Application of Self Assembled Monolayer Approach to Probe Fiber Matrix-Adhesion

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ABSTRACT

Adhesion at the fiber-matrix interface of composites is often related to a combination of factors such as mechanical interlocking, physico-chemical interactions, and chemical bonding of the fiber-matrix interphase region. We demonstrate the use of self-assembled monolayer (SAMs) approach for depositing silane coupling agent on glass fiber and studying the impact of the individual interactions on the adhesion process. Through some unique chemistry, functionalized and non-functionalized C11 chlorosilanes were deposited on to E-glass fiber and modified. The adhesion of diglycidyl ether of bisphenol-A (DGEBA) cured with meta-phenylene diamine (m-PDA) to SAM layer on E-glass fibers was measured by performing single fiber fragmentation tests (SFFT). The extent of adhesion between the fiber and matrix was found to be dependent on carbon chain length of coupling agents, and the functional group at the end of the SAMs layer. Furthermore, the contributions to adhesion by physico-chemical interaction and covalent bonding has been individually assessed.

INTRODUCTION

One of the major technical challenges to a composite's use in high performance applications is the reliable prediction of long-term performance (e.g., failure behavior, fatigue behavior, durability, and stiffness). When composites are manufactured, a small region (< 1 μm), known as the fiber-matrix interphase, forms between the fiber and the matrix [1]. This region exhibits properties similar to, but distinguishably different from the properties of the bulk matrix [2]. Since stress is transferred between the fiber and matrix at the fiber-matrix interphase, the efficiency of this stress-transfer process at the interphase is critical to a composite's ultimate strength and durability. Therefore, the role of the interphase structure, fiber topography, and fiber-matrix chemical bonding on ultimate composite performance needs to be understood fundamentally.

Traditionally, a mole fraction of 50 % ω-aminopropyl trimethoxysilane (APS) coupling agent is applied on glass fiber and this coupling agent promotes adhesion between the glass fiber and epoxy matrix. However, the orientation of bonding sites in coupling agents (i.e., amino group in ω-amino propyl trimethoxysilane on the glass fiber) has been called into question and its impact on covalent bonding to the host matrix (epoxy) has not been fully understood.

In recent years, molecular systems with well defined structural patterns have received growing attention for studying interfaces. A variety of experimental techniques have emerged

which allow one to endow a solid surface with rich, well defined chemical patterns while keeping the surface flat on a molecular scale. SAMs offer one of the highest quality routes for the preparation of chemically and structurally well defined organic surfaces [3-6]. The solvent deposition of the trichlorosilane layer may provide an approach for developing organized self-assembled monolayers [5]. Using this approach, the impact of chemical bonding on interfacial adhesion has been investigated in a more controlled and fundamental manner [4-6]. These studies use the single-fiber fragmentation test (SFFT) to monitor both the fiber strength and the fiber-matrix interface/interphase strength. However there have been difficulties associated with controlling the fiber-matrix interface structure so as to fully understand the impact of interface structure on composites performance.

EXPERIMENTAL

The SFFT specimens were prepared with a DGEBA epoxy, Epon 828 (Shell), cured using m-PDA (Fluka Chemical). One hundred grams of DGEBA and 14.5 grams of m-PDA were weighed out in separate beakers. To lower the viscosity of the resin and melt the m-PDA crystals, both beakers were placed in a vacuum oven set at 65 °C. After the m-PDA crystals were completely melted, the silicone molds containing the coated fibers with silane agent were placed into another vacuum oven that was preheated to 75 °C at –20 kPa, for 20 min. Details of the aqueous coating procedure and SAMs coating procedure can be found elsewhere [7, 8]. The preheating of mold dries the mold and minimizes the formation of air bubbles during the curing process. At approximately 9 min before the preheated molds were removed from the oven, the m-PDA is poured into the DGEBA and mixed thoroughly. The mixture was placed into the vacuum oven and degassed for approximately 7 min. After 20 min, the preheated molds were removed from the oven and filled with the DGEBA/m-PDA resin mixture using 10 ml disposable syringes. The filled molds were then placed into a programmable oven. A cure cycle of 2 h at 75 °C followed by 2 h post-curing at 125 °C was performed.

