

UV-Ozone Surface Modification of Carbon Based Reinforcements for Composite Materials

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A cross-section of carbon based fillers and reinforcing fibers are treated with ultraviolet light in the presence of ozone to determine its efficacy as a new surface treatment. Test samples were chosen to represent the many applications of carbon based materials in industrial applications. A heat/ozone process was used as a comparison to the UV/ozone process. For unexfoliated and exfoliated graphites with a high degree of graphitization, the level of surface treatment was found to be related to the edge groups in the material. It was found that for both materials that even 30 sec. UV/ozone exposure outperformed a 20 min. heat/ozone process. A higher level of oxidation was observed with carbon black, though the heat/ozone process gave significantly greater levels of oxidation than the UV/ozone treatments. Two types of PAN based carbon fibers were examined; an untreated fiber and a milled fiber. Both fibers showed good improvements following UV/ozone treatment. Vapor grown carbon fibers were most susceptible to UV/oxidation, with a five-fold increase in oxygen content following 2 min. of treatment. The effects of starting morphology and surface chemistry are discussed along with an analysis functional group distribution following surface treatment.

1. INTRODUCTION

The light weights, excellent mechanical, thermal and electrical properties of graphite based carbon materials, has prompted a great deal of effort into their study as reinforcements and fillers for polymer matrix composites. Carbon fibers are the most developed graphitic reinforcement, yet recent thrusts to develop cost effective nanoscale materials have pushed the development of graphite or graphite analogs to the forefront of research.

As with many composite systems, good mechanical properties are often dependent upon the polymer-support interface. The ideal interface has excellent chemical or mechanical compatibility between the support and the polymer matrix. Unfortunately, many properties intrinsic to graphite or byproducts of the synthesis of carbon supports are detrimental to good interfacial adhesion. Graphitic materials have a low concentration of functional groups on the surface with reactive sites limited to the free valence bonds found on the edges of the material [1] and are naturally incompatible with many polymer matrices. Additionally, materials with a low degree of graphitization may have poor mechanical properties. For instance, lower modulus PAN based carbon fibers have a defect laden outer surface in conjunction with a weakly bonded outer skin that not only provides poor adhesion but also diminishes the fiber tensile strength. Improving the interfacial properties of graphitic materials mandates the use of some sort of surface treatment.

Carbon fibers are far and away the most studied material in regard to surface treatments to improve adhesion [2-7]. Several surface treatment strategies have been examined including: dry gaseous oxidation, wet chemical oxidation, electrolytic oxidation and plasma treatment. Though these treatments were originally intended for carbon fibers; they could, in some cases, be adapted to other graphitic materials. Wet chemical oxidation by sulfuric or nitric acids is undesirable as it requires aggressive reagents and long treatment times. Electrolytic oxidation is a common technique for surface treating carbon fibers, however as many carbons are in the form of fine powders, insuring good electrical contact

during the surface treatment will become difficult. Plasma treatment is an excellent method to not only for oxidization but also as a pathway for depositing polymeric and non-polymeric materials onto the carbon surface [8]. Unfortunately plasma treatments require vacuum and controlled environments which limit the treatments to batch processes. Also, uniformity of surface treatment is an issue with plasma treatment as not surfaces will be treated evenly, if at all. Additionally, airborne fine graphitic powders have an uncanny ability to short electrical devices and great caution must be taken when treating powders. Dry gaseous oxidation, in the form of ozone or oxygen at elevated temperatures, provides good surface coverage of powders and fibers but requires longer reaction times and may not be aggressive enough to attack all materials effectively.

The use of ultraviolet (UV) light in conjunction with ozone is an alternate surface treatment to more traditional methods. UV treatments have been successfully used for the surface treatment of many polymeric materials [9]. High energy UV photons are able to break many chemical bonds inducing crosslinking in some cases and creating radicals that are available for oxidation or other derivitization. When used in conjunction with ozone and atomic oxygen, UV light can create a highly oxidizing environment by the two pathways described in Eq. (1) – Eq. (3)



Photons with a wavelength of 185 nm decompose molecular oxygen into atomic oxygen, a highly reactive, oxidizing species (Eq. 1). Atomic oxygen may combine with molecular oxygen to form ozone (Eq. 2). Ozone may also disassociate upon absorption of light at 254 nm to give molecular and atomic oxygen (Eq. 3).

