HIGH THROUGHPUT CARBON FIBER SURFACE MODIFICATION

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ABSTRACT

Typical commercial surface treatments for continuous carbon fibers are often unavailable for short fibers. As such, there is little variety of chopped fiber surfaces leading to non-ideal coating solutions which result in poor interfacial compatibility between fibers and matrix. In this work we develop a method of applying a highly effective coating using a high throughput technique for chopped carbon fibers. We show the ability to tune both the coating thickness and chemical functionality using processing parameters. The coatings are evaluated using EDS and X-ray photoelectron spectroscopy (XPS) for uniformity and composition. Using this technique, thermoplastic composites are highlighted showing an increase in interfacial shear strength (IFSS) of 25 MPa. This process shows promise for increasing the throughput of surface treatment of chopped fiber on the industrial scale. With this technique, we hope to increase the overall performance of commercial, discontinuous composites as well as expand the possibilities of carbon fiber technologies.

1. INTRODUCTION

Short (chopped) carbon fibers are a versatile filler used for a variety of high performance polymer composites [1][2]. Utilizing short carbon fibers is beneficial for manufacturing composites of complex geometries using both thermoplastic and thermosetting resins. The success of short carbon fiber composites relies heavily on the interface between fiber and resin. Poor adhesion between resin and carbon leads to poor interfacial shear strength and a loss in translation of properties. While many simple continuous methods for treating carbon fiber tows and fabrics exist in industry, these methods do not apply to short fibers. In this paper we propose a simple method to treat short carbon fibers that allows for tunable surface chemistry.

Many approaches have been used to modify the chemical and physical structure of the carbon fiber surface. These studies have shown that a balance between surface morphology and surface chemistry is required to achieve superior performance [3]. A very common method for chemically modifying surfaces is to apply functional organosilane (shortened here to silane)

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molecules. These molecules typically consist of a central silicon atom bonded to three identical short functional groups by ether linkages (R_1) and a single longer organic functional group (R). These molecules are preferred because of their ease of attachment to solid, inorganic substrates and the wide variety of chemical functionalities commercially available. Silane molecules attach to the inorganic substrates in a variety of complex orientations. Figure 1 illustrates a few of the most typical theoretical orientations of silane molecules at the solid surface. Here R represents the functional moiety and R_1 represents either the native short functional groups or some derivative of that group. Note that silanes often undergo hydrolysis at the ether linkage creating an O^- functional group, however other mechanisms are possible and therefore the chemical interactions depicted vary. Furthermore, the reaction path of silane depends heavily on the chemical composition of the substrate surface.

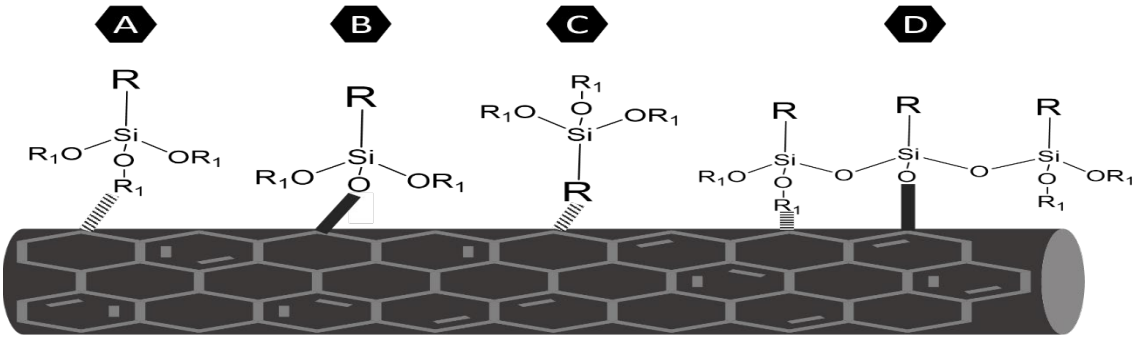


Figure 1. Illustration of typical species of silane on the surface of carbon.

Scenario A and C in Figure 1 depict a physical bond, e.g. a hydrogen bond, between the R1 and R group of the silane and a functional group on the carbon surface, respectively. These interactions are weak and reversible. Scenario B shows the classical covalent bond between the silane and a reactive species on the carbon surface. This is known to occur between hydroxyl surface moieties on the fiber surface and the O^- of the hydrolyzed silane through chemical reaction [4]. For some chemistries, this reaction may be possible between the surface and the R group, however not generally. The last scenario D shows the crosslinked silane, i.e. some number of silanes have been attached to the surface via one of the previous mechanisms. Surrounding silanes react via condensation of two of the short moieties creating a continuous network of silane molecules on the surface. All of these reactions occur at various conditions. The ideal case for most applications is a monolayer of silane.