The SFFT is an indirect micromechanics method used to calculate the degree of adhesion between a rigid fiber coated with silane agent and a more ductile polymeric matrix in fiber reinforced polymer composite. In a single fiber fragmentation test, typically, the fiber is embedded in a matrix material with a higher strain-to-failure than the fiber and the fiber breaks when longitudinal strain is applied. The test is performed by the sequential application of strain increments. The breaks occur at flaws along the fiber length, in a progressive way from the most critical to least critical flaw. A saturation limit is eventually attained, when the fragmented fiber is made up of a large number of very short fragments. Upon reaching the saturation limit, any additional strain does not cause further failure of the fiber. The resulting distribution of fiber fragment lengths represents the raw data from the single fiber fragmentation test. The details of the testing procedure, and the standard error in the testing method can be found elsewhere [9, 10]. All specimens in this research were tested with a 10 min delay between strain increments.

RESULTS AND DISCUSSION

Adhesion at the fiber-matrix interphase of composites is often ascribed to the following factors: (1) mechanical interlocking, (2) physico-chemical interactions, (3) chemical interaction, and (4) mechanical deformation of the fiber-matrix interphase region. Nardin and

Ward [11] appear to be the first to establish that fiber-matrix interface strength as a sum of the first three factors.

$$\tau_{interphase} = \tau_M + \tau_{PCL} + \tau_{CB}$$

where

$\tau_{interphase}$ 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_{PCL} denotes the adhesion at the fiber-matrix interphase due to physico-chemical interactions.

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

By solvent deposition of coupling agent we prepare pure and mixed monolayers fuctionalized and non fuctionalized silane on glass fiber. The monolayer formations provide an approach for studying the impact of the three factors on interfacial adhesion in a more controlled and fundamental manner.

Figure 1 compares the number of fiber break results of aqueous deposited silane and solvent deposited trichlorosilane. The smooth lines drown on each data points in Figure 1 are just to guide the reader's eyes. 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. Because of the non-bonding nature of propyl trimethoxysilane (PTMS) and undecyl trichlorosilane (UTCS) towards epoxy, according to the Nardin and Ward model [11], for glass fibers coated with PTMS and UTCS system the adhesion contribution must come from mechanical interlocking and/or physicochemical interaction. A close examination of SFFT result (fiber breaks) for 100 % mole fraction PTMS coated and 100 % mole fraction UTCS coated glass fiber composite shows higher breaks for PTMS than UTCS. For the 100 % mole fraction PTMS coated glass fiber epoxy composite, the average number of breaks was (44 ± 6), where the number after ± is one standard deviation from the mean and is taken as the standard uncertainty, while for 100 % mol fraction UTCS coated glass fiber epoxy composite, the average number of breaks was (6 ± 2). The comparison of non-bonding coupling agents (PTMS and UTCS) suggests that PTMS coated fiber is more strongly adhered to the epoxy matrix than UTCS. Using atomic force microscopy (AFM), the PTMS coupling agent deposited film on fiber was observed and the film is rougher and non-uniform than the UTCS coupling agent deposited film. Based on AFM images, one can infer that the epoxy resin is likely to penetrate the porous PTMS coupling agent layer and reach the bare glass fiber surface. We expect, mechanical interlocking mechanisms that involves penetration of the epoxy resin through the porous silane layer to the glass surface to have largely contributed to increased adhesion, as measured by single fiber fragmentation test. Solvent deposited UTCS on glass fiber, the long back bone chain promote better packing of coupling agent on glass surface and there is less likelihood for epoxy to penetrate glass surface. As expected, the number of breaks for the UTCS coated glass fibers epoxy composites is small. The adhesion contribution may come largely from physico-chemical interactions.
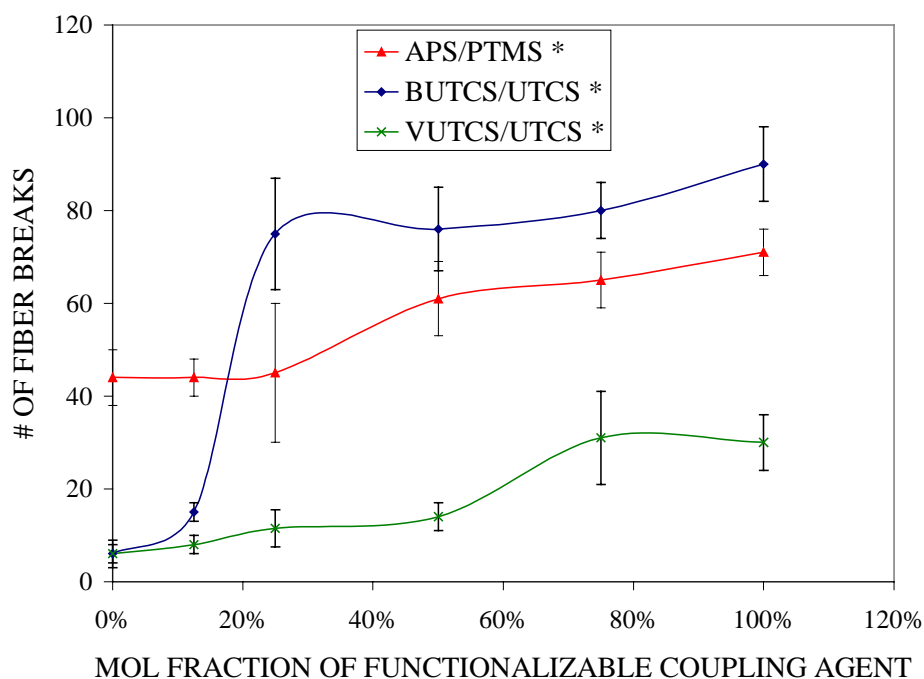
Figure 1. Average number of fiber breaks for E-glass fiber solvent deposited with short chain and long chain coupling agents as the mole fraction of functionalizable terminal groups in solution. The percentage is based on the mixing ratio of the silylating agents in solution during the deposition process [* For example, 0 % in the X-axis represents the mixture of 0 % mole fraction of bonding APS and 100 % mole fraction of non-bonding PTMS.] (Error bar represents one standard deviation from the mean and is taken as the standard uncertainty)

