ROLE OF FIBER ADHESION IN NATURAL FIBER COMPOSITE PROCESSING FOR AUTOMOTIVE APPLICATIONS [1]

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Abstract

The prediction and characterization of the adhesion between fiber, surface treatment, and polymer is critical to the success of large-scale natural fiber based composites into automotive semi-structural applications. The two primary limiting factors in natural fiber composites are in large part dominated by fiber moisture uptake due to fiber structure, and limits in high-temperature processing. In this study, we have developed several fiber surface modification techniques and analyzed the fiber-polymer adhesion to more clearly understand the critical parameters controlling moisture uptake, swelling, and structural degradation due to interface degradation. We will present preliminary surface modification findings on hemp fiber sources, and attempt to resolve the role that fiber interface adhesion characterization plays in understanding and predicting fiber performance within polymer matrices.

Background

Adhesion forces between two surfaces are comprised of both short and long-range forces. Short-range forces play a significant role at atomic or molecular distances (typically a few nm) and are defined by the electronic properties, as in the case of atoms or molecules, or the local chemical and geometrical properties, as in the case of macroscopic bodies in close proximity. Very important is the medium that separates particles (atoms, molecules, or small clusters) or macroscopic bodies; for example, the presence of moisture between a fiber and polymer can significantly impact interface adhesion. Short-range forces arise from either electromagnetic interaction potentials, dominating long-range forces at molecular distances, or can be of a mechanical origin, i.e., due to geometric or steric interaction. The overall sum of the contributing long and short range forces determines whether an interaction between two bodies is attractive or repulsive and thus determines the cohesion or adhesion between identical or different bodies.

A primary consideration in adhering cellulose-based fibers to a polymer is the moisture present in the fiber during reaction. It is costly to dry lignocellulosics to less than 1% moisture, but the -OH group in water is more reactive than the -OH group available in the lignocellulosic components, rendering hydrolysis to be faster than substitution. The most favorable condition for surface reaction is one that requires a trace of moisture and the rate of hydrolysis is relatively slow. Three factors determine the rate at which moisture is removed from lignocellulosic materials: temperature, relative humidity, and air velocity. The ability to control and minimize energy input during this process is one opportunity foreseen within processing cellulose materials, and the forest products industry in general. The ability to eliminate water absorption during service of cellulose-based composite components is paramount in industrial

applications. In sisal fiber/unsaturated-polyester composites, it is readily apparent that storing test samples in water (100% RH) and then drying samples will adversely affect mechanical properties [1]. High water absorption of the samples (10%) will result in a significant reduction in mechanical part properties (up to 50% in bending modulus).

The objective of this paper is to provide a template for fully characterizing the adhesion of natural fibers to polymer surfaces. The methodology contained herein is now being applied to hemp and kenaf fibers that have undergone a number of surface treatments, although preliminary results are not sufficiently supported to report in detail.

Interface Experimental Characterization Methods and Theory

Experimental characterization of the natural fiber interface for composite application requires several techniques to be deployed in order to develop an accurate "picture" of the fiber and polymer characteristics. Other research groups have evaluated many of these techniques and report their attributes in review papers [2, 3, 4]. In this section, we will briefly describe these techniques and the information gleaned from each.

Lignin Determination

As grown, the cellulose in natural fibers are coated with a complex connective tissue that includes lignin, pectin, hemi-cellulose, fats, waxes, proteins, ash, and minerals [4]. The non-cellulose content of fibers, which varies based on many factors including fiber type and growth conditions, can be broadly characterized as "extractives" and "lignin". Lignin content of fibers affects all of the relevant properties of the fibers such as moisture uptake and tensile strength. Lignin can be removed, leaving cellulose intact, through caustic treatment of fibers. The lignin content of samples may be determined using established methods such as TAPPI Test Method T222 om-88 (TAPPI 2004).

Determination of Reaction Sites

In its simplest form cellulose may be thought of as having three hydroxyl groups per monomer unit that may be available for coordination with water molecules in moisture uptake or for reaction with chemical groups to tailor its chemical properties. The actual structure of the natural fiber, with non-cellulose components and cellulose crystalline regions, is much more complicated than this simple picture. It would be beneficial to have an effective method for determining the density of reaction sites (moles of sites per gram fiber) available on a given fiber sample or for a particular fiber source. The number of carbonyl groups per mass of cellulosic material has been determined through the use of fluorescent labels combined with gel permeation chromatograpy (GPC). We are attempting to titrate the number of reactive groups in natural fiber samples by reacting with molecules to produce byproducts, the concentrations of which can be monitored using gas chromatography (GC).

