

The Role of the Terminal Functional Group of Self-assembled Monolayers on Fiber Matrix Adhesion

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ABSTRACT: Adhesion at the fiber-matrix interface of a composite is often influenced by a combination of factors such as mechanical interlocking, physicochemical interactions, and chemical bonding in the fiber-matrix interphase region. We demonstrate the use of an approach using self-assembled monolayers (SAMs) for studying the impact of one of the factors, chemical bonding, on the overall adhesion of the glass-fiber/matrix interface. Transformation of these monolayer surfaces using conventional chemistry with a focus on the creation of a terminal functional group that interacts with epoxy resin is reported. The modified surfaces were characterized by ellipsometry, X-ray photoelectron spectroscopy, and contact angle techniques for chlorosilane

coverage, and *in situ* conversion. The adhesion of diglycidyl ether of bisphenol-A resin to modified SAMs on E-glass fibers was measured by performing single-fiber fragmentation test. The extent of adhesion between the fiber and matrix was found to be dependent on the type of functional group at the terminal end of the SAM in contact with the epoxy matrix. Methyl terminal group resulted in the least adhesion, while amine terminal groups resulted in the most adhesion. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 462–469, 2007

Key words: interfacial shear strength; glass fiber epoxy composite; bonding and non bonding coupling agents; single-fiber fragmentation test; contact angle

INTRODUCTION

A major technical challenge to composite use in aerospace and automotive applications is the reliable prediction of long-term material performance (e.g., failure behavior, fatigue behavior, durability, 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 embedded interphase 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 the stress-transfer process at the interphase is critical to a composite's ultimate strength and durability. Therefore, the role of interphase structure, fiber topography, and fiber-matrix chemical bonding on ultimate composite performance needs to be fundamentally understood.

One approach for improving adhesion in the fiber-matrix interphase region is to use silane-coupling agents (SCAs) that promote environmentally stable adhesion. These difunctional agents covalently bond

to the glass fiber and to the host matrix. Therefore, adhesion between the glass fiber and epoxy matrix depends on the organofunctionality of the SCA and its concentration on the fiber surface. Industrially, a mass fraction of 5% sizing package that typically contains the SCA γ -aminopropyl trimethoxysilane as the active compound is applied on glass fibers to promote adhesion between the glass fiber and epoxy matrix. The extent to which the amino group of the SCA reacts with the epoxy matrix is known to be influenced by the tendency of the amino group to bend inward and interact with the glass surface.³ Furthermore, the coupling agent backbone is short, and the deposited layer is porous, as found through the research of Ishida and Koenig.⁴ Therefore, penetration of epoxy resin to the glass surface is likely. Hence, adhesion at the fiber-matrix interphase region may have contributions from chemical bonding, mechanical interlocking, and physicochemical interactions. Isolating the individual contributions to the overall adhesion in this region is a subject that has not been well addressed.

In recent years, molecular systems that form ultrathin films have found usefulness in investigating interfaces. Self-assembled monolayers (SAMs) offer one of the highest quality routes for the preparation of a chemically and structurally well-defined organic surface.^{5–8} The deposition of a long-chain trichlorosilane layer followed by *in situ* modification of the layer should provide a methodology for investigating the

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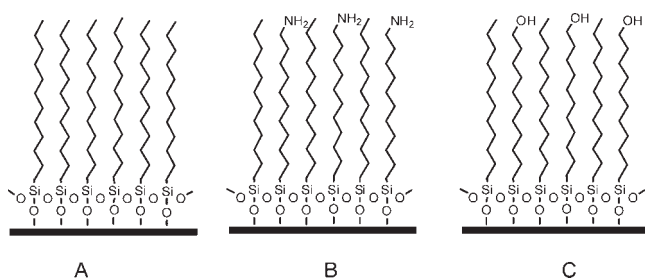


Figure 1 Schematic representation of SAMs. (A) pure methyl terminated SAMs; (B) mixed amino-terminated and methyl terminated SAMs; (C) mixed hydroxyl-terminated and methyl terminated SAMs.

embedded glass fiber/polymer interphase.⁷ Using this approach, we can investigate the impact of chemical bonding on interfacial adhesion in a more controlled and fundamental manner. In this work, undecyl trichlorosilane, amino-terminated SAMs, and hydroxyl-terminated SAMs were used (see Fig. 1). By employing the single-fiber fragmentation test (SFFT), both the fiber strength and the adhesion strength in the embedded interphase can be measured.^{9–11}

EXPERIMENTAL¹

Materials

Pure and mixed SAMs of methyl-terminated, amino-terminated, and hydroxyl-terminated undecyl silane were prepared on glass and silicon surfaces. For preparing methyl-terminated SAMs on glass surfaces, undecyl trichlorosilane (UTCS) was used as received without further purification. Amino-terminated SAMs were prepared by depositing the commercially available bromoundecyl trichlorosilane (BUTCS) onto the appropriate substrate followed by *in situ* modification. Hydroxyl-terminated SAMs were prepared by synthesizing 10-undecenyl trichlorosilane, a vinyl trichlorosilane (VTCS). The Cave and Kinloch¹² procedure was used to synthesize 10-undecenyl trichlorosilane. This procedure subjects 10-undecenol to bromination followed by reaction with a Grignard reagent and addition of SiCl_4 . The VTCS was then deposited onto the substrate followed by *in situ* modification. Details of the SCA deposition process and *in situ* modifications will be described later.