Treatment of carbon surfaces with UV light is an under utilized technique. Research conducted at Michigan State University over the past several years has resulted in US patents covering the UV treatment of carbon fibers [11]. This work aims to survey the efficacy of the UV/ozone process across a spectrum of graphitic supports. The array of specimens analyzed are representative of many different types of graphite supports including crystalline graphite, exfoliated graphite and carbon black as well as vapor grown carbon fibers, milled PAN carbon fibers and PAN carbon fibers.

2. EXPERIMENTAL

A variety of carbon based support materials were chosen to examine the efficacy of the UV/ozone method. The material set includes (i) nanosized carbon black (KETJENBLACK EC-600 JD, Akzo Novel Polymer Chemicals LLC), (ii) unexfoliated crystalline graphite (Aldrich), (iii) exfoliated graphite nanoplatelets (produced by an in-house heat treatment), (iv) vapor grown carbon fibers (Pyrograf III, PR-19 PS grade, Pyrograf Products, Inc.), (v) milled PAN based carbon fibers (PANEX 33 MC Milled Carbon Fibers, Zoltek Co.), and a (vi) polyacrylonitrile based carbon fiber without prior surface treatment (AU4, Hexcel).

UV/ozone treatments were performed with an annular pulsed xenon lamp with a spectral output of 180 nm and greater. Ozone was generated from flowing oxygen through a commercial ozone generator (Ozotech, Inc.). Ozone concentrations of 700 ppm were used for all samples. Carbon fiber specimens were stretched across the length of the lamp and flowing ozone was admitted to sample during treatment. The powdered samples were placed in a reaction chamber as described in Fig. 1. The vessel consists of a 2 cm diameter quartz tube with a reaction volume of approximately 15 cm³ defined by two Teflon plugs. Holes

were drilled into the plugs and filled with glass wool to allow ozone to enter the reaction volume without loss of sample. The tube was rotated at approximately 15 RPM. To ensure good mixing, three quartz tumblers were inserted between the plugs at angles of 120°. Ozone was introduced at low flow rates and the vessel was allowed to purge for 5 minutes prior to irradiation.

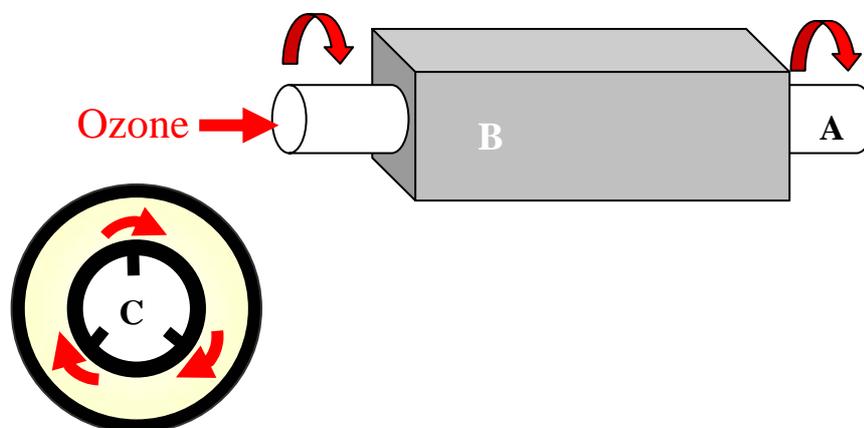


Fig. 1. A schematic representation of the experimental design depicting the quartz tube (A) in the annular lamp (B). The cross section (C) indicates the position of the tumblers in the tube.

For comparison all materials with the exception of the PAN carbon fibers were treated with ozone at 80°C (hereby known as heat/ozone). An oven was purged with ozone for approximately 30 min. prior to heating. After the oven reached temperatures, the samples were introduced and treated for 20 minutes. PAN carbon fibers were exposed to ozone at room temperature for 1, 2, and 10 minutes.