Thermal Gravimetric Analysis (TGA) / Differential Scanning Calorimetry (DSC)

Thermal gravimetric analysis and differential scanning calorimetry are useful methods to determine the moisture content and thermal stability of virgin fibers, treated fibers, and fiber composites [5]. In addition to reducing the moisture uptake of fibers and improving fiber interface with the polymer matrix a primary goal of chemical surface modification of fibers is increase of fiber thermal degradation temperature. Higher temperature stability of fiber can be important for end use application, but is most relevant for the conditions at which polymeric composites are processed.

Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) images of the hemp/kenaf fibers show that they are composed of ~50-µm diameter strands. Close examination confirms the low inherent surface area of the as-grown fibers. Extensive SEM analysis of both treated and embedded composite fibers is important for an understanding of the morphological changes in the fiber brought about by surface treatment [6].

Fluorescence Constituent Mapping

Due to the difference in chemical structure between cellulose and the lignin, etc. present in natural fibers, mapping of the constituent distribution can be accomplished through preferential labeling with fluorescent markers and subsequent investigation in a fluorescent microscope [7]. Confocal Raman microscopy is another method that has similarly been used to visualize mesoscale fiber structure.

Dynamic Contact Angle

The wettability of modified fiber is important both for moisture uptake and for fiber/polymer matrix interaction. Determination of the advancing and receding contact angles of modified fiber surfaces gives direct and predictive information on the fiber wettability [8].

X-Ray Diffraction

The crystallinity of cellulose present in natural fibers has been seen to be affected by chemical treatment of the fiber, including caustic treatment used to remove lignin [5]. Cellulose crystallinity in the fiber is relevant for thermal stability and mechanical strength. Relative crystallinity before and after chemical treatment may be determined using X-ray diffraction.

Fourier Transform Infrared Analysis (FTIR)

Fourier transform infrared spectra of fibers, including the surface-sensitive attenuation total reflection (ATR) technique, before and after modification can be useful for qualitative detection of modifying agents with sufficiently unique vibration signatures [5].

Nuclear Magnetic Resonance (SS-NMR)

Solid-state NMR spectroscopy is useful for characterizing cellulose-based materials since detailed information can be obtained from solid samples. In general, solid state NMR involves proton-carbon cross polarization to enhance the ^{13}C signal, high power decoupling to eliminate dipolar line broadening due to protons and spinning of the sample about the angle of 54.74°, with respect to the static field to reduce the chemical shift anisotropy effects. Specific chemical species provide spectral region peaks and from this data chemical shift data allow quantitative and qualitative of the major components of wood, and associated modifications to the surface. ^{29}Si solid state NMR is also an important technique for characterization of silane coupling chemistry.

X-Ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (otherwise known as electron spectroscopy for chemical analysis (ESCA)) provides a quantitative understanding of both the quality of interfacial bonding and the performance of the bond during service. One is able to determine the presence of non-equivalent carbon (C1s), oxygen (O1s), fluorine (F1s), and silicon (Si2s, Si2p) atomic composition at the surface of modified and unmodified fibers. XPS provides the ability to study surface modification of cellulose fibers and the resulting chemical shifts and peak shapes that reflect molecular structure modification. Coupling agents, or surface monolayer uniformity or specific surface concentrations may be determined. For lignocellulosic materials, oxygen and carbon are the predominant species, as is evident from the absorptions of O1s and C1s peaks occurring at 531 eV and 280 eV, respectively. Other species, such as Ca, Si, etc., may be distinguished in small concentrations, with the advent of silane and isocyanate treated fibers resulting in shift peaks whereby quantitative concentrations may be distinguished.

Dynamic Contact Angle (DCA)

Dynamic contact angle measurements obtain the advancing and receding angles over an approximately 2-mm section of fiber at a constant velocity of 12 µm/second. Typically, a small metal strip is used to minimize the electrostatic effects during the test [9]. Each fiber can be attached to a substrate such as a plastic strip with pressure-sensitive tape, carefully aligning the fiber to the liquid surface during testing.

