PHOTO-OXIDATIVE TREATMENT OF CARBONACEOUS FIBERS TO PROMOTE ADHESION IN POLYMER MATRIX COMPOSITES

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Introduction

It is widely recognized that carbon fibers require surface treatment in order to establish suitable adhesion to polymeric matrices. Three major methods are currently practiced: 1. Anodic oxidation, a wet process where solution concentration and amperage must be maintained; 2. Exposure to ozone gas at elevated temperature; and 3. Treatment in caustic solutions such as nitric acid. Surface treatments result in improved fiber-matrix shear properties through a two part mechanism. First, a weak, defect-laden outer layer is removed from the surface of the fiber which generates a stronger surface to sustain shear loading. The second contribution of surface treatments is the deposition of chemical functionalities, most notably oxygen containing moieties that improve wetting and bonding between the fiber and matrix.

This work describes the use of ultraviolet (UV) light in the presence of ozone (UVO) as a method for treating carbonaceous fibers [1-2]. The UVO method involves several complimentary processes to potentially oxidize a surface. First, photons with wavelengths of less than 300 nm have sufficient energy to break many chemical bonds forming radicals on the surface which are then available to react with oxygen. Second, UV photons with wavelengths of 254 nm have sufficient energy to disassociate ozone into atomic oxygen, a highly reactive species, which can oxidize the surface. Additionally, UV photons with wavelengths of 185 nm can react with oxygen to form ozone, which is a very reactive species that can oxidize the graphitic surface.

Carbonaceous fibers made from polyacrylonitrile (PAN) and from coal tar pitch were used to demonstrate the efficacy of this method. The effect of UVO treatments on fiber surface chemistry, topography, tensile strength, and interfacial adhesion to an epoxy matrix were investigated.

Experimental

Carbon fibers from 2 different precursors were obtained from the manufacturer in their “as received” state without any surface treatment. PAN based AU4 (Hexcel) has a tensile modulus of 228 GPa. The commercially treated variation of this fiber was also evaluated and is identified as AS4. The other fiber type evaluated was derived from coal tar pitch, Dialead K63712 (Mitsubishi Chemical), and has a modulus of 634 GPa. The PAN and Pitch fibers were exposed to ultraviolet light in the presence of ozone for time periods ranging from 5 seconds up to several minutes. The source of the UV flux was a 300W pulsed Xenon flash lamp with wavelength emission below 200 nm. Approximately 700 ppm of ozone was passed over the sample during UV irradiation.

Changes in surface chemistry as a function of treatment were evaluated using x-ray photoelectron spectroscopy (XPS). XPS measurements were performed using a Physical Electronics PHI-5400 ESCA work station. X-Ray photons were generated from a polychromatic Mg anode (1254 eV). The analyzer was operated in the fixed energy mode employing a pass energy of 89.45 eV for survey scans and 17.9 eV for utility scans.

For scanning tunneling microscopy, as received and UVO treated fibers were adhered to steel disks using silver paste on each end of small bundles of fibers. Low current STM images were collected in constant current mode using a Nanoscope IV Multimode SPM (Digital Instruments, Santa Barbara, CA) equipped with an E scanner.

Tensile strength measurements were conducted on single filaments prior to and following 90 second UVO treatment to ascertain if the treatment caused structural damage to the fibers.

The single fiber fragmentation test was used to quantify the interfacial shear strength of PAN and Pitch fibers treated for 90 seconds in UVO. The matrix was diglycidyl ether of bisphenol A, Epon 828 (Resolution Performance Products, Houston, TX) cured with the stoichiometric amount (14.5 g/100 g resin) of m-phenylene diamine (Sigma-Aldrich Corp., St. Louis, MO). A schedule of 2 h at 75 °C followed by 2 h at 125 °C was used to process the single fiber fragmentation coupons. The embedded fiber diameters were measured using an optical microscope fitted with a video caliper. Details of this test can be found elsewhere [3-4].