The effectiveness of the surface treatments were determined by increases in the oxygen to carbon atomic ratios as measured by 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 standard 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. Powdered samples were affixed to the specimen holder with double sided tape. The ends of the carbon fiber specimens were crimped with aluminum foil and the sample was attached to the specimen holder by a molybdenum mask. Semi-quantitative information was obtained by measuring the C 1s and O 1s peak areas and applying the appropriate sensitivity factors. Deconvolution was performed using the Multipak software package. The C 1s spectral envelope using a non-linear least-squares curve fitting routine. The graphitic peak for carbon (corrected to 284.6 eV) was fit using an asymmetric Gaussian-Lorentzian peak, while the oxides of graphite were fit with Gaussian-Lorentzian peaks assuming an approximate 1.5 eV chemical shift per bond to oxygen [12-14]. Goodness of fit was tested with a simple materials balance by comparing the O/C atomic ratio estimated from the deconvolution to the actual value. A fit that produced an error of less than 10% was deemed worthy and subsequently accepted.

3. RESULTS AND DISCUSSION

Ozone reacts with carbon surfaces by addition across unsaturated carbon bonds via the Criegee mechanism forming an ozonide [15]. Degradation of the ozonide, by heat, reducing, or oxidizing agents leads to the formation of hydroxyls, carbonyl groups or carboxylic acids. Unsaturated carbon bonds not present in an aromatic ring structure are most vulnerable to oxidation as the aromaticity of benzene and larger ringed networks (such as graphite) hinder ozonolysis. When UV photons are added to the ozone treatment, there are most likely three general pathways to oxidize the surface. The first involves cleavage of chemical bonds at the surface to form free radicals which can then react with ozone, molecular or atomic oxygen to form oxidized species. Though the aromatic network that makes up the graphene sheets should readily absorb the UV photons, the same aromaticity should protect the sheets from any photo-induced bond cleavage. Thus any photoinitiation is constrained to the edge planes of the carbon sheets. The second pathway involves the attack of the material by atomic oxygen formed from photo-dissociation of molecular oxygen or ozone. Similarly the graphene sheets should be well protected against this type of oxidation (particularly at lower temperatures) and any reaction will occur along edges or defect sites in the material. The final process involves the ozonation and photo-cleaving of the resulting ozonide to give various oxidation products. As with the previous examples, this too should be relegated to the edge or defect sites.

Whereas the treatment time and temperatures of the heat/ozone process should limit any reaction to just the unsaturated carbons on the surface, it should be noted that most of the oxidation products are chromophores with absorption bands occurring at wavelengths higher than the lower limit of the UV lamp used in this study (180 nm). These chromophores act as sites for further oxidation leading to a gradual etching of the surface to form CO₂, H₂O or other incomplete combustion products. Thus, the UV/ozone treatment should be considered a continuous process that gradually erodes graphite from the edges in. Additionally, any functional groups on the surface may serve as initiation sites for photo-oxidation.

As such, with both the heat/ozone and UV/ozone treatment of graphite, it is expected that the amount of oxygen uptake will be related to the concentration of edge planes or defect sites in each sample. Two types of carbon with a high degree of graphitization are examined in this study, unexfoliated crystalline graphite and exfoliated graphite. The unexfoliated graphite should have a low concentration of edge atoms, and thus only small increases in the O/C atomic ratio are expected following surface treatment. The oxygen uptake for these materials (along with carbon black) is described in Fig. 1 and indeed, only a slight increase in oxygen concentration for the unexfoliated graphite is observed. In fact, following UV/ozone treatment, the oxidation levels are very similar to the heat/ozone treated graphite. This suggests that both processes react with similar surface species. The exfoliation process which increases the surface area of the material from roughly 0.2 m²/g to 100 m²/g [16] should also increase the concentration of edge groups available for reaction. So it comes as no surprise that for exfoliated graphite, which has roughly the same starting oxygen content as the crystalline graphite, a more substantial level of oxidation is seen. However the oxygen concentration is greater than what is observed with the heat/ozone process, with even the 30 sec. UV/ozone treatment outperforming the 20 min. heat/ozone treatment in regards to oxygen uptake. In comparison with unexfoliated graphite, where the heat/ozone and UV/ozone treatments have similar oxygen uptake, this is somewhat of a surprise. Perhaps the exfoliation process introduces surface sites that are more susceptible to attack by UV/ozone.