Typical application of silanes to inorganic surfaces is done using solution based formulations, wherein a good solvent is pH adjusted to catalyze hydrolysis of the silane. The substrate is immersed and removed such that a thin layer of bound silane layer is achieved. This method has been used for most applications with many modifications. For short carbon fibers, these methods have been applied directly [5][6], however controlling the silane layer is difficult and techniques are often chemistry specific. Vapor phase silanization has been previously developed where silane solutions are evaporated to form silane layers on the substrate surface giving rise to controllable monolayers of silanes [7].

In this work we introduce a vapor phase silanization technique wherein a highly tunable functional surface is achieved on short carbon fibers. To demonstrate this technique we use an example silane which we deposit on the surface of a model carbon fiber. We use spectroscopy to confirm the silane layer and show a favorable increase in the surface properties. With this method we show that highly tailored carbon fiber surfaces are achievable by high throughput processing, leading to superior composite materials and expanding the possibilities for utilizing carbon fibers in a variety of chemical processes.

2. NOVEL PROCESSING TECHNIQUE

In this technique, outlined in Figure 2, short fibers are suspended over pure liquid silane and enclosed in a sealed vessel. Vacuum is applied to the chamber until an equilibrium pressure is achieved. During the pump down, silane evaporates. In the vapor phase, silane has two options: to interact with functional groups on the fiber surface or coalesce onto the surface as very fine droplets. The chamber remains under vacuum for a given period of time until it is opened to the atmosphere.

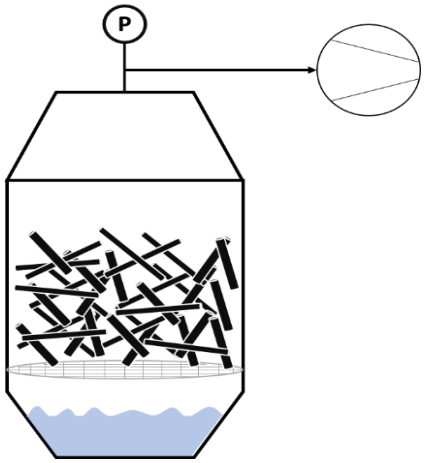


Figure 2. Schematic of the vapor phase deposition process.

After vacuum processing, fibers are heated to promote surface reactions and to crosslink the silane molecules. This accomplishes two things: it builds the average number of silane molecules attached to a single surface site and solidifies unreacted silane droplets, forming an adherent layer on the surface. The resulting carbon surface contains both chemically linked and adsorbed silane molecules in both crosslinked layers and as single molecules. This method expands upon previous methods with several advantages: (i) only a dilute amount of silane is available for surface reactions, (ii) the silane vapor readily fills all available space, (iii) does not require expensive solvents for deposition and rinsing, and (iv) silane deposition occurs via condensation regardless of covalent bonding to the surface.

2.1 Demonstration of application

To demonstrate the technique, we deposit triethoxysilyl propylsuccinic anhydride, AnhPES, (Gelest Inc.) onto the surface of petroleum pitch based carbon fiber. for 1 hr at pressures below

0.1 torr and crosslinked at 100 ℃ for at least 24 hr. The chemical structure of the silane is shown in Figure 3.

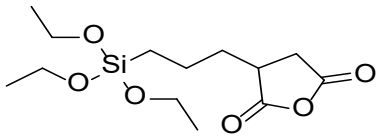


Figure 3. Chemical structure of AnhPES.

Prior to silanization, fiber surfaces were oxidized via ozone treatment. Further detail of this procedure is given in [8]. The oxidized surface was chosen to enhance the attachment of silane due to increased surface oxygen containing moieties. Both chopped and long tows of fibers were treated using identical methods to be used in different characterization techniques and to assess process variability.