Results And Discussion

XPS. The surface of the untreated "as received" AU4 fibers possessed an O/C of 0.02. Following just 5 seconds of exposure to a UVO treatment this ratio increased to 0.12 (Figure 1), a tremendous level of oxygen uptake. The fibers continued to oxidize with UVO treatment times of up to 90s where it reached a plateau with an O/C atomic ratio of 0.22. Following a UVO treatment of 10 minutes, the O/C atomic ratio increased to 0.27. The observed levels of surface oxidation go well beyond what is expected for a graphitic surface, where only the edge groups are considered vulnerable to oxidative attack. However, the structure of the outer defect layer is most likely nongraphitic or amorphous in nature and is expected to be more susceptible to oxidation. Treatments with ozone alone in the absence of ultraviolet light and UV in air without supplemental ozone also lead to oxidation of the surface (Figure 1), but to a lesser extent. More detailed discussion on the surface chemical effects of UVO treatments on AU4 fibers are found elsewhere [5]. The highly graphitic as received pitch fibers had an O/C atomic ratio of

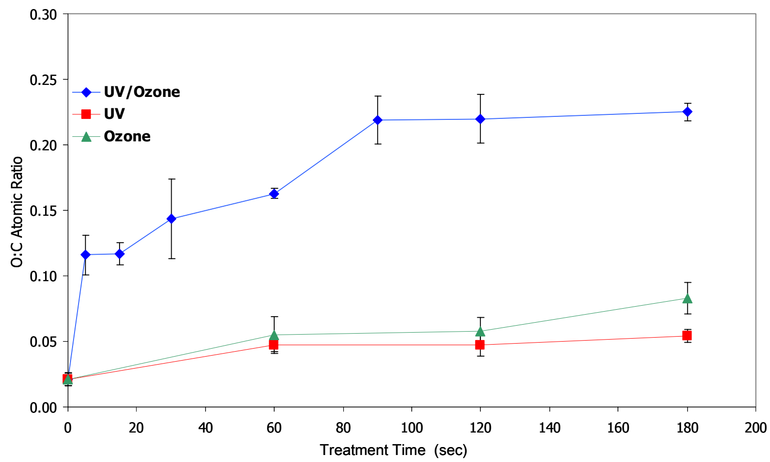

Figure 1. Effect of surface treatment on AU4 O:C atomic ratio

0.02, the same as the untreated AU4 pan fiber. Following 90 sec UVO treatment, the O/C atomic ratio increased to 0.06, much less than the increase achieved in AU4 under the same treatment conditions. The graphitic pitch fibers have fewer lattice edges compared to the AU4 fibers, resulting in less opportunity for oxidation of the fiber surface by the UVO treatment.

STM. The surface roughness of both the PAN and PITCH fibers were slightly increased following UVO treatment (Figure 2). Typical STM images for the PAN based fibers are shown in Figure 3. The nodular, graphitic crystallites are more clearly defined in the STM images of AU4+UVO and the commercially treated AS4, with UVO treated fibers having the largest nodular structure as measured from the STM micrographs (Table 1.) It is suspected that the UVO treatment removes a weakly bound, incoherent layer on the fiber surface which results in a structurally stronger surface for the development of interfacial bonds.

Table 1. Size of graphitic crystallites as a function of treatment.

Size of Graphitic Crystallites (nm)		
AU4 As Recd	AU4-UVO	AS4
12-15	12-18	9-12

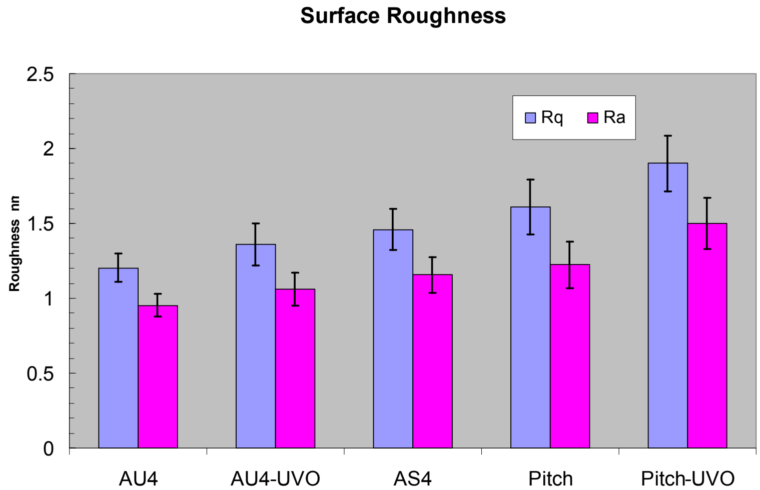

Figure 2. The effect of UVO treatment on carbon fiber surface roughness.