The total surface concentrations of oxygen-containing functional groups as a function of surface treatment for all tested materials are described in Table 1. Deconvolution lead to three classifications of functional groups, hydroxyl/ether, carbonyl and carboxyl. For the

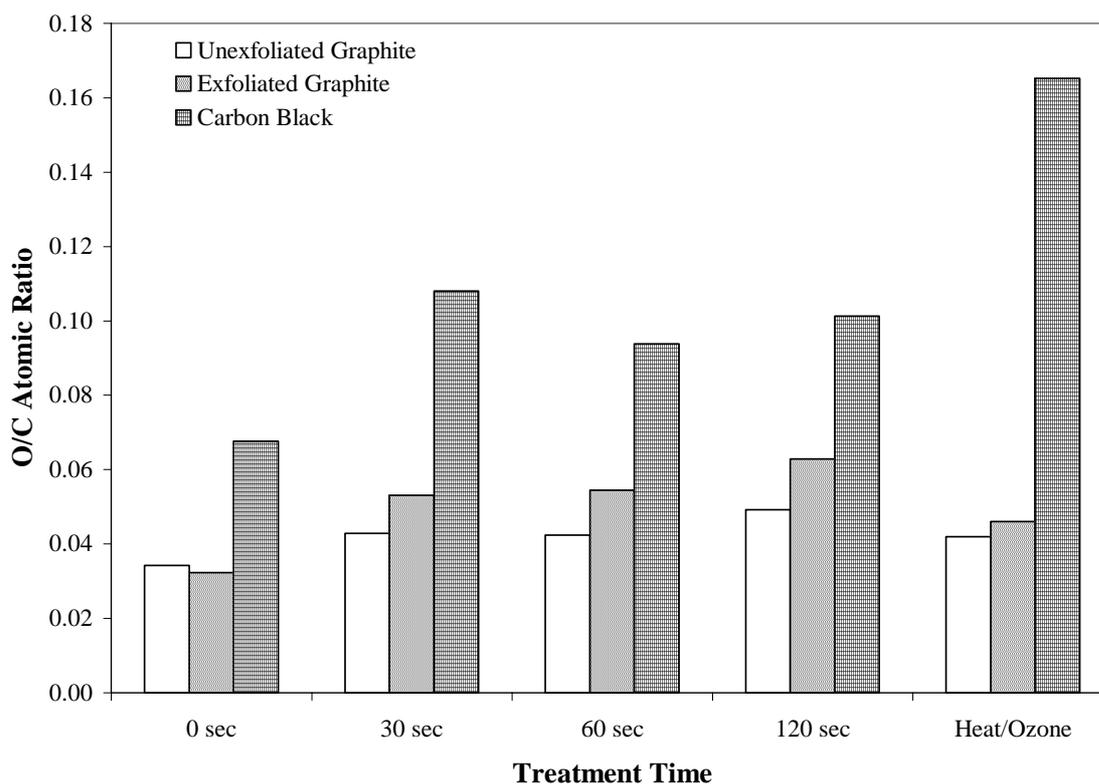


Fig. 2. The variation in the O/C atomic ratio for unexfoliated graphite, exfoliated graphite and carbon black. Treatment time refers to the length of the UV/ozone treatment. Heat/Ozone treatment has a duration of 20 minutes

unexfoliated and exfoliated graphite, the UV/ozone treatment produces a slight increase in

For carbon with a low degree of graphitization, other sites in addition to edge groups are available for chemical attack. These include non-aromatic carbon that is a byproduct of incomplete graphitization and amorphous carbon that is graphitic in structure but lacks long range order. The former case should be highly susceptible to oxidation by both the UV/ozone and heat/ozone treatments. Non-aromatic unsaturated hydrocarbons are particularly vulnerable to ozonolysis and should be readily oxidized by either treatment.

Carbon black is an amorphous graphitic material whose edge/plane ratio should be very high when compared to the exfoliated and crystalline graphite. As such, the greater extent of oxygen uptake is not surprising. As with the previous materials, oxidation is very rapid, reaching a steady state after 30 sec. Unlike the crystalline and exfoliated graphite, however, there is a wholesale increase in functionalization of the carbon surface with UV/ozone treatment with significant increases in the hydroxyl/ether, carbonyl and carboxyl groups. The functional group distributions are of different proportions when compared to crystalline graphite suggesting that the edge groups themselves are not the reaction site. Most likely, non-graphitic carbon is also being oxidized.