Since "mechanical interlocking" is minimal for long chain non-bonding silane coupling agent (UTCS), we can study the impact of purely covalent bonding on overall adhesion by considering long chain bonding silane coupling agent i.e, amino undecyl trichlorosilane (AUTCS).

Figure 1 shows the result for number of fiber breaks as a function of mole fraction of functionizable coupling agent in the solution. The deposited BUTCS was in-situ modified to AUTCS. This approach allows all amine groups of the long chain silane coupling agent on glass fiber to be oriented away from the fiber surface, and will be available for reaction with the epoxy resin. It can be seen that the magnitude of fiber breaks increases initially (shown by the line corresponding to ◆) and reaches 85 % of the saturation value at 25 % mole fraction of functionalizable coupling agent in solution and marginally increases with further increase in functional coupling agent component above this concentration.

A plausible explanation for saturation at a mole fraction of 25 % of functionalizable coupling agent is that DGEBA is a large monomeric molecule and may sterically hinder the accessibility of neighboring reactive groups (amine) to react with the epoxy functional group of another DEGBA molecule [12]. Consequently, a large fraction of the groups registered on the fiber may not have participated in the epoxy/amine reaction. Therefore, the amount of adhesion between glass fiber and epoxy is dependent not only on the bonding/non-bonding type of coupling agents, the composition of bonding/non-bonding coupling agent mixture, and the

packing/registering of coupling agent molecules, but also on the structure of the reacting matrix.