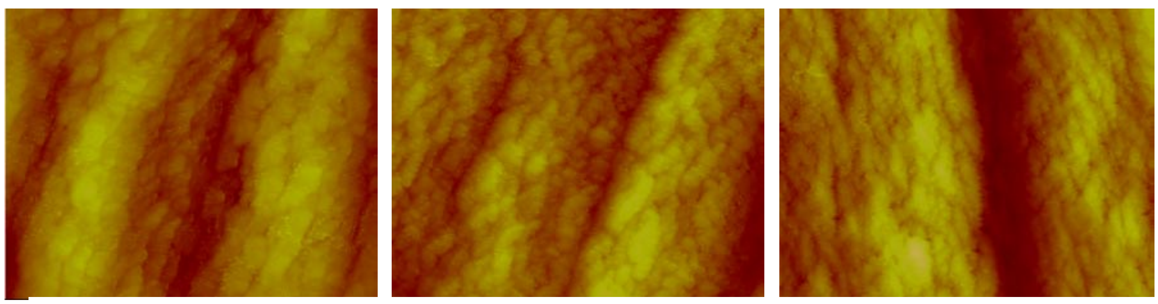

Figure 3. Typical STM images of AU4, AU4+UVO, and AS4 carbon fibers.
X-Y scale collected at 300 nm, z range is 30 nm.

Fiber Tensile Strength. One benefit of the UVO process is the improvement in tensile strength following treatment (Figure 4). The tensile strength of the AU4+UV-Ozone treated fibers was 11% greater than the baseline AU4 system. The t-test confirms that the difference in tensile strength is statistically significant at the 0.10 probability level. Similar findings have been reported by others [6]. It is also noteworthy that the mean diameter of the UV-Ozone treated fiber is less following UV-Ozone treatment, which suggests that the photo-oxidative process is simultaneously removing material from the fiber surface as well as changing the surface chemistry. It has been shown in earlier published work [4] that this outer layer of material contains defects, and removal of the defective outer layers results in greater tensile strength of the carbon fiber following UV-Ozone treatment. From the diameter measurements, it is estimated that 100-300 nm of material is removed during the 90 second treatment used in this study. Similar improvements in tensile strength were found for the Dialead Pitch fibers following UVO treatment. Following treatment, the tensile strength exhibited a 10.5% improvement. Pitch fibers are inherently weaker than PAN fibers, and the scatter in strength data for high modulus fibers is greater than lower modulus materials. A large sample set is required to statistically confirm the improvement in strength, which is currently underway.

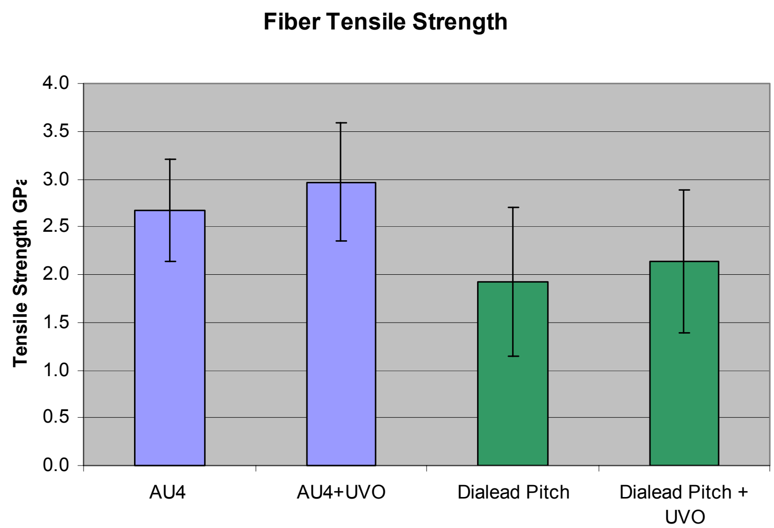

Figure 4. Single filament tensile strength.