It should also be noted that all UV/ozone treatments of carbon black reach oxidation levels below what is observed for the heat/ozone treatment. Quite possibly this is due to the remarkably high surface area of carbon black ($1400 \text{ m}^2/\text{g}$) and its small particle size (average diameter 10-30 nm) which might allow ozone to penetrate into the micropores of the material some of which are inaccessible to incoming UV photons. Obviously, UV treatment is a line of sight process and many of the pore walls do not have a direct pathway for exposure. Thus, oxidation from heat/ozone may very well be away from the surface available for UV exposure but still within the sampling depth of XPS. Finally, the carbon distribution following heat/ozone treatment is different than what is observed following UV/ozone treatment. The carbonyl carbon, a typical byproduct of ozonolysis, is proportionally higher

Table 1. Surface concentrations of carbon species.

Sample	Hydroxyl/Ether (%)	Carbonyl (%)	Carboxyl (%)
<i>Crystalline Graphite</i>			
Untreated	2.0	0.0	1.1
30 seconds	2.8	0.0	1.1
60 seconds	2.6	0.0	1.3
120 seconds	2.8	0.2	1.3
Heat/Ozone 20 min.	2.5	0.0	1.3
<i>Exfoliated Graphite</i>			
Untreated	2.3	0.6	1.0
30 seconds	4.2	0.3	1.1
60 seconds	3.9	0.6	1.3
120 seconds	3.8	1.1	1.2
Heat/Ozone 20 min.	3.3	0.0	1.4
<i>Carbon Black</i>			
Untreated	4.1	0.1	2.5
30 seconds	5.9	0.4	3.3
60 seconds	6.1	0.5	2.7
120 seconds	5.7	0.6	3.3
Heat/Ozone 20 min.	7.5	1.8	5.2
<i>Milled Carbon Fibers</i>			
Untreated	3.1	1.4	1.6
30 seconds	6.6	2.5	2.1
60 seconds	6.5	2.9	3.0
120 seconds	7.3	2.2	3.1
Heat/Ozone 20 min.	8.2	2.9	4.6
<i>Vapor Grown Carbon Fibers</i>			
Untreated	4.2	0.9	2.0
30 seconds	7.2	4.1	4.9
60 seconds	7.5	4.0	5.4
120 seconds	8.6	4.2	8.9
Heat/Ozone 20 min.	6.1	1.2	2.8
<i>AU4 Carbon Fibers</i>			
Untreated	1.5	0.4	1.2
30 seconds	5.5	2.5	2.8
60 seconds	6.0	2.4	3.3
120 seconds	6.1	3.3	4.5
Ambient/Ozone 60 sec.	4.8	1.0	1.0
Ambient/Ozone 120 sec.	5.5	0.8	1.0
Ambient/Ozone 10 min.	6.3	1.9	0.9

following the heat/ozone treatment.

The effects of treatment time on the O/C atomic ratio for the milled fibers, vapor grown carbon fibers and the AU4 fibers are shown on Fig. 3. Both are PAN based carbon fibers, but the surface chemistries are significantly different. Most likely this is due to different processing temperatures used in the manufacture of the fibers. The AU4 carbon fibers emerge from the reactor with a defect laden surface layer. The fiber surface is carbon rich with an O/C of 0.02. Following 30 sec. of UV/ozone treatment, the O/C ratio rises to 0.14 and continues to increase to 0.22 after 120 sec. of exposure. 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 this