The Wilhelmy equation is used to determine the dynamic contact angles of the fibers:

$$F = \gamma_{lv} P \cos(\Theta) \tag{1}$$

Where F = force, γ_{lv} = probe liquid surface tension, P = perimeter, and Θ = dynamic contact angle. The advancing contact angles can be calculated using equation (2):

$$\cos\Theta = \frac{F_a}{F_r} \tag{2}$$

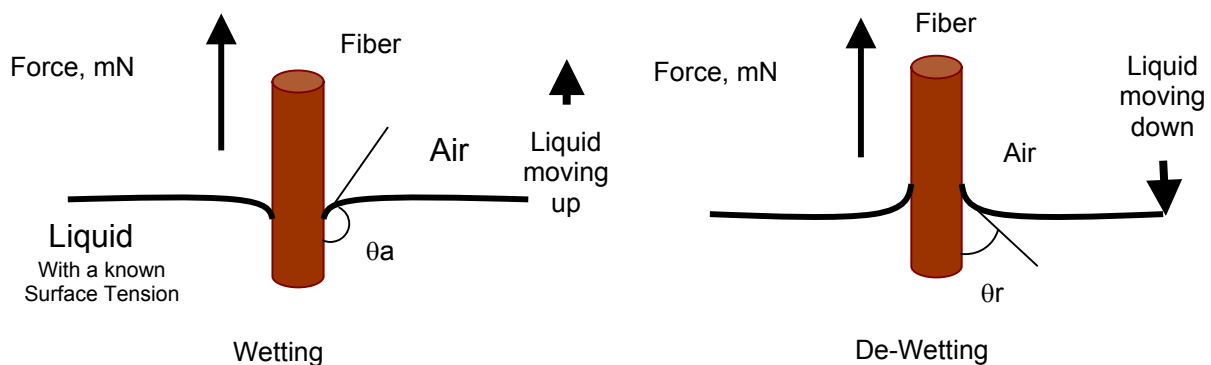Where F_a = force for advancing and F_r = force for receding. A schematic of the test is provided in Figure 1.

Figure 1: Schematic of the procedure to obtain single fiber contact angle measurement.

Zeta (ζ) Potential

Due to the known hydrophilic character of cellulose-based materials, suitable methods that allow characterization of the 'wet-state' of these materials are typically applied to study their surface properties [4]. For this reason, the ζ-potential measurements have been established to characterize the potential difference in an otherwise practically uniform medium between a point some distance from the surface and a point on the plane of shear. The plane of slip between the double layer and the medium involved (in this case water) may be interpreted in terms of charge density. Thus, changes in surface composition and in the water uptake behavior due to fiber separation and subsequent surface treatment may be quantified by measuring the ζ-potential. Additionally, it will be useful to quantify trends in the ζ-potential as a function of pH and subsequent fiber swelling.

The quotient $\Delta\zeta - (\zeta_o - \zeta_\infty)/\zeta_o$ should correspond to the water uptake at 100% relative humidity (RH – the sorption capacity) of the investigated solid. The decrease of the ζ-potential as a function of time due to the water uptake can be described as follows:

$$-\frac{d\zeta}{dt} = \kappa \bullet \left(\zeta - \zeta_\infty\right) \tag{3}$$

Which leads to:

$$-\ln\frac{\zeta - \zeta_\infty}{\zeta_o - \zeta_\infty} = \kappa \bullet t \tag{4}$$

Where ζ is the measured ζ-potential value at a certain time, ζ_∞ the ζ-potential value which reaches the function $\zeta = f(t)$ asymptotically to κ, a constant depending on the surface of the investigated coating.

Atomic Force Microscopy (AFM) Adhesion Testing

This procedure utilizes atomic force microscopy (AFM) to measure the attractive or repulsive forces between a known polymer sphere and a fiber surface. A polymer particle (in this case, a polystyrene or polypropylene sphere) is attached to a cantilever and held a fixed distance above a fiber bonded to a substrate [10]. As the substrate is moved towards the suspended particle, sensing the deflection of the cantilever monitors the interaction between the particle and substrate. Knowing the spring constant of the cantilever allows for a conversion between the cantilever motion and the relevant force. The force exerted on the particle as a function of the substrate displacement is shown in schematic at the bottom of Figure 2. In this figure, the region labeled D-E is most sensitive to the surface-force interactions that are of interest, although the approach (A) reveals insight into the effect of the solution medium.