10-Undecenyltrichlorosilane

We report infrared (IR) and nuclear magnetic resonance (NMR) data of the final compound: ¹H-NMR

¹Certain commercial instruments and supplies are identified in this article to adequately describe the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that instruments and supplies are best available for this purpose.

(CDCl_3) 1.14–1.54 (m, 16 H), 1.84 (m, 2 H), 5.80–5.92 (m, 1 H); IR (2929, 2855, 1641, 1465, 1437, 993, 909, 721) cm^{-1} ; ¹³C-NMR (CDCl_3) δ (139.0, 114.0, 33.9, 31.9, 29.5, 29.4, 29.2, 29.1, 29.0, 24.5, 22.4). The reported NMR and Fourier transformed infrared (FTIR) data were in agreement with published results.^{12,13} NMR and FTIR characterizations were also performed on the intermediate compounds.¹⁴

Preparation of substrates for silane deposition

A 30-cm long tow was cut from a spool of E-glass fibers (from Owens-Corning) previously shown to be free of processing aids by X-ray photoelectron spectroscopy (XPS).² The tow was washed with spectrophotometric grade acetone, vacuum dried at 110°C for 2 h, and cooled prior to use. To model the behavior of the coupling agent film on the E-glass fiber, SCA was also sorbed on glass plates or silicon wafers. The procedures adopted for cleaning the glass plates (Fisher Scientific, Pittsburgh, PA, premium cover glass) and silicon wafer (Wacker-Siltronic, Corp., San Jose, CA) were similar to that used for glass fibers.

Adsorption of pure and mixed silanes onto substrate

For adsorption of pure and mixed BUTCS, the silane solution of BUTCS and UTCS, (the amount-of-substance fraction is 0.30 in hexadecane) was prepared and mixed in a vial to the desired ratio. The acetone-cleaned substrate was immediately immersed in the silane solution. The vial along with the substrate was then placed in an oven, and heated to 40–50°C for 4–6 h. Subsequently, the coated substrate was withdrawn from the solution and carefully handled by rinsing with methylene chloride (CH_2Cl_2). The substrate was further rinsed with acetone. Similarly, for adsorption of pure and mixed vinylundecyl trichlorosilane (VUTCS), the silane solution of VUTCS and UTCS was prepared and mixed in the desired ratio, and the glass substrate was immersed in the solution.

In situ conversion of pure and mixed bromo-terminated silane to amine terminated silane

The procedure of Heise et al.¹⁵ was adopted, for *in situ* modification of pure and mixed bromo-terminated SAMs to pure and mixed amine-terminated SAMs. Pure and mixed bromo-terminated SAMs were placed in a saturated solution of sodium azide (NaN_3) in dry dimethylformamide (1.5 g in 100 mL). The solution (together with the undissolved NaN_3) was stirred at room temperature. After 24 h, the SAMs coated glass substrate was rinsed with distilled

²Based on report provided by Evans East and contracted by NIST.

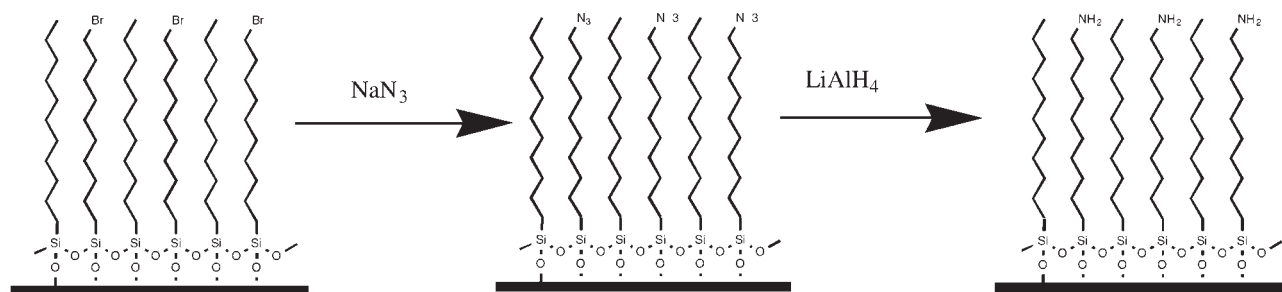


Figure 2 Schematic representation of the *in situ* modification of the mixed (methyl terminated and bromo terminated) SAMs.

water several times. Figure 2 shows the schematic representation of *in situ* modification of mixed methyl terminated and bromo terminated SAMs.

