

Retraction

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The article was originally submitted to the editor of this volume but was withdrawn by the authors who subsequently submitted the work to the journal *IEEE Transactions on Plasma Science*, where it has since been published, [1]. As the publication in [1] pre-dates the publication in JPCS we are withdrawing this version to remove the duplication. The editor of this volume, L Soto, apologises for any inconvenience caused to the authors and to readers.

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Atmospheric Plasma Treatment of Carbon Fibers for Enhancement of Their Adhesion Properties

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Abstract. Plasma processing of carbon fibers is aimed to provide better contact and adhesion between individual plies without decrease of the carbon fiber (CF) mechanical resistance. This work deals with surface modification of CFs by atmospheric pressure dielectric barrier discharge (DBD) in air. Scanning electron microscopy (SEM) of a single untreated fiber showed many thin tracks aligned along the fiber. This feature can be explained by the fiber manufacturing process. SEM of the treated samples revealed many small particles distributed over entire surface of the fiber. These particles are product of the fibers surface etching during the DBD treatment that removes the epoxy layer covering as-received samples. The alteration of CF surface morphology was also confirmed by the Atomic force microscopy (AFM), which indicated that the CF roughness increased as a result of the plasma treatment. Analysis of the surface chemical composition provided by X-ray photoelectron spectroscopy (XPS) showed that oxygen and nitrogen atoms are incorporated onto the surface. The polar oxygen radicals formed on the surface lead to increasing of the CF surface energy. Both, the increase of surface roughness and the surface oxidation contribute for enhancement of CF adhesion properties.

1. Introduction

In the last decade carbon fibers (CFs) have been extensively used for manufacturing of thermoplastic composites, such as carbon-reinforced polyetherimide (CF/PEI). This high-performance material has found multiple applications in aerospace, marine and automobile industry due to its favorable engineering properties, such as lower density, enhanced toughness, excellent fire resistance and easy recyclability. One problem that can seriously compromise the performance of this material (when no previous surface treatment of CFs is applied) is to obtain composites with low interlaminar shear strength [1]. Therefore plasma processing of carbon fibers is aimed to provide better contact and adhesion between individual plies without decrease of the carbon fiber mechanical resistance [2-3]. This surface modification is originated by introduction of chemical functional groups and surface morphology alteration during the treatment [4]. Plasma treatment of carbon fibers by air dielectric barrier discharge (DBD) at atmospheric pressure is more economical than other plasma treatments



because it needs no closed chambers, special gases and expensive vacuum equipment [3]. Therefore it permits large-scale industrial processing more easily than low pressure plasmas [2].

Currently other materials, such as polyester textile materials [5], Twaron fibers [4], polyester fabric with fluoropolymers [6] and epoxy composites [7], have been treated with atmospheric pressure plasmas in order to improve their adhesion properties.

This work deals with surface modification of CFs by an atmospheric pressure dielectric barrier discharge (DBD) in air. The treated and untreated carbon fibers were characterized by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and atomic force microscopy (AFM).

2. Experimental

The polyacrylonitrile fibers were purchased from Hexcel in the form of plain weave fabric containing 3000 monofilaments in each tow with epoxy coating (sizing). Each CF monofilament has diameter of about 8 μm . The fibers were used as-received. The plasma reactor (15.5-cm-diam cylindrical enclosure made of Plexiglas) operates in air with essentially uniform electric field, generating DBD between two circular aluminum electrodes with diameter of 9.5 cm. The bottom reactor electrode was connected to a high-voltage source while the upper electrode was grounded. The power supply consists of a high-voltage transformer (V_{rms} 110/20000), powered by an auto transformer Variac operating at frequency of 60 Hz. A high voltage resistance (1 k Ω) protects the transformer in the event of electric arc. Both reactor electrodes were covered by dielectric barriers. The dielectric used was Mylar[®] with a thickness of 0.5mm. The distance between the electrodes was set at 2.5 mm for all treatments. CF samples with area of 5.0x5.0 cm² were placed on the dielectric layer covering the bottom electrode. The DBD consists of large number of filamentary discharges randomly distributed over entire dielectric. Time for plasma treatment was set at 2, 5, 7.5 and 10 minutes while the voltage magnitude was kept the fixed at 35 kV peak to peak.