A. Approach

C. Withdrawing

Direction of
Substrate
Motion

B. Loaded

D-E. Release (Adhesive Force)

**Load
Force**

B

A.
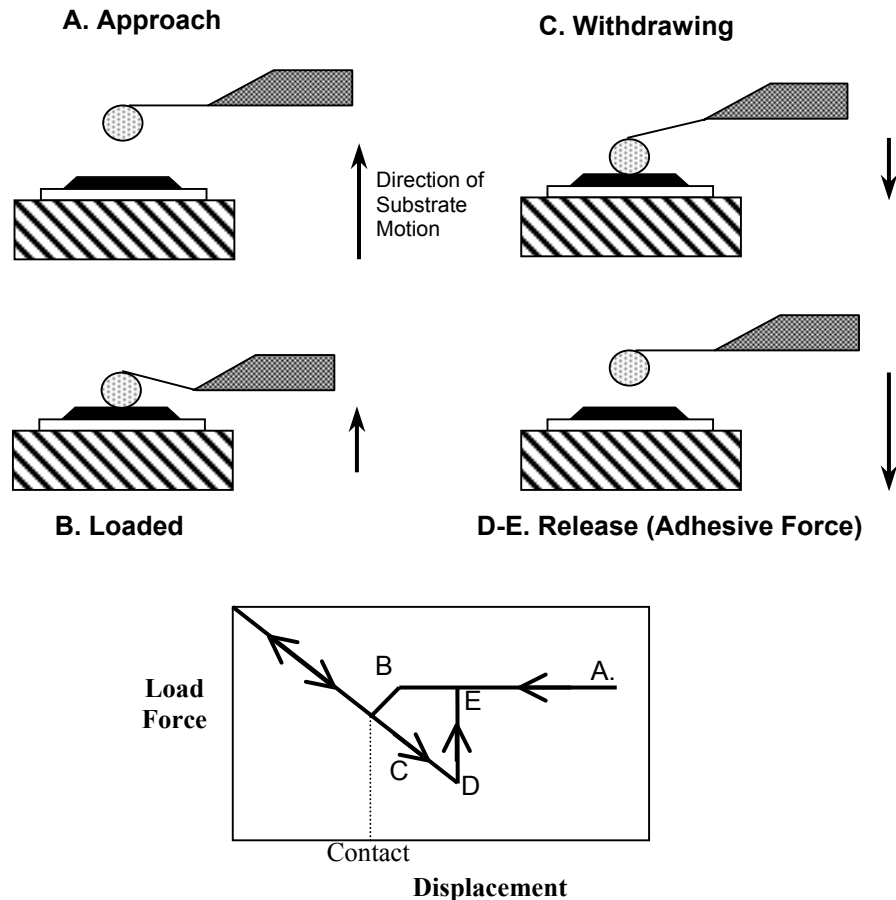
E

C

D

Contact

Displacement

Figure 2: Schematic of the procedure to obtain the force of interaction between a micrometer-size sphere mounted and a fiber. In the Load Force – Displacement diagram, the regions of interest on the force curve are labeled to show the approach (A), jump-to-contact (B), loading (C), unloading (D to E), and removal regions of the experiment. The adhesive force is measured from points D to E in the diagram.

Fiber Treatment Methodology

Reinforcing fibers can be modified by physical and chemical methods to correct for deficiencies in these materials, especially to impart bonding and adhesion, dimensional stability, and thermoplasticity. Surface modification of natural fibers can be used to optimize properties of the fiber-matrix interface.