In situ reduction of pure and mixed azide-terminated SAMs to pure and mixed amine-terminated SAMs was performed by placing the substrate in lithium aluminum hydride solution (0.2 mol/L in tetrahydrofuran (THF)) for 24 h, followed by soaking in THF for an additional 24 h. The modified glass fiber was then placed in a mass fraction of 5% hydrochloric acid solution for 5 h to achieve complete hydrolysis of the aluminum complex. The modified glass fiber was rinsed with distilled water several times, then with acetone, and placed in triethylamine for 24 h to convert the $-\text{NH}_3^+$ into $-\text{NH}_2$ groups. The final step involved air-drying for 1 h.

***In situ* conversion of vinylic group to hydroxyl terminal group**

The procedure of Heise et al.¹⁵ was adopted, for *in situ* modification of pure and mixed vinyl-terminated SAMs to pure and mixed hydroxyl-terminated SAMs (refer to Fig. 3). The terminal vinyl group has the advantage that it can be easily converted into the hydroxyl functional group. The pure and mixed VTCS pretreated glass fiber was dipped for 2 min in a 1 mol/L solution of diborane tetrahydrofuran (Aldrich, St. Louis, MO) and stored under dry argon at room temperature. The substrate was dipped for 2 min in a mass fraction of 30% hydrogen peroxide solution in 0.1 mol/L NaOH and rinsed with distilled water several times and dried using hot air.

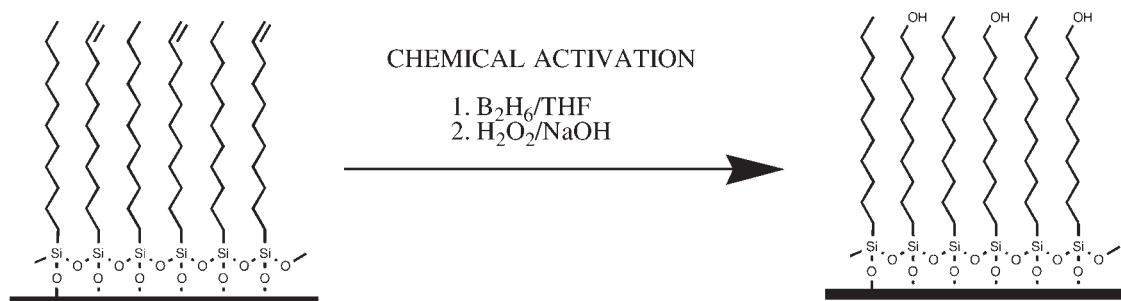


Figure 3 Schematic representation of the *in situ* modification of the mixed (methyl terminated and vinyl terminated).

Contact angle measurements

To determine the polarity of a pure or mixed SAM layer deposited on a glass substrate, water contact angle measurements were performed on flat glass plates and glass fibers using a dynamic contact angle analyzer (CAHN DCA 322, Gaithersburg, MD). The platform was raised at a speed of 80.0 $\mu\text{m/s}$. Four runs were performed for each specimen and the standard uncertainty in each measurement was approximately $\pm 2.0^\circ$.

X-ray photoelectron spectroscopy

The SAM layer deposited on a silicon wafer was characterized on a VSW 5000 XPS spectrometer (Gaithersburg, MD). The spectra were obtained using Al K α radiation with an energy of 1638.4 eV, at a pressure between 10^{-6} and 10^{-7} Pa, with an experimental resolution of 0.5 eV and an electron take-off angle of 70° .

Ellipsometry measurements

All measurements were performed on Discrete Polarization Modulation Automatic Ellipsometer (INOMTECH, Hartford, CT) equipped with a He-Ne laser (632.8 nm) operated at an incident angle of 70° . The thickness was calculated with a two layer step profile model by assuming the refractive indices for the coupling agent films adsorbed on the silicon wafer to be 1.42. This is based on reported refractive index values of 1.42–1.44 for straight-chain hydrocarbons.^{16,17} To obtain the coupling agent layer thickness, the oxide

layer thickness of silicon wafer was subtracted from the total thickness of the oxide layer on silicon wafer plus coupling agent layer. Five different spots on each film were recorded.

