SURFACE TREATMENT OF PITCH-BASED DISCONTINUOUS CARBON FIBERS

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ABSTRACT

Given the exponential growth in carbon fiber products, it is both environmentally and economically practical to recycle carbon fibers. Instead of being disposed in landfills, recycled carbon fibers can fill the anticipated gap between supply and demand, especially because the production costs of carbon fibers remain high. One of the barriers to reintroducing recovered and recycled carbon fibers is the lack of an efficient method for surface treating reclaimed chopped fibers that have undergone recycling processes (e.g. pyrolysis) that leave the fiber surface essentially without functional groups that are required to ensure good fiber-matrix adhesion. For example, discontinuous fibers cannot be surface treated using conventional roll-to-roll electrochemical surface treatments that are used for continuous pitch- and poly(acrylonitrile)-based fibers. In this presentation, we describe novel methods for applying surface treatments to these discontinuous fibers via both electrochemical and wet chemical means. Changes in surface chemistry, and surface topology were quantified/monitored using X-ray photoelectron spectroscopy, and scanning electron microscopy. Specifically, we demonstrate broad control over surface oxygen and nitrogen concentrations and demonstrate that these are similar to those achieved via conventional surface treatments of continuous fibers by varying processing conditions (e.g., temperature, electrolyte concentration, ionic conductivity, reagent composition). Overall, our new method provides a scalable, effective means of surface treatment for discontinuous carbon fibers.

1. INTRODUCTION

Because of the recent and continuing exponential growth of carbon fiber products, it is both environmentally and economically practical to recycle carbon fibers [1]. Recycled carbon fibers can fill the anticipated gap between supply and demand, which would result from the high production costs of carbon fibers. A major barrier to reintroducing recovered and recycled carbon fibers is the lack of an efficient method for surface treating reclaimed chopped fibers that have undergone pyrolysis and other recycling processes that leave the fiber surface essentially without functional groups needed for good fiber-matrix adhesion. For example, discontinuous fibers cannot be treated using conventional roll-to-roll electrochemical surface treatments that are used for continuous pitch- and poly(acrylonitrile)-based fibers [2]. Because of their relatively fast and uniform treatment, electrochemical methods for discontinuous fibers have already been

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developed for carbon fiber tows and filaments [3−5]. However, these methods are not scalable or would damage fibers that are longer than filaments.

Herein, we describe a novel and scalable electrochemical method for surface treatment of discontinuous, pitched-based carbon fibers. Changes in surface chemistry and topology were quantified/monitored using X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). Single fiber tensile tests were performed to assess the effects of the electrochemical treatment on tensile properties.

2. EXPERIMENTATION

Untreated, de-sized discontinuous chopped carbon fibers (pitch-based, K223HE) with lengths 6 mm and 25 mm were obtained from Mitsubishi Chemical Carbon Fiber and Composites. Platinum mesh (2.54 cm x 2.54 cm) electrodes were purchased from Ametek Scientific Instruments, Mueller BU-60C alligator clips were obtained from McMaster-Carr, and carbon felt was purchased from Metaullics Systems Company, L.P. Electrolyte solutions were prepared from ammonium bicarbonate (≥99.5 %, Sigma Aldrich) and Milli-Q water (18 MΩ·cm^{-1}). Teflon tape (12.7 mm width x 0.07 μm thickness) was purchased from ULINE.

Electrochemical surface treatment was performed according to Figure 1, and a Laboratory DC Power Supply Model 4025 was used to apply voltage. Experiments were performed for 10 min. under varying applied voltages (1−18 V). These experiments were non-isothermal. The resulting fibers were thrice washed with Milli-Q water (18 MΩ·cm^{-1}) and filtered, followed by drying under vacuum overnight at 100 °C.

Table 1. Processing conditions and surface elemental compositions based on x-ray photoelectron spectroscopy

experiment	Time at anode (min)	Time at cathode (min)	Electrolyte concentration (M)	Applied voltage (V)	T (°C)	%C	%O	%N
Bare	---	---	---	---	---	98.7	1.3	0
1	10	0	0.5	4	21.0	90.8	6.5	2.7
2	10	0	0.5	21	19.5	87.6	5.2	7.2
3	5	5	0.5	16	22.0	85.7	9.4	5.0

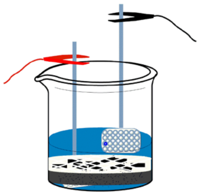

Figure 1. Experimental apparatus for electrochemical treatment of discontinuous carbon fibers.