Chemical Modification – Mercerization

Mercerization increases the amount of amorphous cellulose at the expense of crystalline cellulose. The important modification is removal of hydrogen bonding in the network structure. For example, the following reaction proceeds as a result of treatment with alkali:

$$\text{Fiber} -OH + NaOH \qquad \text{Fiber} -O^{-}Na^{+} + H_2O \qquad\qquad (5)$$
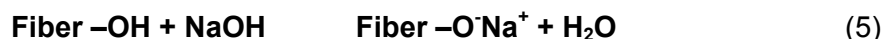
As a result of sodium hydroxide penetration into crystalline regions of the parent cellulose, alkali cellulose is formed. Then, after unreacted Na is leached, regenerated cellulose is formed. The transformation is an irreversible exothermic process resulting in the modification of elementary cells. The effect of NaOH treatment depends on the concentration of alkaline

solution, its temperature, and the duration of treatment. Optimum conditions for mercerization increase the degree of bonding at the polymer-fiber interface and lead to a rise in the rupture stress of cellulose.}

Conventional Chemical Modification

Conventional chemical modification is usually carried out through typical esterification and etherification reactions. Esterfication involves the reaction of lignocellulose hydroxyl groups with organic acids or anhydrides. A disadvantage of this approach is the requirement that fibers must be dry to obtain a good reaction yield. Many esters are possible depending on the nature of the organic acid (anhydride) used in the reaction, with double-bond-containing esters with longer chains conferring thermoplasticity on the lignocellulosic materials.
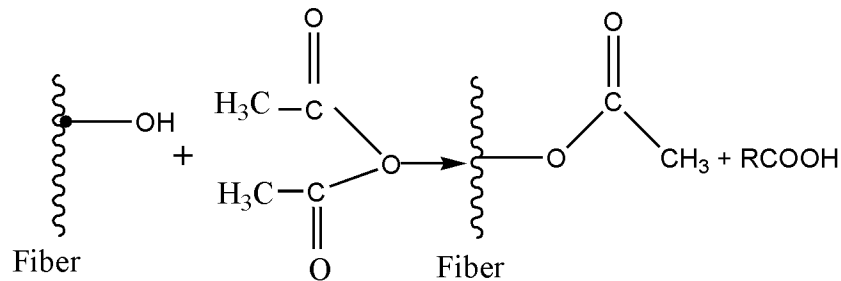
Figure 3: Schematic of the acetylation of hydroxyl groups from cellulose to lignin.

Silane Coupling Agents

Organosilanes are the main group of coupling agents for glass-fiber-reinforced polymers. Among them, alkoxysines can be represented by the following formula:

$$(R^1O)_3\text{-Si-}R_2\text{-}X \tag{6}$$

Where R^1O is a hydrolyzable alkoxy group, and X is a functional organic group. The R^1O groups are capable of hydrolyzing in an aqueous media, forming hydrogen bridges between cellulose hydroxyl groups and hydroxyl groups created as a result of the hydrolysis. Terminal groups present in silane molecules react with the polymer matrix and chemically bond cellulose to the polymer matrix. Hydrolysis of alkoxysilanes, e.g., vinyltriethoxysilane, which proceeds in the presence of moisture, leads to the formation of silanols, subsequently reacting with the fiber.

Silanization of natural fibers minimizes the deleterious effect of moisture on composite properties and increases adhesion between fibers and the polymer matrix. The effectiveness of the modification depends on the silane type, its concentration in solution, the temperature and time of fiber silanization, the moisture content, and the volume fraction of fibers in the composite.

Interface Surface Characterization – Preliminary Findings

Reinforcing fibers that emanate from natural sources are complex entities in and of themselves that comprise several different polymeric materials including cellulose, hemi-cellulose, lignin, pectin, and others extractives. This has been illustrated in extractive experiments conducted on both kenaf and hemp fiber sources per the TAPPI Test Method T222 OM-88. Results indicate the lignin content in kenaf to be twice that of hemp, and that the kenaf extractives content is 6.2% and for hemp is 4.9% (Table I). This poses a challenge when depositing preferential chemistries on these surfaces; the chemical uniformity and subsequent adhesion to the surface will be greatly impacted by the non-uniform nature of the surface (Figure 4). We have determined that in order to achieve the most efficient fiber surface coverage, fibers should be pre-treated to remove residual compounds. Whether this can be achieved in a cost-effective manner within the industrial environment remains to be determined.

Table I: Chemical digestion experiments conducted per TAPPI Test Method T222 om-88 (TAPPI 2004).