Preparation of SFFT specimens

The molds for preparing SFFT specimens were made with silicone rubber (RTV-664, General Electric, Fairfield, CT) following the procedure described by Drzal and Herrera-Franco.¹¹ All molds were post cured at 150°C and rinsed with acetone prior to use. Single filaments of the E-glass fiber modified with the SAM layer were carefully separated from the 30-cm tow. The individual fibers were aligned in the mold cavity via the sprue slots in the center of each cavity. The fibers were temporarily fixed in place by pressing them onto double-stick tape. Small strips of double-stick tape were placed over each fiber end to hold them in place until each fiber was permanently mounted with 5 min epoxy.

The SFFT specimens were prepared with a diglycidyl ether of bisphenol-A (DGEBA) epoxy, Epon 828 (Shell, Calgary, Alberta, Canada), cured using *meta*-phenylenediamine (*m*-PDA) (Fluka Chemical, Pittsburgh, PA). One hundred grams of DGEBA and 14.5 g of *m*-PDA were weighed out in separate beakers. To lower the viscosity of the resin and melt the *m*-PDA crystals, the beakers were placed in separate vacuum ovens set at 75°C. After the *m*-PDA crystals were completely melted, the silicone molds containing the fibers were placed into another vacuum oven that was preheated to 75°C. The silicone molds were heated at this temperature under a pressure of -20 kPa for 20 min. This last procedure 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 ~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, and a cure cycle of 2 h at 75°C followed by 2 h at 125°C was used.

Testing of SFFT specimens

The single-fiber fragmentation test (SFFT) is an indirect micromechanics method used to calculate the degree of adhesion between a rigid fiber coated with silane agent in a more ductile polymeric matrix (typically three to five times the fiber failure strain). 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 the least critical flaw. A saturation limit is eventually attained, when additional strain does not cause further failure of the fiber. The resulting distribution of fiber fragment lengths represents the raw data from the SFFT. The details of the testing procedure, and the standard error in the testing method can be found elsewhere.^{9,17} All specimens in this research were tested with a 10-min delay between strain increments.

RESULTS AND DISCUSSION

Surface characterization studies

Figure 4 shows the water contact angle as a percentage of silane coupling agent composition (the percentage is based on the mixing ratio of the methylated and bromine-terminated silylating agents in solution). For a glass fiber treated with a mass fraction of 100% undecyl SAMs, the water contact angle was ($110^\circ \pm 2^\circ$). Unless otherwise specified, the \pm refers to the standard uncertainty based on one standard deviation. The water contact angle for a mass fraction of 100% bromo-terminated undecyl SAMs on glass fiber is $95^\circ \pm 2^\circ$ and $68^\circ \pm 2^\circ$ for the bromo-terminated undecyl SAMs *in situ* modified to amine-terminated undecyl SAMs. The contact angle values for the mixed system are in good agreement with the literature values reported for similar mixed system.¹⁵ As expected, the conversion of bromo-terminated silanized surface to amine-terminated silanized surface led to an increase in hydrophilic character. However, based on water contact angle measurements, it was difficult to estimate the extent of conversion of bromo functionality to amine functionality. As the percent of bromo functionality in the mixed SAM layer increases, we expect, after conversion, a higher density of amine groups to be present on the SAM layer. This is because a greater number of bromo groups will be available for *in situ* modification to amine functionality. Further studies are needed to quantify the extent of the conversion of bromo functionality to amino functionality. However, these results indicate that amination of bromo-terminated SAM surface increases the polarity of the surface, thereby suggesting the participation of a bromo functional group in the conversion to an amino functional group.

The vinyl group to hydroxyl group conversion in mixed vinyl SAMs on glass fibers also resulted in a decrease in advancing water contact angle from 110° to 60° (Fig. 5). The measured contact angle values for mixed SAMs are in general agreement with the literature values for similar systems on glass plate.¹²

Table I presents the pure and mixed methyl- and amine-terminated C11 SAM coupling agent thickness