3. Results and discussions

3.1. Electric Measurements of DBD reactor

The discharge current was obtained through measuring the potential drop across a serial resistor of 1200 Ω . The voltage applied on the reactor was measured by a 1000:1 high-voltage probe (Tektronix P6015A) and displayed on a digital oscilloscope (Tektronix TDS 2024B). Figure 1 shows the typical waveforms of DBD voltage and current.

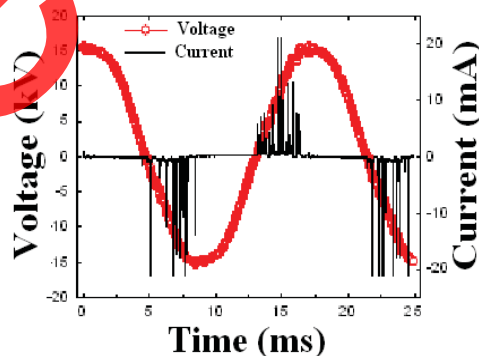


Figure 1: Typical waveforms of DBD voltage and current.

The charge transported in the discharges was calculated from the measurement of potential drop on a serial capacitor of 0.91 μF .

The charge $Q(t)$ stored on the electrodes is represented as a function of $V(t)$ for one period to form so-called Lissajous figure (see figure 2). In case of filamentary DBD driven by a sinusoidal power source the typical shape of its Q - V curve is a parallelogram. The area enclosed by the Lissajous figure gives the electrical energy consumed for voltage cycle. The discharge power of 6.6W was then calculated by multiplying the electrical energy by the frequency of the applied voltage (60 Hz).

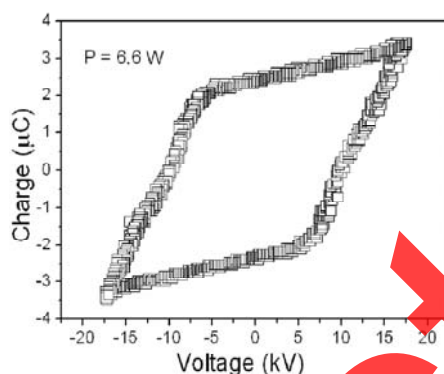


Figure 2: Lissajous figure ($Q \times V$) of DBD

Discharge power as a function of the applied ac voltage is presented in figure 3. Beyond the onset voltage of 11 kV the discharge power scales linearly with the voltage amplitude. This linear behavior is a typical feature of DBDs.

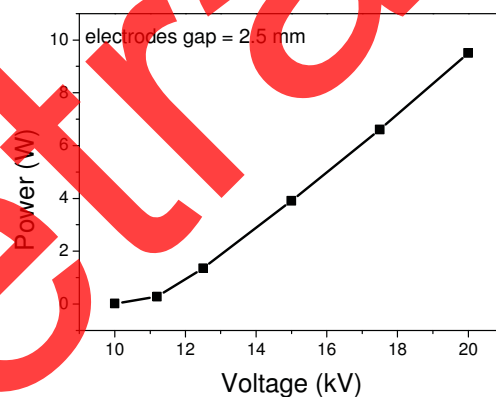


Figure 3: Power as a function of the applied a.c. voltage in DBD reactor.

3.2 Scanning electron microscopy analysis (SEM)

The effect of DBD on surface morphology of the carbon fibers was investigated by SEM analysis. Figure 4 depicts the images of the treated and untreated samples. The micrograph of the untreated sample shows many thin tracks aligned along each fiber. This characteristic of CF was also observed by other authors [8] and was attributed to the wet spinning process employed to produce the polyacrylonitrile (PAN) filaments used as raw material in carbon fiber processing. SEM of the sample treated during 2 min reveals many small particles distributed over entire surface of the fiber. These particles are product of the fibers surface etching during the DBD treatment that removes the epoxy

layer covering as-received samples. As the DBD-treatment time increases the quantity of epoxy covering removed by the DBD also increases.