Fiber	Extractives Content (% dry weight basis)	Lignin (% dry weight basis)
Kenaf	6.2	**10.4**
Hemp	**4.9**	5.0

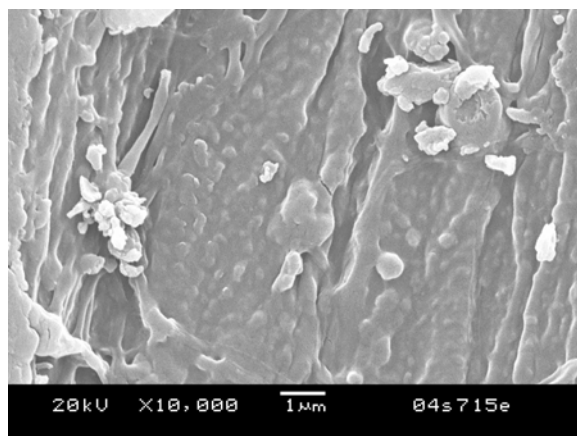

Figure 4: Scanning electron micrograph of a hemp fiber surface. Scale bar is 1 μm.

FTIR analysis assists in understanding the bonding between a fiber and a modified fiber, although the interpretation of the data can prove to be very challenging. For this reason, possessing a full database of chemical bonding that is expected in the deposition process for comparison is important for efficiently elucidating data from FTIR measurements. For example, Figure 5 depicts a comparison of a scan of an untreated hemp fiber (red) with a fiber that has been treated with C6 silane. It is clear that precision analysis of peak differences requires an electronic algorithm to achieve an accurate comparison. As this project has proceeded, a database has been developed of various fibers and treatments to better understand the fiber-treatment interaction and the bonding characteristic of each combination.
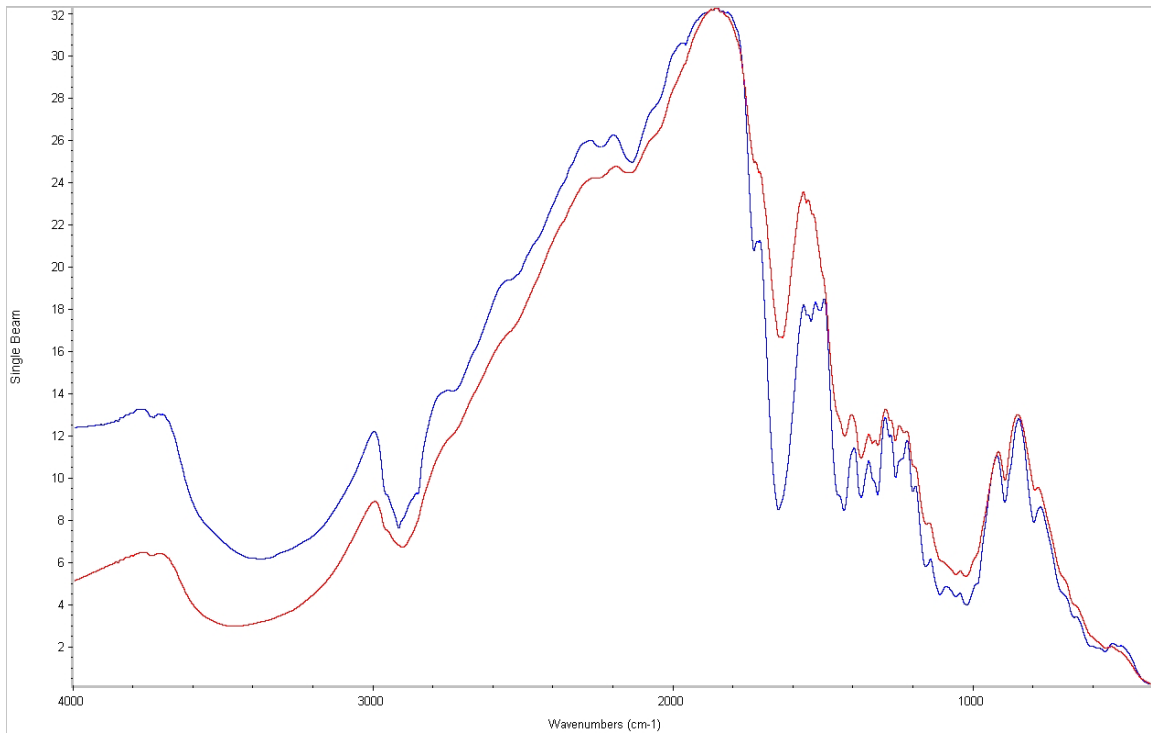
Figure 5: FTIR comparison of hemp (red) and C6 silane treated h hemp (blue).