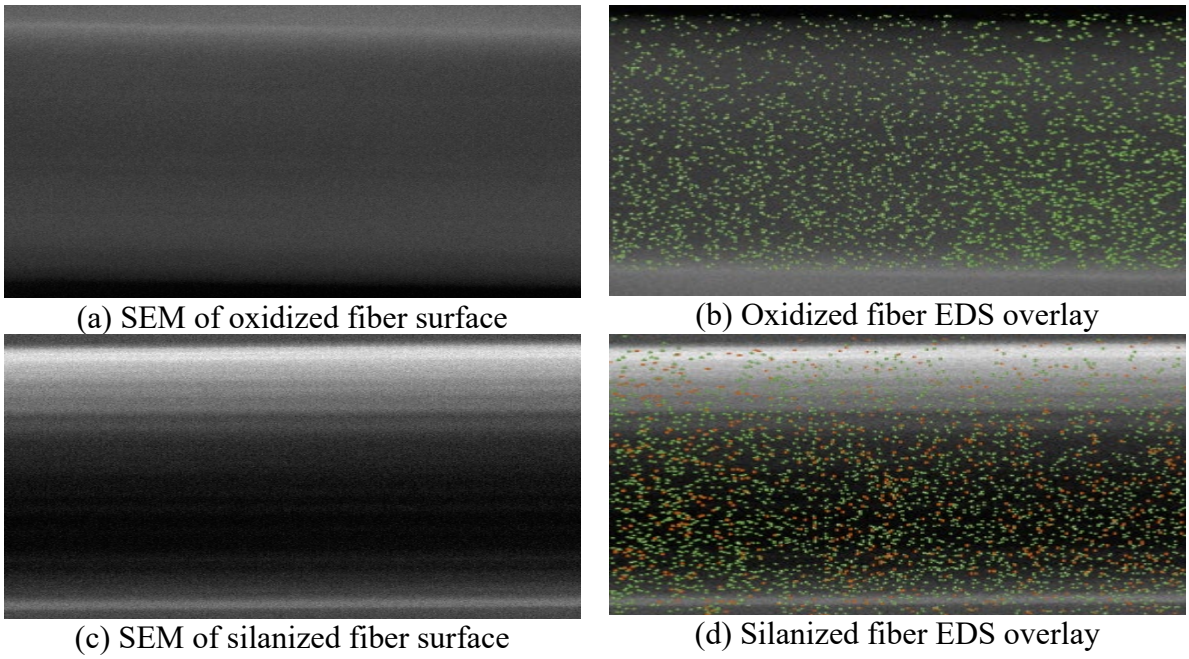
3. SURFACE ANALYSIS

The modified carbon fiber surface was analyzed using Energy Dispersive Spectroscopy (EDS) performed on a Zeiss scanning electron microscope (SEM). This technique gives a good measure of the presence and homogeneity of silane molecules on a single fiber surface. These maps are used to demonstrate uniformity of the silane deposition across the surface of a single fiber. More quantitative analysis on the bulk fibers is performed using a Phi Versaprobe X-ray photoelectron spectrometer (XPS).

Contact angle was measured using a Cahn Dynamic Contact Angle Analyzer (DCA-322). Single fibers were immersed at a speed of 20 μm into water up to 1 mm during which an average advancing angle is recorded. The fiber is withdrawn and an average receding contact angle recorded. Measurements were done on 5 individual fibers sampled from the same batch. The individual contact angles are averaged to determine characteristic dynamic contact angles. Interfacial shear strength (IFSS) was determined using single fiber fragmentation (SFF) testing. Fiber samples were produced using molten polyetherimide (PEI) and single long carbon fibers. These results were averaged over multiple fiber composites, with additional details given in [8].

4. RESULTS

After treatment, single chopped fibers were characterized using SEM/EDS. The SEM micrograph in Figure 4a shows an oxidized fiber surface. As shown by Figure 4c, the silanized fiber surface shows no observable physical change over the oxidized fiber. This confirms the thickness of the coating is minute, meaning there are no macroscale deposits and adhesion potential is optimal for composite manufacture. The element maps in Figure 4b show an even distribution of oxygen sites due to the oxidation treatment. After silane treatment, the fiber contains an even distribution of silicon atoms that correspond to only a fraction of the original oxygen atoms. Additional oxygen from the silane molecule is also present. These results from EDS should be interpreted to show a generally favorable uniformity, however no direct observation of the silane molecule can be made and quantitative measures are not made.



(a) SEM of oxidized fiber surface

(b) Oxidized fiber EDS overlay

(c) SEM of silanized fiber surface

(d) Silanized fiber EDS overlay

Figure 4. SEM micrograph and EDS element maps for fiber surface after before and after treatment with AnhPES. Green dots indicate elemental oxygen. Orange dots indicate elemental silicon. Note the fiber diameter is 5 μm.