From the data, it can be concluded that the UVO treatment did not damage the pitch fiber.

Interfacial Shear Strength. The untreated AU4 in Epon 828-MPDA matrix exhibited a weak, diffuse birefringent stress pattern with stick-slip bands that arise from arrested crack advancement followed by rapid crack propagation (Figure 5). This behavior has been correlated with systems having low levels of fiber-matrix adhesion [3-4]. Following photo-oxidative treatment, the AU4+UVO fiber exhibited much shorter fragment lengths accompanied with an intense birefringent stress pattern. The fracturing mode for the commercial AS4 fiber was similar to AU4+UVO, and this mode is a qualitative indicator of relatively greater levels of adhesion between the carbon fiber and epoxy matrix. The Dialead coal tar pitch fiber exhibited the same change in failure mechanism. The "as received" pitch fiber had a diffuse birefringent pattern

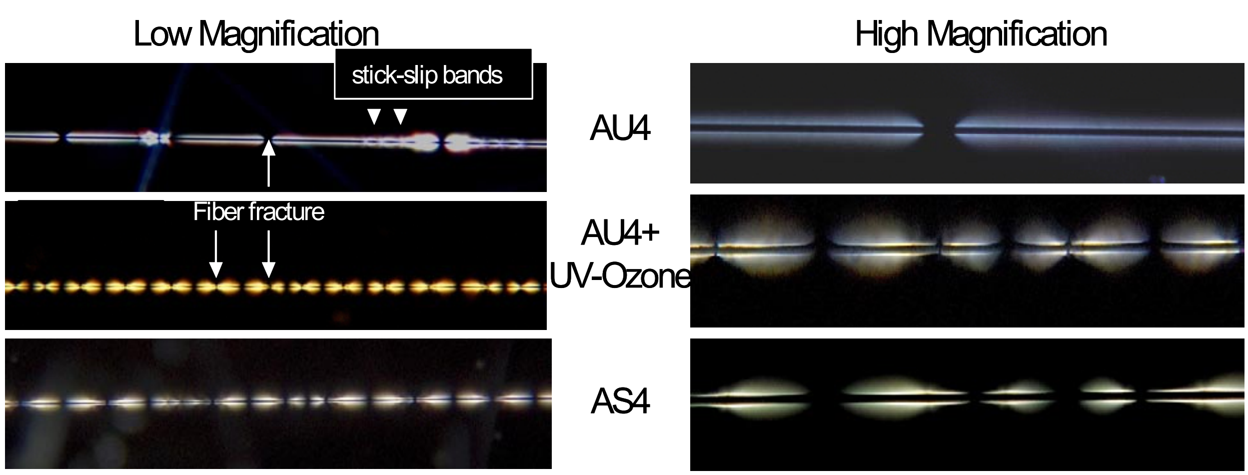

Figure 5. Birefringent stress pattern collected at high coupon strain showing differences in failure mode of AU4 (top), AU4+UV-Ozone (middle), and AS4. Fiber diameter is approximately 8 um.