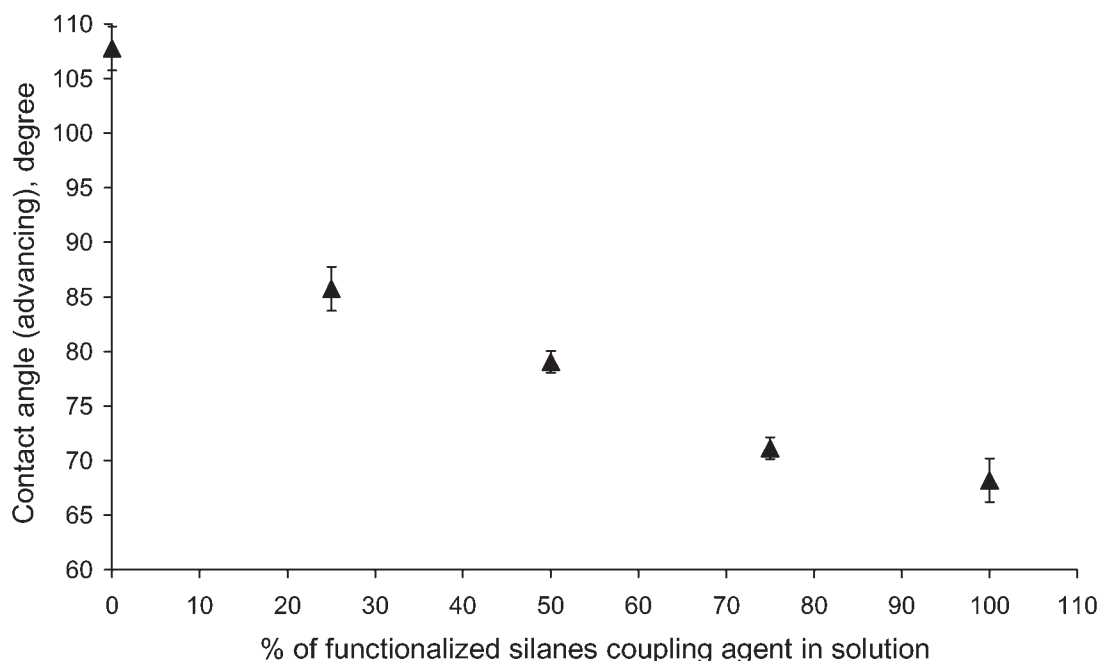


Figure 4 The advancing contact angle (water) on long-chain silane as the percentage of functionalizable terminal groups. The percentage is based on the mixing ratio of the silylating agents in solution during the preparation (for example, 0% on the abscissa represents the mixture of 0% mass fraction of bonding *in situ* modified BUTCS and 100% mass fraction of non-bonding UTCS). (Error bar represents one standard deviation from the mean and is an estimate of the standard uncertainty.)

data on silicon wafers, as determined by ellipsometry. The results indicate that the average thickness of the SAM layer was 24.5 ± 2.0 Å on silicon wafer. These thickness measurements are in excellent agreement with similar estimated value of C18 long-chain

SAMs on silicon substrate made by Heise et al.¹⁵ These researchers^{15,16} based their estimates on the following assumptions: (1) the alkyl chain is fully extended; (2) the projection of the carbon-carbon bond length of the *trans*-extended chain onto the sur-

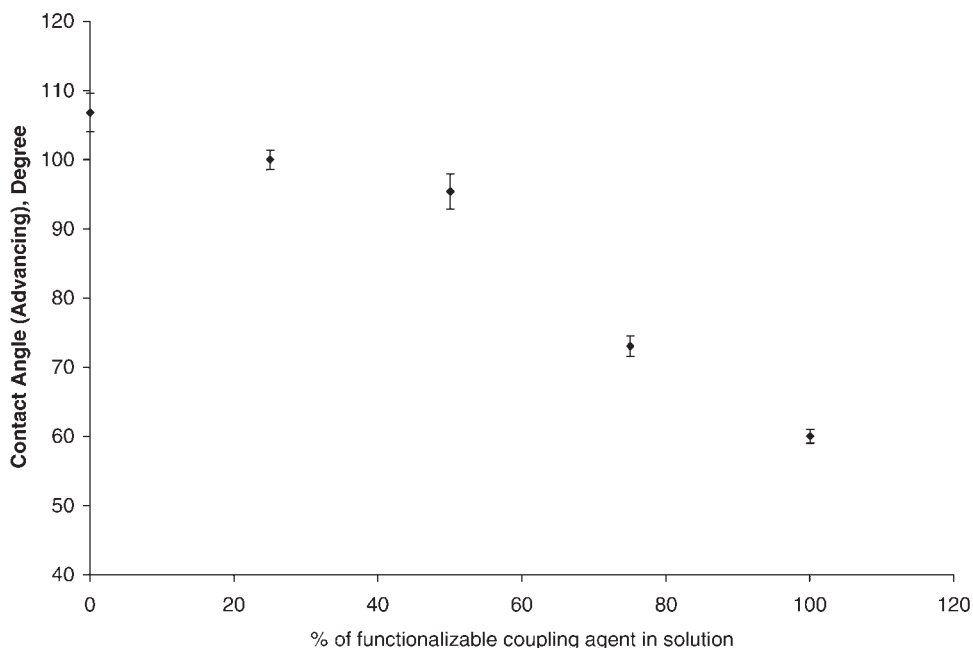


Figure 5 The advancing contact angle (water) on long-chain silane as the percentage of functionalizable terminal groups. The percentage is based on the mixing ratio of the silylating agents in solution during the preparation (for example, 0% on the abscissa represents the mixture of 0% mass fraction of bonding *in situ* modified VUTCS and 100% mass fraction of non-bonding UTCS). (Error bar represents one standard deviation from the mean and is an estimate of the standard uncertainty.)