Quantitative surface analysis was performed using X-ray photoelectron spectroscopy (XPS). Contrary to EDS, XPS probes only the first few nanometers of the sample surface. Additionally, the X-ray beam covers a spot size of diameter 200 μm, meaning the measurement averages over approximately 40 fibers. Figure 5 shows the XPS spectra measured for oxidized fibers and both long and short batches of AnhPES treated fibers. The oxidized fibers show only carbon and oxygen present on the surface. This is expected, as the oxidation increases the oxygen content of the neat carbon surface. The magnitude of the peak corresponding to O_{1s} is slightly increased for the silanized samples corresponding to the oxygen from the silane molecule. Note that this value is not predictable because it depends on the number of chemically bound silane molecules and crosslinked molecules which individually alter the number of oxygens present in the silane layer. Additionally, the inset shows clearly the existence of an Si_{2s} and Si_{2p} peak in only the silanized samples, confirming successful application to the fiber surfaces.

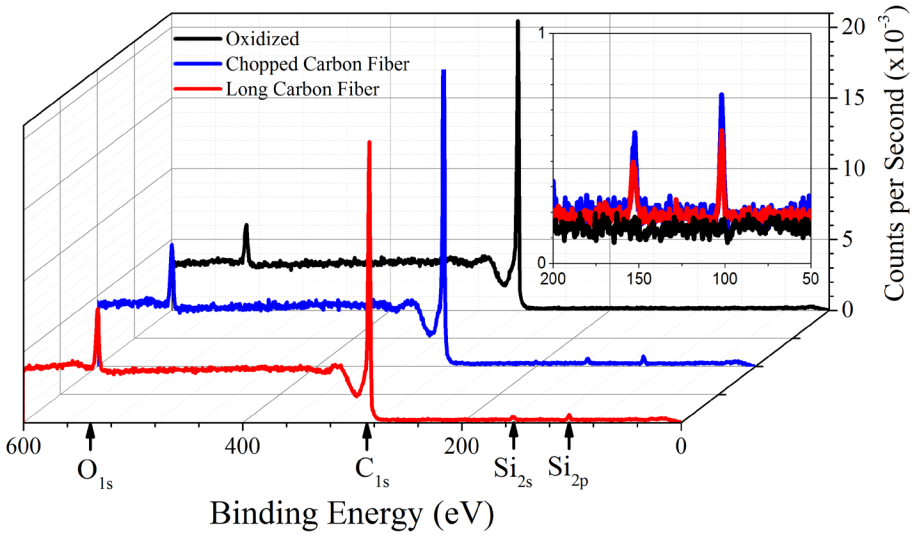


Figure 5. XPS spectra for oxidized and silanized carbon fibers. Inset shows peaks corresponding to surface Si. Note that only a select range of binding energies are shown.

The atomic concentrations measured via peak integrations using XPS spectra are summarized in Figure 6. This confirms the absence of Si in the oxidized samples, which is increased to just greater than 1 % for both silanized samples. The chopped fibers show a marked increase in the concentration of oxygen (>2 %) from oxidized to treated, corresponding to the oxygen of the silane molecule. Interestingly this increase is less pronounced for the continuous tow fibers. While the two batches have different starting oxygen (binding site) content, the same amount of silane is deposited (as determined by the silicon content). This suggests that either there is a fixed number of accessible sites (hydroxyls) on the fiber surface or that the process is limited by some other factor. More investigation would be needed to determine the cause of the discrepancy.

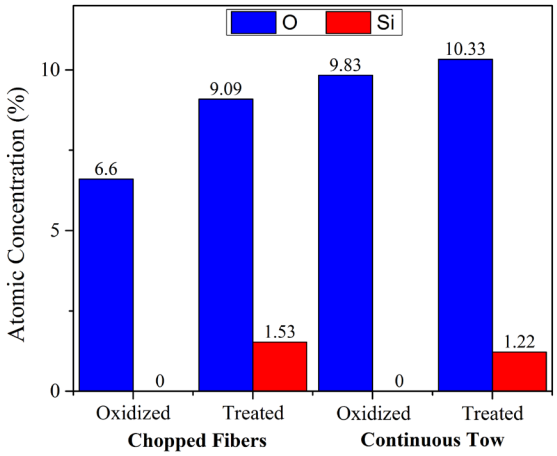


Figure 6. XPS atomic concentrations for O and Si on oxidized and treated (silanized) fibers.

