

THE EFFECT OF SELF-ASSEMBLED MONOLAYER TECHNOLOGY ON FIBER-MATRIX ADHESION

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Introduction

The concept of an interphase region between an adherent and a matrix or adhesive was first introduced in 1972 by Sharpe.¹ Since its introduction, the role of the interphase region in controlling the performance of fibrous composites has been extensively investigated. As noted by Drzal² the interphase region is a complicated three-dimensional construction consisting of the bulk adherent, the adherent surface layer, the adsorbed material, the polymer surface layer, and the bulk adhesive. This complexity coupled with the difficulties associated with investigating an embedded organic-inorganic interphase region has minimized the progress of fundamental research on this area.

Adhesion in the interphase region of fibrous composites is often ascribed to (1) mechanical interlocking, (2) physicochemical interactions, (3) chemical bonding, and (4) mechanical deformation of the fiber-matrix interphase region (Sharpe and Drzal). In 1987, Nardin and Ward³ suggested that the contributions of the first three parameters to fiber-matrix interphase adhesion between polyethylene fiber and low viscosity epoxy resin was additive.

$$\tau_{\text{interphase}} = \tau_M + \tau_{PCI} + \tau_{CB} \quad (1)$$

where

$\tau_{\text{interphase}}$ denotes the total fiber-matrix adhesion as measured by the interphase strength parameter.

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.

Nardin and Ward proposed that the contribution to interfacial adhesion due to physicochemical interactions could be quantified by the following expression:

$$\tau_{PI} = \alpha(\gamma_S - \gamma_C) \quad (2)$$

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 .

In addition, Nardin and Ward proposed that the contribution to interfacial adhesion due to mechanical interlocking is related to the rugosity of the fiber surface and the maximum contribution to interfacial adhesion from physicochemical interactions (τ_{PCI}^{\max}).

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

where

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

a is a constant

These authors noted that it is difficult to separate the contributions to interfacial adhesion by the second and third terms in equation 1. In addition, they speculated that the contribution to interfacial adhesion by chemical bonding is related to the number of chemical bonds in the fiber-matrix interphase region. For E-glass fibers embedded in a diglycidyl ether of Bisphenol-A (DGEBA) epoxy resin cured with meta-phenylene diamine (m-PDA), MacTurk *et al.*⁴ observed a correlation between the number of chemical bonding sites on the fiber and the total fiber-matrix adhesion. Interestingly, at zero bonding these researchers observed a finite level of adhesion significantly higher than the level of adhesion between carbon/DGEBA/m-PDA epoxy resin interfaces, where the degree of chemical bonding in the untreated carbon fibers has been estimated by Drzal to be approximately 5%.⁵ This would suggest that the increased adhesion in the E-glass/DGEBA/m-PDA systems at zero bonding is due to incomplete coverage of the glass surface by the non-bonding silane coupling agent or increased rugosity of the fiber surface that arises from the process used to deposit the silane layer. These observations suggest that the dynamics of stress transfer at the fiber-matrix interface can only be understood by a fundamental understanding of the interplay between mechanical interlocking, physicochemical interactions, and chemical bonding.

The deposition of the silane-coupling agent by self-assembled monolayer technology may provide an approach for resolving these research issues. This technology provides a methodology for compressing the three-dimensionality of the interphase region in glass-fiber reinforced composites. Using this technology, the roughness of the glass surface induced by the industrial water-deposition process can be minimized and the contribution of adsorbed material in the interphase region can be eliminated. Hence the impact of the first three factors on interfacial adhesion can be investigated in a more controlled and fundamental manner.

Experimental

Fiber-Coating Procedures. Details of the industrial coating procedure used in the laboratory and the SAM coating procedure can be found elsewhere.^{6,7}

Preparation of Single Fiber Test Specimens. Details of the specimen preparation can be found elsewhere.^{8,9}

Single Fiber Fragmentation Testing Procedure. The details of the testing procedure and the standard error in the testing method can be found elsewhere.^{8,9} All specimens in this research were tested with a 10 min delay between strain increments.

