessed independently of the other mechanisms for the hydrophobic E-glass fiber / amine epoxy resin interface.

The average number of fiber breaks for hydrophobic E-glass SFFT specimens prepared using the SAM technology with undecane trichlorosilane (UTCS) as the silane coupling agent are shown in Figure 1 by the open square symbol at zero percent amine concentration (6 ± 2). Dynamic contact angle measurements on the fibers and companion glass plates indicate a modest increase of the surface hydrophobicity for the SAM coated fiber relative to surfaces prepared by the aqueous deposition process (see Table 1). Therefore, we interpret the dramatic drop in the number of fiber breaks in the hydrophobic E-glass /

amine cured epoxy SFFT specimens to be due to the elimination of ì mechanical interlockingî as a mechanism for adhesion in the SAM specimens. These results also suggest that physicochemical interactions between amine cured epoxy resins and predominately hydrophobic fiber surfaces result in minimal adhesion at the fiber-matrix interface.

Consistent with these results, a dramatic change in the extent of debonding at the fiber matrix interface was observed during the fragmentation tests. In Figure 2, the unstressed debond region associated with the fracture of a hydrophobic E-glass specimen prepared by the aqueous deposition process is shown. The debond region is approximately 25 μm. The interpretation of the darkened region as being matrix material debonding from the embedded glass fiber is based on previous research.[7] In Figure 3, the unstressed debond region associated with the fracture of a hydrophobic E-glass SFFT specimen prepared by the SAM technology is shown. The total length of the debonded region is greater than 200 μm. The original fiber fracture site with debond region is delineated on the figure (≈ 30 μm). Additional debonding occurred as the strain was continually increased during the test. The extensive secondary debonding after initial fiber fracture is similar in magnitude to that found by Galiotis *et al.*[8] for carbon fibers embedded in Ciba-Geigy resin MY750 cured with the amine hardener HY951. However, this magnitude of debonding after initial fiber fracture has not been observed for E-glass fibers coated with silane coupling agents using the aqueous deposition process.[7]

In their research, Nardin and Ward discovered a simple relationship between the surface roughness (i.e., the depth of the pits or valleys on the fiber surface) and the degree of interfacial adhesion due to mechanical interlocking.

$$\tau_M = ae + \tau_{PCI}^{max} \qquad (3)$$

where

e denotes the mean depth of the pits or valleys on the fiber surface.

a is a constant

This expression also depends on the maximum contribution to interfacial adhesion from physicochemical interactions (τ_{PCI}^{max}). Initial AFM pictures and surface roughness analyses of the hydrophobic silane layers deposited by the two deposition processes (**not shown**) suggests that the SAM surface is rougher than the aqueous deposition surface. Hence,a more elaborate ì mechanical interlockingî mechanism may be needed to explain the differences in debonding discussed above and the AFM results.

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Table 1
Contact Angle of Hydrophobic Surfaces
Aqueous versus SAM Deposition

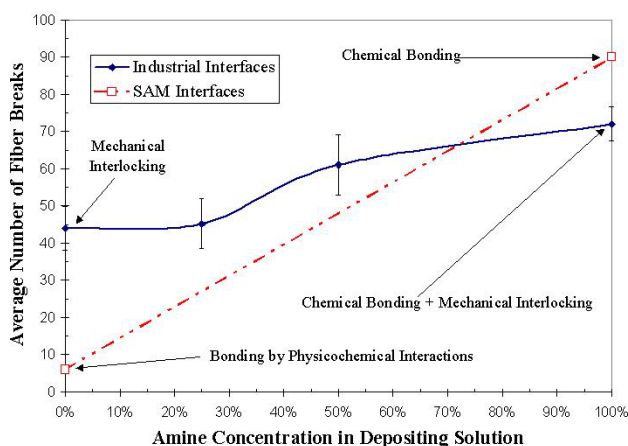| Specimen Identification	Contact Angles	
	Advancing	Receding
PTMS ñ Plates (Aqueous)	97 ± 4	64 ± 2
PTMS ñ Fibers (Aqueous)	95 ± 2	61 ± 2
Undecane ñ Plates (SAM)	107 ± 3	69 ± 1
Undecane ñ Fibers (SAM)	103 ± 3	67 ± 1

Figure 1. A plot of the number of fiber-breaks versus the amine concentration of the depositing solution.
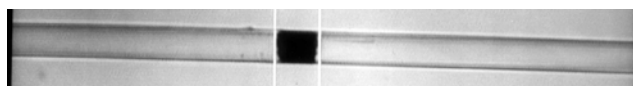

Figure 2. Unstressed debond region associated with fiber break in hydrophobic E-glass specimens prepared by aqueous deposition process (25 µm).
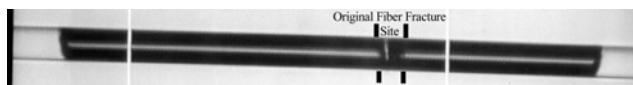

Figure 3. Unstressed debond region associated with fiber break in hydrophobic E-glass specimens prepared by SAM technology (≈ 220 µm).
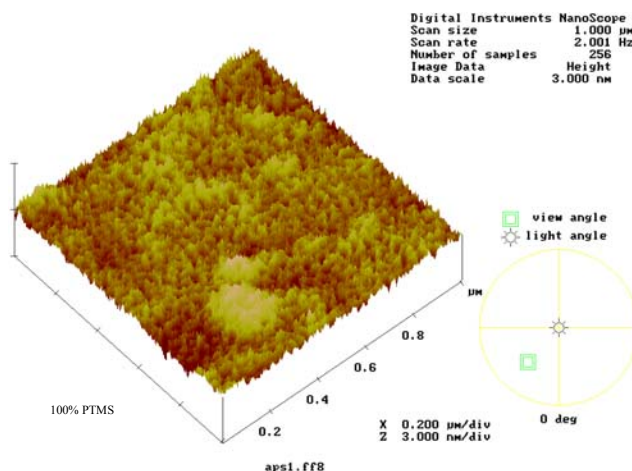

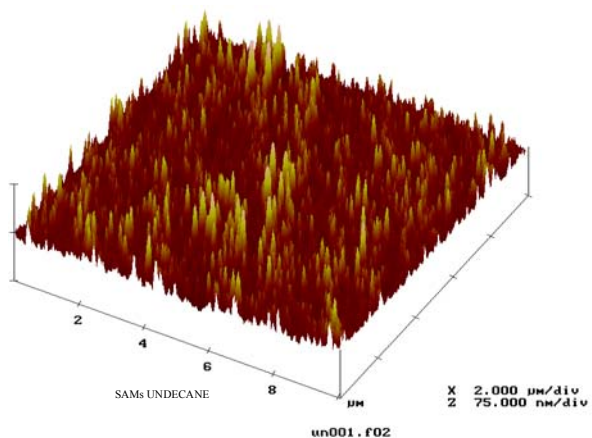**Figure 4.** AFM of 100 % PTMS surface deposited by aqueous deposition process.

Figure 5. AFM of 100 % Undecane trichlorosilane (UTCS) surface deposited by SAM process.