TABLE I
Thickness of Coupling Agent Film on Silicon Wafers
as Measured by Ellipsometry

Coupling agent concentration in 0.3% (v/v) solution	Thickness of coupling agent layer (deposited/in situ modified) on silicon wafers (Å)
UTCS (100%)	22.8 ± 2.0
BUTCS/UTCS (25%:75%)	25.5 ± 1.8
BUTCS/UTCS (50%:50%)	25.5 ± 1.6
BUTCS/UTCS (75%:25%)	24.5 ± 2.8
BUTCS (100%)	24.3 ± 0.5
UTCS (100%)	20.9 ± 0.2
VUTCS/UTCS (25%:75%)	20.0 ± 0.4
VUTCS/UTCS (50%:50%)	22.2 ± 0.1
VUTCS/UTCS (75%:25%)	22.7 ± 0.1
VUTCS (100%)	21.9 ± 0.1

BUTCS, bromoundecyl trichlorosilane; VUTCS, vinylundecyl trichlorosilane; UTCS, undecyl trichlorosilane.

face normal (z axis) is 1.26 Å, with distances being derived from standard bond lengths; (3) the C—Si and Si—O bond lengths are 1.52 and 1.33 Å, respectively; and (4) an additional 1.92 Å is included for the terminal methyl group. The contribution of the methyl group is the total of the covalent radii of carbon (0.77 Å), hydrogen (0.37 Å), and the van der Waals radius of hydrogen (1.2 Å) and projecting this sum onto the normal axis. Table I summarizes the thickness data of pure and mixed vinyl- and methyl-terminated UTCS coupling agent deposited on silicon wafer. The ellipsometric results again indicate that there is approximately monolayer coverage of coupling agent 21 ± 2 Å on the silicon wafer for both pure and mixed solution.

XPS measurements were performed qualitatively to study the *in situ* conversion of the bromo-terminated undecyl SAMs to amine-terminated undecyl SAMs. Figure 6(a) shows a broad Br (3 d) peak at 75 eV before *in situ* modification and Figure 6(b) shows the appearance of strong N (1 s) peak at 400 eV after *in situ* modi-

fication. The absence of strong N (1 s) peak before *in situ* modification and the lack of broad Br (3 d) peak after *in situ* modification was also noticed.¹⁴ The disappearance of Br (3 d) and appearance of N (1 s) peaks in XPS spectra support our earlier finding that the bromoundecyl silane has indeed been *in situ* modified to amine-terminated undecyl silane.

To determine if the vinyl groups were transformed to hydroxyl groups, we used XPS in conjunction with a chemical derivatization technique. Derivatization of terminal hydroxyl group was achieved by immersing *in situ* modified vinyl-terminated (hydroxyl converted) SAMs in butyl isocyanate at room temperature for 20 min.¹² Figures 7(a,b) show XPS spectra before and after derivatization of the *in situ* modified vinyl-terminated SAM layer. We observed the origin of N (1 s) peak at 400 eV after reacting with isocyanate, indicating that the terminal hydroxyl groups had indeed reacted with butyl isocyanate.

Single fiber fragmentation tests data analysis

Figure 8, compares the number of fiber breaks versus the solution composition of coupling agent deposited on glass fiber and *in situ* modified. The number of fiber breaks is directly proportional to the adhesion at the fiber-matrix interface.^{9,10} Hence, an increase in the number of breaks in the test specimen reflects an increase in the adhesion at the fiber-matrix interface.⁹ Adhesion at the fiber-matrix interface is based on contributions from covalent bonding, mechanical interlocking, and physicochemical interaction. Because of the nonbonding (only van der Waals forces) nature of undecyl SAMs, we expect the fiber-matrix adhesion to have contribution from mechanical interlocking and/or physicochemical interaction and no contribution from covalent bonding.¹⁸ SFFT for the mass fraction of 100% UTCS-coated glass fiber epoxy composite yielded the average number of breaks to be 6 ± 2 . We