X-ray photoelectron spectroscopy aids in understanding the quantity of surface treatment deposited on a fiber surface by providing atomic percentages of the elemental compounds at the surface. This is particularly useful for determining the deposition concentration of unique elements, such as silicon, on the surface as a function of deposition parameters (a sample output is provided in Figure 6).

Changing the deposition parameters will affect the amount or rate of deposition, which can be determined by comparing samples. For example, Table II illustrates the Si/C ratio of two deposition runs of similar silane chemistry. Note that the two unique deposition techniques resulted in nearly a 2x increase in the amount of Si on the fiber surface. This provides a basis for understanding the appropriate process for achieving the desired fiber treatment goal and subsequent surface adhesion characteristics.
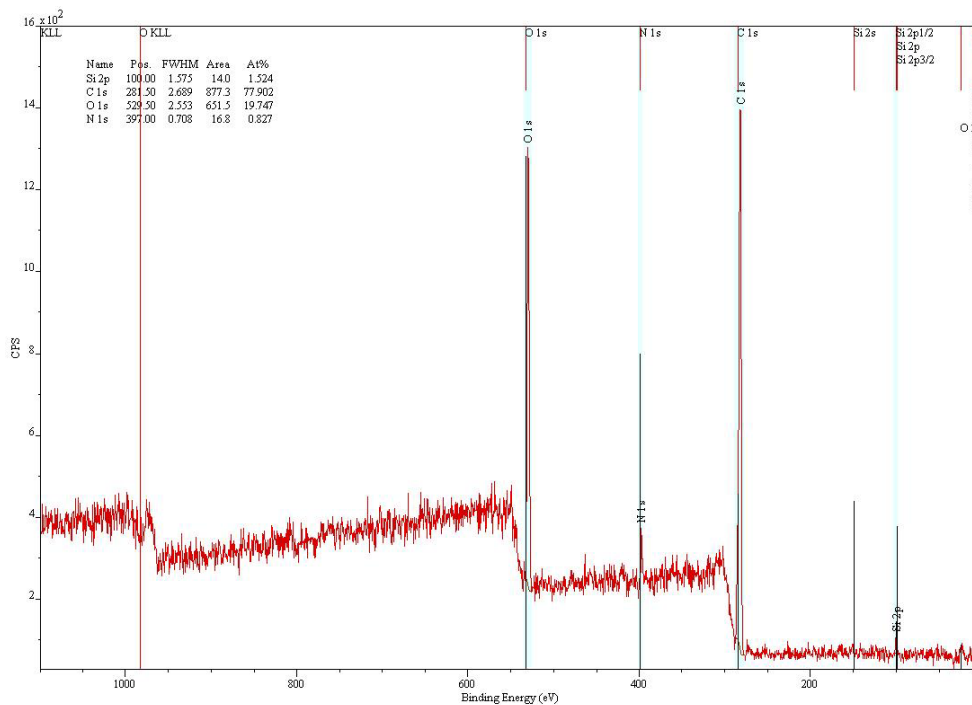
Figure 6: Sample XPS spectra of a treated hemp fiber.

Table II: XPS Results of hemp and modified hemp fibers.

Treatment	Carbon (%)	Oxygen (%)	Nitrogen (%)	Silicon (%)	Si/C
Dried Hemp	75.3	22.4	2.4	0	-
Silane-Single Step	77.9	19.7	0.8	1.5	**0.0196**
Silane-Modified	**80.6**	**15.9**	**0.005**	**2.9**	**0.0365**

Summary and Future Work

This paper highlights the scope of our research program focusing on the role of fiber adhesion in natural fiber composite processing applicable to automotive applications. Future challenges reside in several important tasks: fiber treatment, deposition chemistry characterization, and the processing of the treated fibers into composites for automotive applications. Our near term goal is to focus on the front end of these tasks utilizing the techniques outlined in this paper. In the future, we will report on our fiber treatment and subsequent adhesion characterization progress in greater detail.

Acknowledgements

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