A large difference in the extent of debonding for UTCS and BUTCS/ in-situ modified glass epoxy composites at the fiber matrix interface was observed during the fragmentation tests. The debond area is indirectly proportional to adhesion at the glass/fiber interface. Figure 2, shows the unstressed debond region associated with the fracture of glass specimen coated with 100 % mole fraction of in-situ modified BUTCS. The debond region is approximately 20 μm. When the fiber fractures, a matrix crack perpendicular to the fiber axis is formed in addition to the matrix debond region. Figure 3, shows the unstressed debond region associated with the fracture of a glass specimen coated with 100 % mole fraction of non-bonding UTCS. The total length of the debonded region is greater than 200 μm. These results further confirm that the covalent bonding in in-situ modified BUTCS largely contributes to adhesion at E-glass fiber/epoxy composite interface. This contribution was minimal in UTCS systems. To establish that indeed covalent bond contributes to enhanced adhesion, we compared the number of fiber breaks for PTMS with APS coated glass fiber epoxy composites. As expected, the number of fiber breaks for glass fibers treated with mixed APS and PTMS increased with increase in the APS concentration in the mixture. We performed statistical analysis of the results and detailed analysis of the results can be found elsewhere [13].

We also studied the role of terminal hydroxyl functional group on the overall adhesion of fiber/epoxy composite by solvent depositing vinyl undecyl trichlorosilane (VUTCS) (bonding silane coupling agent) and UTCS (non-bonding silane coupling agent) on glass fiber. The deposited VUTCS was in-situ modified to create hydroxyl terminal group so that hydroxyl groups can hydrogen bond to the epoxy resin matrix. The plot (Figure 1) shows a steady increase in the number of fiber breaks (shown by line correspond to ✕) as the percent of functionalizable group on the fiber surface is increased and then plateau at higher concentration of functionalizable groups on the E-glass fiber surface. The difference in the number of fiber breaks between the modified BUTCS interface and modified VUTCS interface is due to the type of chemical bonds formed with epoxy resin. In the case of amine terminated glass (modified BUTCS) surface, covalent bonding of terminal amine with the epoxy resin can result in strong adhesion, while hydroxyl terminal glass surface, it is speculated that hydrogen bonding of the hydroxyl group with the cured epoxy resin explain weak adhesion. Our comparison is based on the assumption that the extent of in situ modification of BUTCS to amine and VUTCS to hydroxyl-functionalized E-glass fiber is very similar. Further studies are needed to quantify the extent of in-situ modification in both systems and confirm our observations.
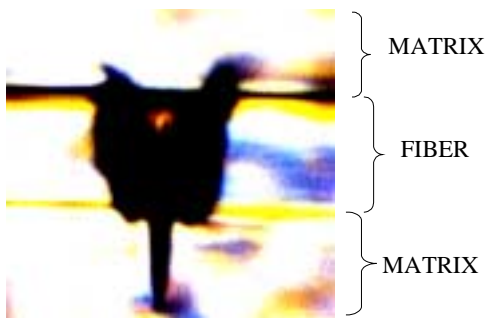

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Figure 2. Debond regions associated with the fiber breaks in in-situ modified 100 % BUTCS coated glass fiber epoxy composite.
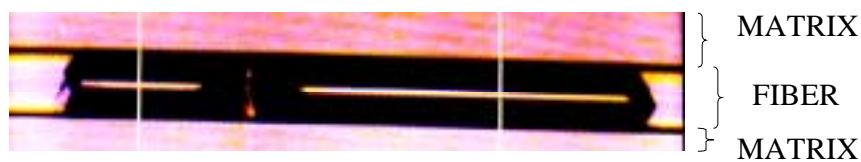
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Figure 3. Debond regions associated with the fiber breaks in 100 % UTCS coated glass fiber epoxy composite.

CONCLUSION

1. The results from aqueous phase deposited silanes indicates that ~85% of the fiber breaks is obtained with ~50% of the surface covered with amino groups.
2. Solvent deposition and in-situ modification of silane was used to prepare pure and mixed functionalized silane monolayers on E-glass fiber surfaces.
3. The fragmentation data for SAMs modified glass fiber/epoxy composite indicate that ~85% of fiber breaks is obtained with ~25% of the surface covered with amino groups.
4. Hydroxyl terminated SAM was used to probe the strength of hydroxyl-hydroxyl bonding at the fiber matrix interphase. The adhesion for hydroxyl terminated SAM was found to be much lower than the adhesion results exhibited by amine functionalized SAMs surface.

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