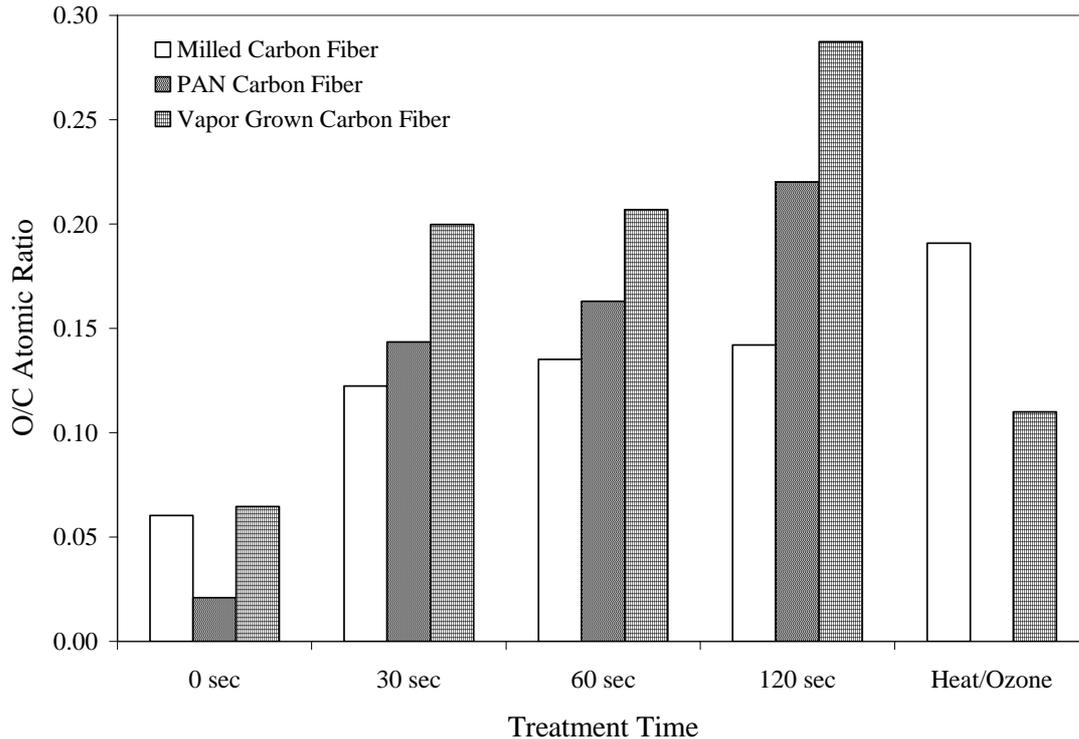


Fig. 3. Variation in the O/C atomic ratio for milled carbon fibers, PAN carbon fibers and vapor grown carbon fibers. Treatment time refers to the length of the UV/ozone treatment. Heat/Ozone treat has a duration of 20 minutes

outer defect layer is most likely nongraphitic or amorphous in nature and quite susceptible to oxidation. Initially, the untreated carbon fiber consists of approximately 2% hydroxyl and trace amounts of carbonyl and carboxylate groups. After 30 sec. of UVO treatment, the hydroxyl concentration increases to about 6% of the total surface where it remains independent of the increasing irradiance. The total surface carbonyl and carboxylate concentrations rise to 2.5% and 2.8%, respectively. Both functionalities track the increase in treatment time with the carboxylate concentration slightly outpacing the carbonyl concentration. Since more oxidized carbons form after longer exposures, it is quite possible to tune the surface chemistry of the carbon fibers by simply lengthening or shortening the exposure time.

In an effort to elucidate a mechanism for surface oxidation, the AU4 fibers were exposed to ozone at ambient temperatures. Following 1 min. of treatment, the O/C ratio for the ambient/ozone treatment is around 0.05 and remains relatively constant through 10 min. of exposure. An increase in the hydroxyl concentration is also observed, but unlike the UV/ozone treated fibers, the carbonyl and carboxyl carbon concentration remains low. It is believed that the predominate mechanism for oxidation of the AU4 fibers consists of ozone absorption to form an ozonide group followed by photo-cleavage to yield oxidation products. As mentioned previously, these groups may also serve initiation sites for further oxidation. UV/ozone is a fairly aggressive surface treatment on carbon fibers and significant etching of the fibers are observed. Following surface treatment the fibers diameters decrease from 8.3 μm to 7.8 μm . This decrease is actually quite beneficial as it removes many surface defects which weaken the fiber. Thus following treatment the average tensile strength of the AU4 fibers increases from 2.7 GPa to 3.0 GPa, an 11% improvement. Etching may also occur with the amorphous or partially amorphous powders and work is currently underway to determine if this is true.