As Received

UVO Treated

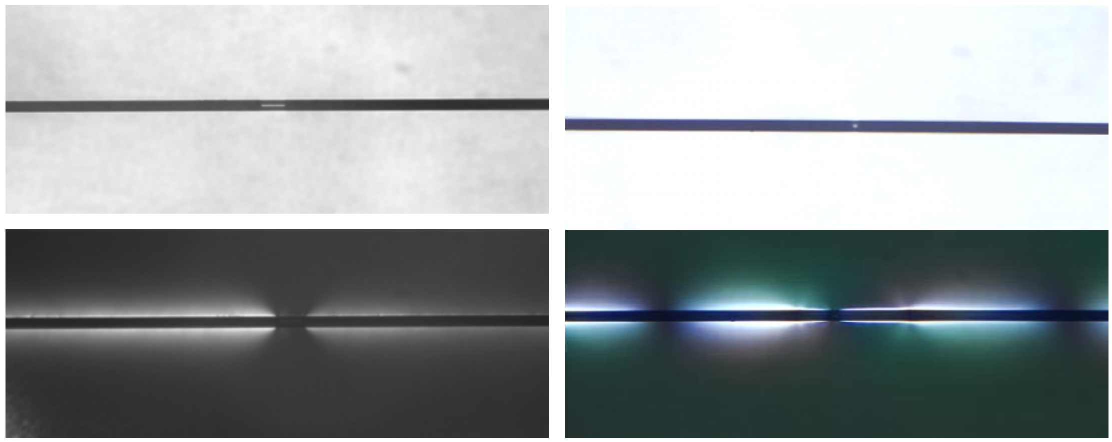

Figure 6. Failure mode of Dialead pitch fiber As Received (left) and UVO treated. Top photographs in transmitted light showing fiber fracture. Fiber diameter is nominal 12 um.

indistinguishable from the untreated AU4 system (Figure 6). Following UVO treatment, the pitch fiber failure mode was observed to have an intense and symmetrically distributed birefringent stress pattern on each side of the locus of fiber fracture. This failure mode is indicative of high levels of fiber-matrix adhesion.

Figure 7 presents the results of the fragmentation test used to quantify the interfacial shear strength of the fibers evaluated in this study. Using the measured values of the single filament tensile strengths in the computation of the interfacial shear strength, AU4+UVO was more than twice the baseline value for the “as received” AU4 system. Furthermore, the interfacial shear strength of the AU4+UVO fiber was greater than the commercially treated AS4 system.

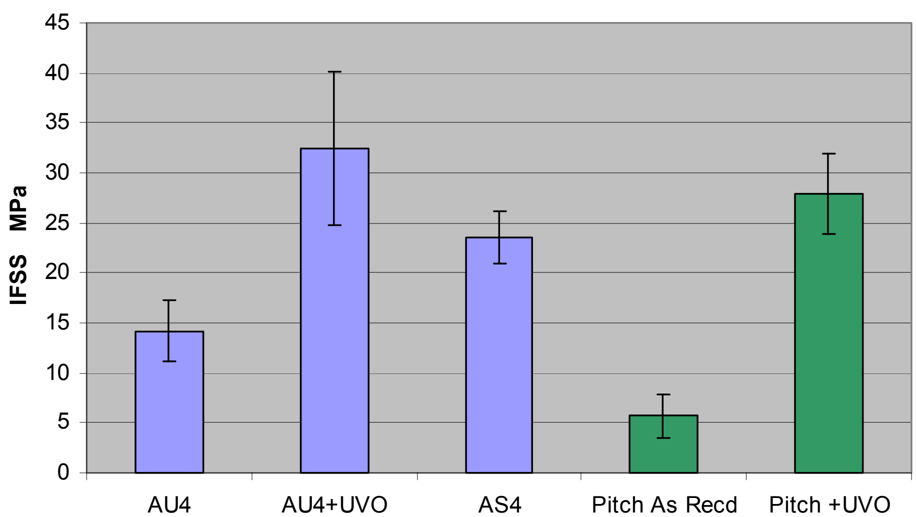

Figure 7. Interfacial shear strength from fragmentation test.

The IFSS for the untreated Pitch fiber, 5.67 MPa, was much lower than the PAN fibers. After UVO treatment, the IFSS increased nearly 400% to 27.89 MPa, surpassing the commercially treated AS4 fibers. The brief exposure to energetic light in the presence of ozone produced a substantial increase in the interfacial shear strength.

CONCLUSIONS

The application of energetic ultraviolet light was demonstrated to be an effective method to treat PAN and Pitch based carbon fibers.

- The UVO treatment resulted in significant enhancement of fiber surface oxygen.
- UVO causes oxidation of the carbon fibers while removing a weak, incoherent surface layer.
- Surface roughness was slightly increased following UVO treatment.
- Fiber tensile strength increased more than 10% after UVO treatment.
- The interfacial shear strength for fibers having UVO treatments is comparable or superior to levels of commercially treated fibers.

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