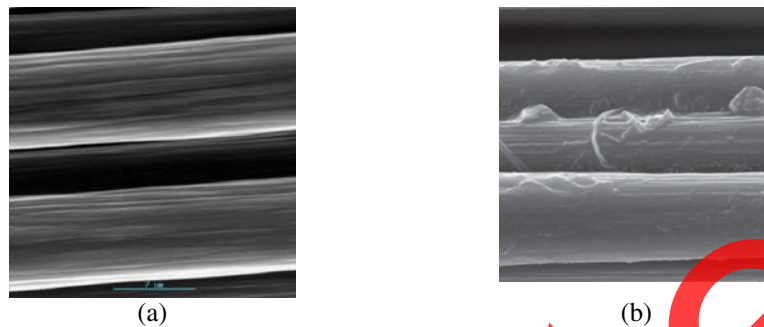


Figure 4: SEM images of carbon fibers: a) untreated sample; b) DBD treated sample

This kind of carbon fiber surface layer etching was also reported by other authors [1-10] after using RF plasma processing. The alteration of CF surface morphology was also confirmed by the AFM analysis.

3.3 Atomic Force Microscope analysis (AFM)

Results from AFM analysis indicate that the carbon fiber roughness increases as a result of the plasma treatment. Figure 5 and table 1 present the AFM images and the rms roughness values (R_q) of the untreated and treated specimens, respectively. The analyzed area was $64 \mu\text{m}^2$.

The samples treated during 2 and 5 min showed up to two-fold increase of their roughness in comparison with the untreated fiber ($R_q=14 \text{ nm}$). This CF roughness enhancement would result in a better adhesion between the polymer matrix and the carbon fibers by enlarging the surface area, which provides more points of contact/anchorage between the fiber and the matrix [9].

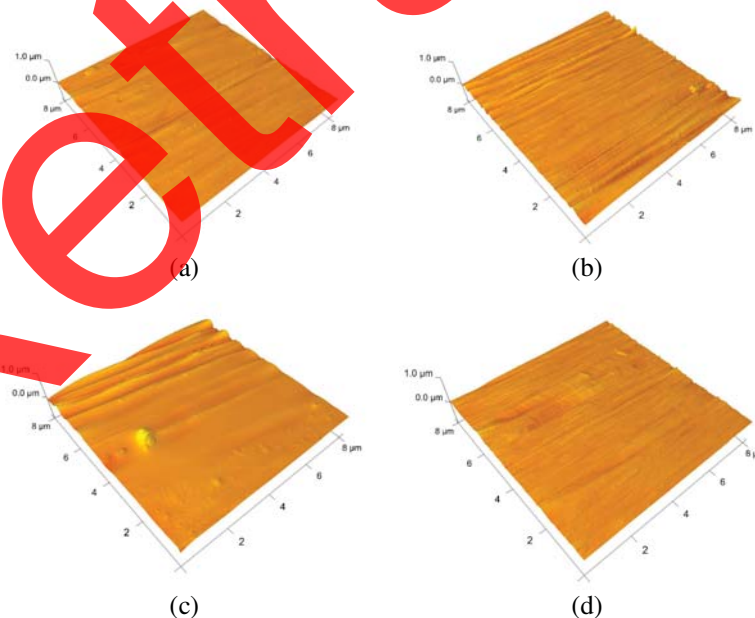


Figure 5: AFM images of the carbon fibers: a) untreated sample; DBD – treated samples b) 2min. c) 5min d) 10min

However the sample treated at 10 minutes shows roughness increase of only 20% in comparison with the standard specimen. This finding can be explained by the fact that during the first several minutes of treatment the soft epoxy layer covering the CF had been already removed and after that the etching goes on the naked CF with lower etching rate.

Table 1: Roughness values from AFM analysis.

Treatment time (min.)	Roughness – Rq (nm)
As received	14.0
2	26.7
5	29.5
10	17.3

This result suggests that there exists an optimal processing time (on the order of 5min) which would favor good adhesion between two phases of composite material. Longer DBD treatment times cause decreasing of the CF surface roughness. Additionally, decrease of the mechanical resistance of the CF fiber can be expected due to the excessive etching. Further mechanical tests will be imperative to prove this.