Conventional XPS was performed on a Physical Elec-tronics VersaProbeII, using a monochromatic Al Kα X-ray source. High resolution scans were obtained for C 1*s*, N 1*s*, and O 1*s* regions with a pass energy of 23.5 eV, a 0.05 eV step size, and averaging of 3-6 scans. All regions were calibrated to the aliphatic component of the C 1*s* peak centered at 284.8 eV. XPS curve fitting was performed using CasaXPS software.

Scanning electron microscopy (SEM) was performed on a Hitachi S-4700 at an accelerating voltage of 5 kV. Prior to imaging, samples were sputtered with an approximately 2 nm thick coating of iridium.

Single fiber tensile tests were performed on 25 mm long carbon fibers using an automatic single-fiber test system (Favimat, Textechno H. Stein GmbH & Co. KG, Germany). The experiments were performed using grips supplied with the Favimat that are designed to grip carbon fibers between surfaces of hard and soft rubber. Testing parameters include a pretension of 0.5 cN/tex, a displacement rate of 0.9 mm/min, a gauge length of 15 mm, a load cell capacity of 210 cN, a force resolution of 0.0001 cN, a maximum possible travel of 100mm, and an elongation resolution of 0.1 µm. Single fibers were loaded directly into the Favimat's grips without the assistance of paper or cardstock tabbing. Eleven tests are reported for the untreated fibers, and twenty-one tests are reported for treated fibers. Physical properties, including diameter, break strength, and initial modulus, were collected from the software program included with the Favimat, Textechno35 (Version 3.0.3547).

3. RESULTS

Proof-of-concept for electrochemical treatment of multiple discontinuous carbon fibers were confirmed by X-ray photoelectron spectroscopy (XPS). Starting at an applied voltage of 4 V, significant increases in the surface atomic concentrations of oxygen and nitrogen were observed after only 10 min. of anodic oxidation in ammonium bicarbonate solution (aq., 0.5 M) and initial temperature of ~23 °C (Figure 2).

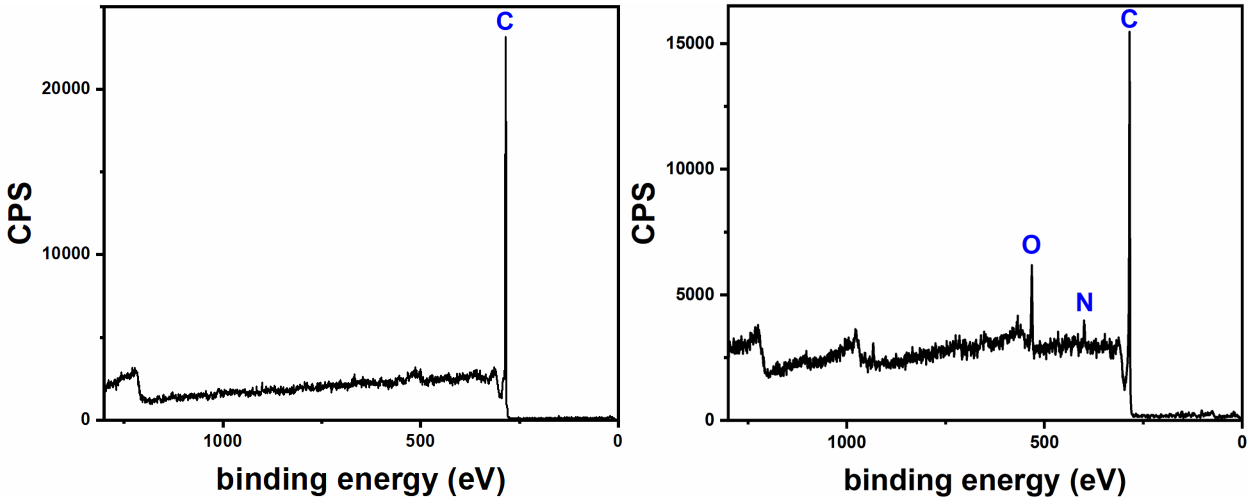

Figure 2. XPS survey scans of untreated (left) and electrochemically treated (right) discontinuous fibers.