The untreated milled fibers are fairly oxidized with an O/C ratio of 0.06. Following 30 sec. of UVO treatment, the O/C atomic ratio doubles and remains steady with increasing treatment time. Examination of the carbon distribution finds that the hydroxyl/ether concentration rises to around 6.5% from 3.1% for the untreated material. A slight increase is observed with increasing treatment time. The carbonyl concentration increases to about 2.5% constant while the carboxyl concentration steadily increases to around 3.0% from 1.6%. While all of these increases are significant, they fall substantially beneath what is observed for the heat/ozone treatment where the O/C ratio reaches 0.19 and obviously the functional group concentrations are all much larger than what is observed for the UV/ozone treated materials.

The vapor grown carbon fibers were the most aggressively oxidized materials encountered in this study. The surface concentration of oxygen increased from an O/C atomic ratio of 0.06 to 0.20 following 30 sec. of treatment and increased to 0.29 after 120 sec. of treatment, a five fold increase. The hydroxyl/ether concentration increases from 4.2% to 8.6% and the carbonyl concentration increases from 0.9% to 4.2% but perhaps the most striking result is the increase in carboxyl concentration from 2.0% to 8.9%. Both hydroxyl and carboxyl carbons are quite reactive with many polymer matrices and the UV/ozone treated VGCF show excellent interfacial adhesion. Raman studies indicate that a high concentration of sp^3 carbon is present in the material which may be quite reactive [18]. The lower oxygen concentration of the heat/ozone treated material indicates that VGCF is quite sensitive to photoinitiation. Darmstadt, *et al.* [18] have raised the possibility that due to small diameters of VGCF, that excessive surface treatment may lead to changes in the bulk properties. Closer examination of the bulk properties after UV/ozone treatment is needed to accurately evaluate its effectiveness as a surface treatment.

4. CONCLUSIONS

The surface chemistry of carbon based fillers and reinforcing fibers is the determining factor in regards to the effectiveness of the UV/ozone process. Reaction sites are restricted to edge groups and defect sites for materials with a high degree of graphitization. Unexfoliated, crystalline graphite has the lowest level of oxygen uptake and it is believed to react in a similar fashion to the heat/ozone treatments. Exfoliated graphite should have a higher concentration of edge groups and thus the increase in the level of oxygen uptake was not unexpected. UV/ozone treatment oxidizes the exfoliated graphite to a greater extent than the heat/ozone treatment. It is believed that exfoliation may create sites that are more susceptible to oxidation by UV/ozone than with heat/ozone.

Materials with lower degrees of graphitization were found to be more susceptible to surface oxidation. Carbon black had roughly a 30% increase in surface oxygen concentration following UV/ozone treatment. Significant increases in the hydroxyl, carbonyl and carboxyl carbons were observed. A disadvantage of the line of sight treatment involved the UV process was exposed as well, as the heat/ozone process was believed to treat a greater portion of the available surface area.

The UV/ozone treatment was found to be particularly effective in oxidizing vapor grown carbon fibers, where the material experienced a five fold increase in oxygen content. Two minutes of UV/ozone treatment found the material to be quite oxidized with close to 9% of the surface carbon assigned to carboxylate carbons. Though this should lead to a remarkable improvement in polymer wetting and adhesion, the effect of this level of treatment on the mechanical properties of fibers have yet to be determined.

The two PAN based carbon fibers also had substantial increases in the O/C atomic ratios. In particular the AU4 fiber went from a very carbon rich surface to a highly oxidized surface at short exposures. Functional group analysis of both the UV/ozone treatment and ambient temperature/ozone treatments for the AU4 fiber suggest that ozone absorption

followed by photo-disassociation of the ozonide is a predominate route for oxidation. The weakly bound outer layer of the AU4 fiber is quite vulnerable to the UV/ozone treatment and significant etching of the material is observed. The milled carbon fibers are a higher modulus fiber compared to the AU4 fibers and have a different surface reactivity.

For the materials tested in this work, the UV/ozone treatment was found to be effective at adding oxygen to the surface of the material. The effect on the mechanical properties as well as the thermal and electrical conductivities of these materials is currently being investigated.

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