Results and Discussion

In Figure 1, the number of fiber breaks versus the amine concentration in the depositing solution is shown. The number of fiber breaks is directly proportional to the adhesion at the fiber-matrix interface. Hence, an increase in the number of breaks in the test specimen reflects an increase in the adhesion at the fiber-matrix interface.

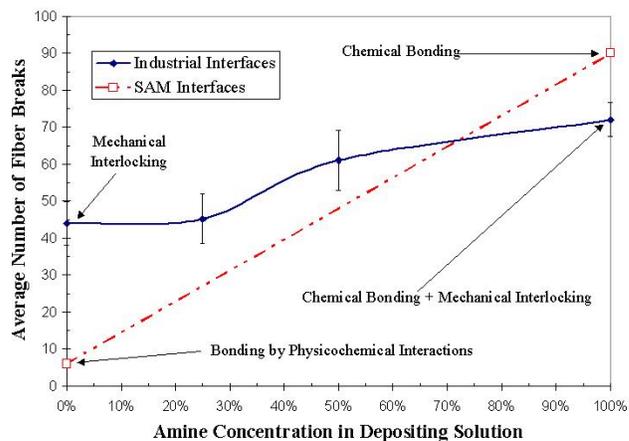


Figure 1. A plot of the number of fiber breaks versus the amine concentration in the depositing solution.

For the industrial type interfaces, mixtures of γ -aminopropyl trimethoxysilane (bonding silane coupling agent) and propyl trimethoxysilane (non-bonding silane coupling agent) were used to vary the amine concentration in the depositing solution (water) and hence on the fiber surface. This S-shaped plot shows an increase in adhesion at the fiber-matrix interface as the amine concentration is increased. Of particular interest at this point is the finite number of breaks at zero percent concentration of amine. These results parallel previous research by MacTurk *et al.*,⁴ where they used n-octadecyl triethoxysilane for the non-bonding silane-coupling agent. Interestingly, dynamic contact angle measurements of the fiber surfaces coated with 100 % non-bonding silane coupling indicated complete hydrophobic character.

Contrasting these results at zero percent bonding is the number of fiber breaks obtained from a non-bonding interface prepared using self-assembled monolayer technology. For the industrial type interface the average number of breaks in a specimen with zero percent bonding was (44 ± 6) , while in the SAMs interface the average number of breaks was (6 ± 2) . Since the SAM interface at zero percent bonding also exhibited complete hydrophobic character, the increased adhesion at the fiber-matrix interface prepared by the industrial process appears to be due to mechanical interlocking. Consistent with these results, the extent of debonding associated with fiber fracture was found to be greater in the SAM non-bonding interface than the industrial non-bonding interface.

At 100 % bonding (γ -aminopropyl trimethoxysilane), the average number of breaks in the industrial interface is (72 ± 5) . Since the industrial interface at zero bonding exhibits adhesion due to mechanical interlocking, the adhesion in the industrial 100 % bonding interface is probably due to a combination of mechanical interlocking and chemical bonding.

The average number of breaks in the 100 % bonding SAM interface is (90 ± 8) . This represents a significant increase in adhesion over the industrial interface with 100 % bonding, where we have speculated that mechanical interlocking and chemical bonding contribute to the adhesion process. Since the SAM deposition process should minimize the contribution to mechanical interlocking the adhesion in the 100 % bonding interface should be due primarily to chemical bonding. The difference in adhesion between the 100 % bonding industrial interface and the 100 % bonding SAM interface may be related to the propensity of the γ -aminopropyl moiety to turn upside-down during the industrial deposition process. These molecules would not bond to the matrix when the fiber-matrix interphase is formed. Dynamic contact angle measurements on 100 % bonding specimens deposited by the industrial process, indicates a significant amount of hydrophobic character. This result is also consistent with a significant amount of the γ -aminopropyl moiety exhibiting an upside-down orientation on the fiber surface. Considerable research is still needed, however, to substantiate these experimental results.

Conclusions

The SAM procedure appears to separate the contributions to adhesion between physicochemical interactions and covalent bonding. By comparing the SAM process with the industrial process, the adhesion in the 100 % bonding interfaces produced by the industrial process seems to be due primarily to mechanical interlocking and chemical bonding.

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