After confirmation of the existence of silane molecules on the fiber surface, we next demonstrate the change in bulk fiber properties due to silanization. Contact angle is typically used as an indirect measure of surface chemistry. It is also a critical property in determining the resin compatibility of the fibers. Figure 7a shows the water dynamic contact angles for oxidized and AnhPES treated fibers. The oxidized fiber surface is moderately hydrophilic, due to the hydroxyl groups on the surface. The advancing and receding angles are separated by less than 0.5°. This suggests a highly heterogeneous surface with defects (functional groups in this case) of very small, uniform length scales. For the silanized fibers there is a slight increase in the advancing water contact angle. Additionally there is higher variability in the advancing contact angle. The receding contact angle for the silanized fiber is identical to the oxidized surface. These results suggest that the surface is heterogeneous. Overall the surface has become slightly more hydrophobic in the treated case due to the presence of silane. This is favorable for hydrophobic resins used in the ultimate composite.

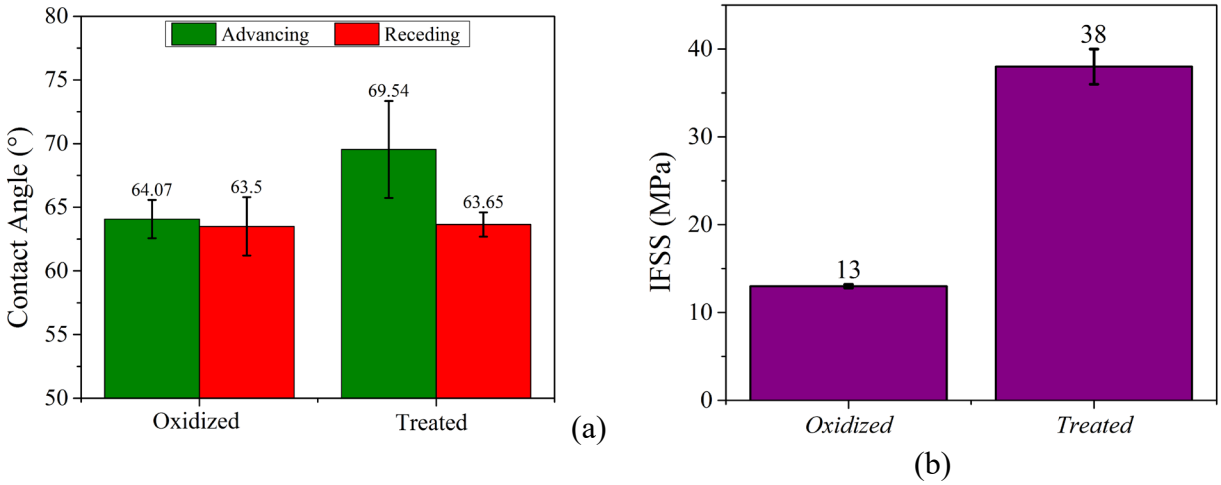


Figure 7. Comparison of (a) water contact angle and (b) IFSS for the oxidized versus the AnhPES treated fibers. Error bars in contact angle represent 95% confidence intervals on the mean. IFSS errors are reported as standard deviations.

To quantify the adhesion of the silanized fiber in the ultimate composite, interfacial shear strength (IFSS) is measured for the fibers embedded in a polyetherimide, thermoplastic resin. The resulting IFSS values for the oxidized and silanized fibers are shown in Figure 7b. As shown, the IFSS is consistently increased by 25 MPa after silanization over the neat oxidized fibers. This shows that adhesion between the matrix and the fiber surface is greatly increased by silanization and the ultimate composite strength is significantly improved. The increased adhesion is likely due to a combination of increased hydrophobicity of the surface, and chemical groups which are able to physically interact with the polymer matrix. Notice that IFSS variability is increased after silanization because of some heterogeneity of the fiber surfaces.

5. CONCLUSIONS

In this work we have introduced a novel technique for applying highly tailored functionality to the surface of chopped carbon fibers. Unlike conventional methods, this technique applies pure silane via vapor phase deposition. This minimizes the concentration of silane exposed to the surface leading to very fine layers of silane. Silane molecules are physically or chemically attached to the surface. After crosslinking, a higher amount of silane remains bound to the fiber surface.

Using a model case, we demonstrate the proposed technique using triethoxysilyl propylsuccinic anhydride deposited onto the surface of oxidized pitch based short carbon fiber. EDS and XPS results show randomly distributed silane molecules are deposited repeatably with a surface concentration of > 1 %. Overall water contact angle shows the silane increases the hydrophobicity of the fiber surface by heterogeneous surface features. The resulting silanized fibers show an increased interfacial shear strength of >25 MPa in thermoplastic polyimide.

Depending on the application, specific functional groups can be selected from known silane chemistries. Using this process, large quantities of short fibers are treated repeatably and uniformly with no use of solvent and very fast coating times.

6. ACKNOWLEDGEMENTS

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