Scanning electron microscopy (SEM) images indicate no obvious surface damage for fibers that were electrochemically treated (see experimental details above) up to an applied voltage of 21 V (Figure 3). Moreover, single fiber tensile tests confirmed that our electrochemical method did not adversely affect the tensile properties of carbon fibers because the tensile strength for untreated and treated fibers (at 16 V) were statistically indistinguishable.

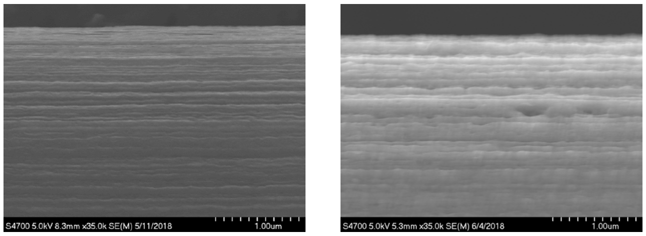

Figure 3. SEM micrographs (x35 k) of discontinuous carbon fibers (left) without treatment and (right) electrochemically treated with ammonium bicarbonate (0.5 M in water, 10 min. anodic oxidation, and applied voltage of 21 V).

The oxygen-to-nitrogen (O:N) ratio as well as the total surface contents of oxygen and nitrogen are highly tunable. Figure 4 illustrates that oxygen-rich surfaces are favored at relatively low voltages (e.g. 4 V) while nitrogen-rich surfaces are favored at relatively high voltages (e.g. 21 V). The O:N ratio changed from ~7:3 to ~2:3 when the applied voltage increased from 4 to 21 V. As expected, higher loading of oxygen and nitrogen were observed with increasing applied voltages but that trend eventually levels off at approximately 15 atomic %.

Optimization of the electrochemical processing parameters led to surface contents (i.e., 85.7 %C, 9.4 %O, and 5.0 %N) that are similar to those of commercially available PAN-based fibers.

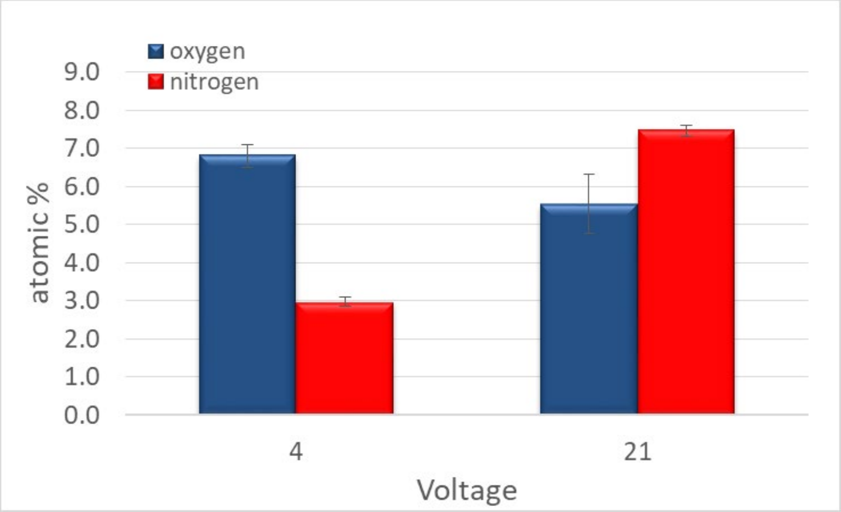

Figure 4. Atomic % of oxygen and nitrogen on carbon fiber surfaces following 10 min. anodic oxidation in ammonium bicarbonate (aq., 0.5 M) at starting temperature of ~23 °C.

4. CONCLUSIONS

We developed a scalable and reproducible electrochemical method for surface treatment of discontinuous carbon fibers. Based on SEM and single fiber tensile tests, our electrochemical method does not cause obvious surface damage nor adversely affect the tensile properties of carbon fibers.

Broad control over O:N ratio and total surface functionalization can be achieved by varying the electrochemical parameters. Low applied voltages (~4 V) tend to favor oxygen-rich surfaces whereas higher applied voltages (~21 V) tend to favor nitrogen-rich surfaces. The total surface contents of oxygen and nitrogen levels off at approximately 15 atomic % for all tested parameters. More details will be available in upcoming publications.

5. REFERENCES

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