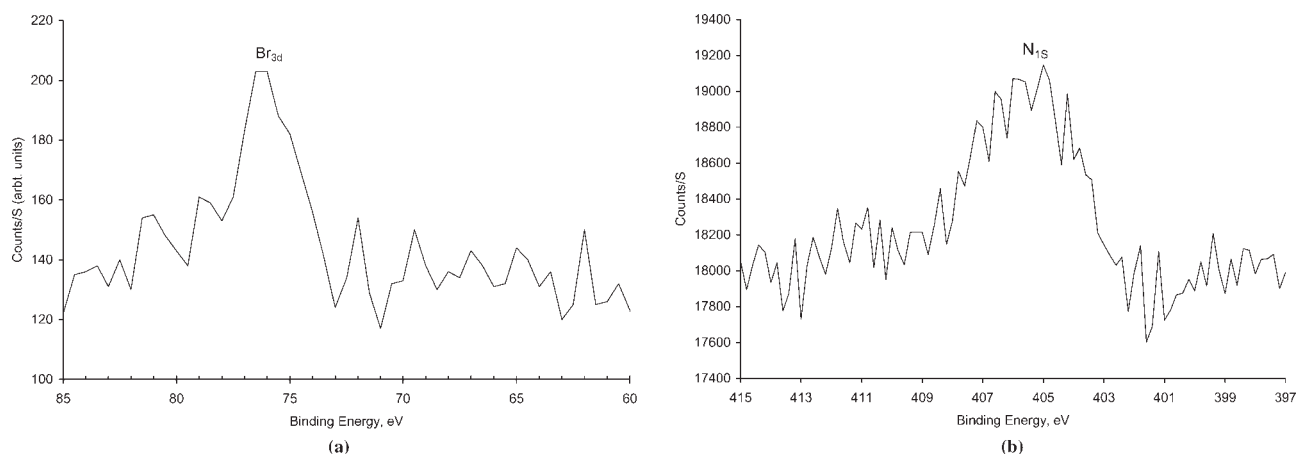


Figure 6 Expanded XPS spectra of 100% bromo-terminated UTCS film on silicon wafer (a) before and (b) after *in situ* modification.

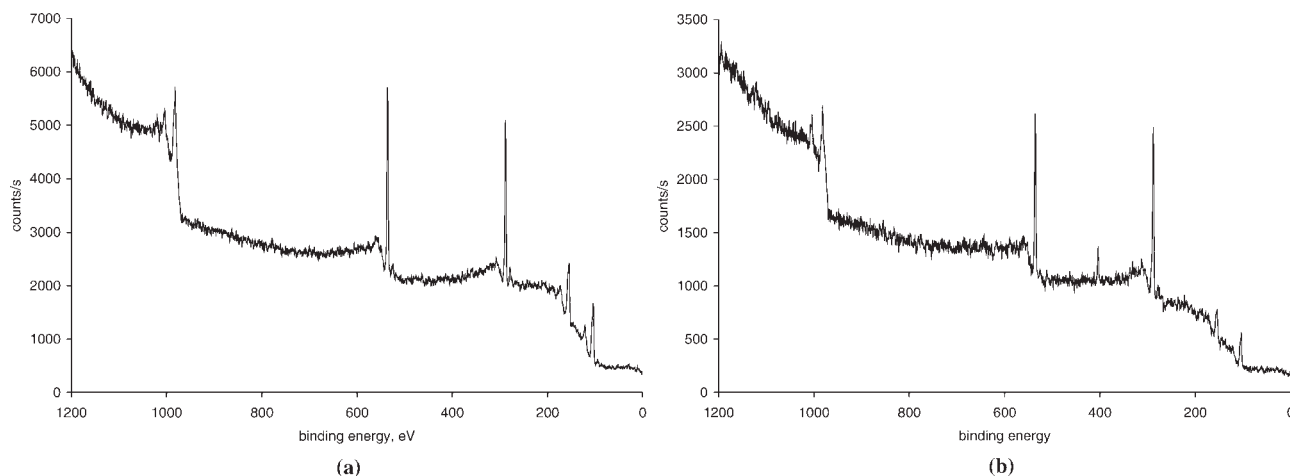


Figure 7 XPS spectra of 100% VUTCS film on silicon wafer (a) before and (b) after derivatization.

interpret the low number of fiber breaks in the UTCS long chain SAM-coated E-glass fiber to the virtual elimination/minimal presence of mechanical interlocking as a mechanism for adhesion in SAMs specimen, because of monolayer coverage on the smooth glass surface and the long back bone of the SAM layer that hinders the epoxy resin from reaching the bare glass fiber. Since mechanical interlocking is virtually nonexistent for long chain nonbonding SCAs deposited by the SAM technique, the impact of purely covalent bonding on overall adhesion can be investigated by considering pure and mixed long-chain amine-terminated undecyl SAMs. By depositing brominated long-chain trichlorosilane on glass fibers that are subsequently modified to amine functionality, Heise et al.¹⁵ have shown that the NH_2 functional group is oriented away from the fiber surface. Therefore, all the amine groups in amine-terminated undecyl SAMs are expected to be available for reaction with the epoxy matrix.

Since the amine functional groups are derived *in situ*, our comparisons are based on the assumption that the concentration of amine functional groups is proportional to the bromine functional groups deposited from the solution. Figure 8 shows the result for number of fiber breaks as a function of mass fraction of the percent of functionalized coupling agent in the solution. The magnitude of fiber breaks increases initially and reaches 85% of the saturation value at a mass fraction of 25% functionalizable coupling agent composition in solution and marginally increases with any further increase in functional coupling agent component in the SAM layer.