3.4 Photoelectron Spectroscopy (XPS)

Analysis of the CFs chemical composition, provided by the XPS analysis, showed that plasma treatment incorporate oxygen and nitrogen atoms onto the surface. The O/C and N/C ratios of CFs are shown in table 2. The increase of the treatment time leads to more incorporation of O on the surface. The polar oxygen and nitrogen radicals formed on the surface will lead to increasing of the CF surface energy.

Table 2: Atomic percentage of the bond specimens from XPS analysis

	C1 C-C or C-H	C2 C-O	C3 C=O	C4 O-C=O	O/C	N/C
As received	62	28	10	0	0.24	0
2 minutes	43	41	10	6	0.49	0.075
10 minutes	35	44	11	10	0.6	0.081

To trace the effect of plasma treatment on CF surface the C 1s peak was investigated in details. Figure 6 depicts the deconvolution of C 1s peaks of untreated and plasma treated CFs. The as-received CF's peak was resolved into 3 contributions, whose binding energies are presented in figure 6. As a result of the plasma exposure the C1 peak decreases while C2 peak increases and a new contribution C4 at 289.7 eV due to O-C=O bonding appears. Table 2 presents the relative area of each contribution together with its assignment.

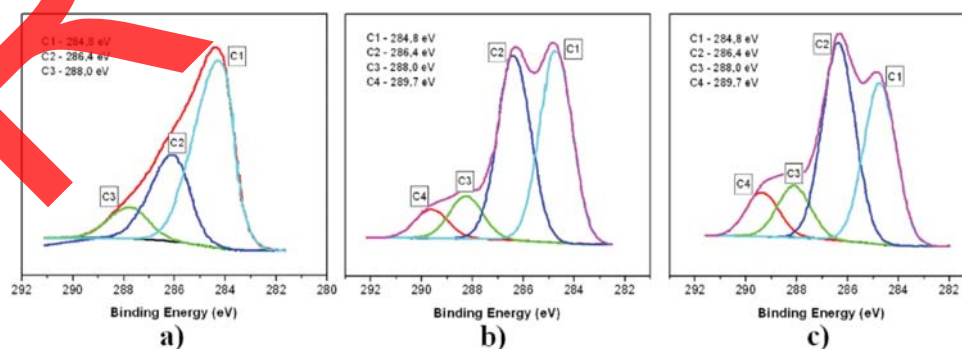


Figure 6: XPS of carbon fibers: a) untreated sample; DBD – treated samples b) 2min. c) 10min.

The N atoms detected on the surface of DBD-treated CF probably come from two sources: first the DBD discharge in air and in second place from the fiber itself. The polyacrylonitrile (PAN), which contains nitrogen, was used as fiber pre-cursor in the fiber manufacturing process. As long as the plasma treatment removes the epoxy layer and uncovers the CF naked surface the XPS analysis starts detecting N atoms from the fiber precursor.

From the XPS analysis one can conclude that oxygen atoms were efficiently incorporated on the surface of the treated fibers mainly in the form of C-O and O-C=O bondings. It was also observed a considerable increase of the O/C ratio (up to 250% for 10 min. DBD treatment). The polar oxygen radicals formed on the surface lead to increasing of the CF surface energy. Both, the modification of surface roughness and the surface oxidation contribute for enhancement of CF adhesion properties. These results are in agreement with the results of J. Li [3] that presents a significant increase in oxygen and nitrogen concentration after the CF treatment with DBD at atmospheric pressure.

4. Conclusion

Carbon fibers were treated by DBD varying the treatment time while the applied voltage was fixed. SEM and AFM images showed surface morphological modifications of the carbon fibers after DBD process that resulted in two-fold increase of the roughness in comparison with the untreated sample (14 nm). XPS results determined that oxygen atoms were incorporated on the surface of the treated carbon fibers. Both the increase of surface roughness and the surface oxidation contribute for enhancement of CF adhesion properties.

Acknowledgments

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