A plausible explanation for saturation at a mass 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 DGEBA molecule. Therefore,

only a fraction of the groups registered on the fiber may be participating in the epoxy/amine reaction. In other words, the amount of adhesion between glass fiber and epoxy is dependent on the composition of bonding/nonbonding coupling agent mixture, the packing/registering of coupling agent molecules, and the structure of the reacting matrix. Further studies need to be conducted with epoxy of different chemical structure to support the explanation.

To study the effect of the type of functional group on the overall adhesion, VUTCS (bonding silane coupling agent) and UTCS (nonbonding silane coupling agent) were deposited on glass fibers. The pure and mixed vinyl-terminated SAM layers were *in situ*

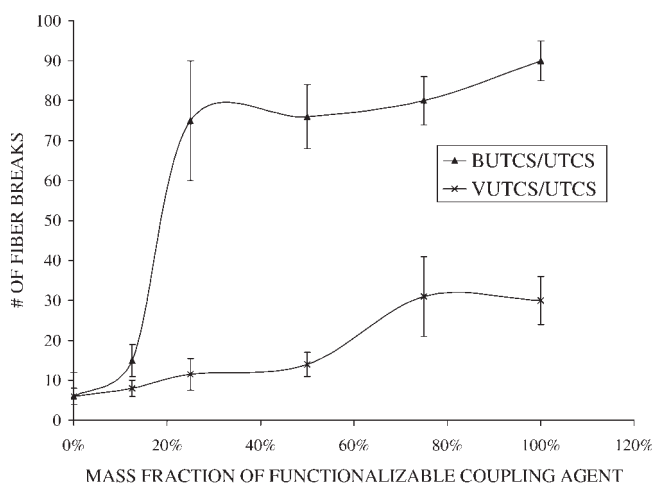


Figure 8 Average number of fiber breaks for E-glass fiber deposited with long-chain coupling agents as the percentage of functionalizable terminal groups. The percentage is based on the mixing ratio of the silylating agents in solution during the deposition process (for example, 0% on the abscissa represents the mixture of 0% mass fraction of bonding *in situ* modified BUTCS or VUTCS and 100% mass fraction of nonbonding UTCS). (Error bar represents one standard deviation from the mean.)

modified to pure and mixed hydroxyl-terminated SAM layers by reacting with diborane/H₂O₂ mixture. It is expected that the hydroxyl groups on the SAM layer can hydrogen bond to the hydroxyl group in the cured epoxy resin matrix. Figure 8 shows a steady increase in adhesion at the fiber-matrix interface, as the mass fraction of functionalizable coupling agent in solution is increased until reaching a plateau at higher concentration of functionalizable coupling agent in solution. The difference in the number of fiber breaks (a measure of adhesion) between the *in situ* modified pure and mixed bromo-terminated SAM layer and *in situ* modified pure and mixed vinyl-terminated SAM layer on glass fiber is due to the type of chemical bonds formed by the SAM layer with epoxy resin. In the case of amine-terminated SAM interface, covalent bonding of amine with epoxy resin can result in strong adhesion, whereas in the case of hydroxyl-terminated SAM interface, it is speculated that hydrogen bonding of the hydroxyl group with the cured epoxy resin forms a weaker bond. However, this observation is based on the assumption that the extent of *in situ* modification of bromo-terminated SAMs to amine-terminated SAMs and vinyl-terminated SAM to hydroxyl-terminated SAMs on E-glass fibers are very similar in their individual reaction medium.

CONCLUSIONS

1. A solvent-based method was used to deposit trichlorosilane on E-glass fiber surfaces followed by *in situ* modification of the deposited layer to prepare pure and mixed amine and pure and mixed hydroxyl functionalized undecyl SAM. The SAM layer was characterized by ellipsometric, XPS, and contact angle measurement techniques. Using silicon wafer as a suitable substitute for glass fibers, it was established that the glass surface has monolayer coverage of long-chain trichlorosilane. XPS spectra showed a decrease in the broad peak of bromo functionality and an increase in the intensity of N functionality upon *in situ* modification of bromo-terminated undecyl SAMs to amine-terminated undecyl SAMs. Simi-

larly, XPS data in conjunction with chemical derivatization established the presence of terminal hydroxyl groups in the SAM layer.

2. The SAM's data indicate that ~85% of fiber breaks obtained for epoxy composite occurs at a mass fraction of ~25% of the glass surface covered with amine functional groups.
3. Hydroxyl-terminated SAM layer was useful in probing the strength of hydroxyl-hydroxyl bonding at the fiber matrix interphase. The number of fiber breaks for hydroxyl-terminated SAM system was found to be much lower than the number of fiber breaks for amine-terminated SAM system.

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