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Influence of surface defects on the tensile strength of carbon fibers

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ABSTRACT

The mechanical properties of carbon fibers, especially their tensile properties, are affected by internal and surface defects. In order to asses in what extent the generation of surface defects can result in a loss of the mechanical properties, non-surface treated carbon fibers were oxidized with three different surface treatment processes: electro-chemical oxidation, oxidation in nitric acid, and oxidation in oxygen plasma. Different surface topographies and surface chemistries were obtained, as well as different types and densities of surface defects. The density of surface defects was measured with both a physical approach (Raman spectroscopy) and a chemical approach (Active Surface Area). The tensile properties were evaluated by determining the Weibull modulus and the scale parameter of each reference, after measuring the tensile strength for four different gauge lengths. A relationship between the tensile properties and the nature and density of surface defects was noticed, as large defects largely control the value of the tensile strength. When optimized, some oxidation surface treatment processes can generate surface functional groups as well as an increase of the mechanical properties of the fibers, because of the removal of the contamination layer of pyrolytic carbon generated during the carbonization of the polyacrylonitrile precursor. Oxidation in oxygen plasma revealed to be a promising technology for alternative surface treatment processes, as high levels of functionalization were achieved and a slight improvement of the mechanical properties was obtained too.

1. Introduction

Carbon fibers are widely used in applications requiring outstanding mechanical properties associated to a low density. That is why carbon fiber reinforced composites are more and more used in aerospace, aeronautics, sport and recreation goods. Moreover, with the recent development of more cost-effective carbon fibers, the range of applications could also be extended to the automotive industry. Carbon fibers can be made from different precursors (rayon, mesophase pitch, polyacrylonitrile, polyethylene, and lignin) but the precursor that is mostly used currently is polyacrylonitrile (PAN). The manufacture of carbon fibers involves several steps which are the spinning of the precursor followed by stabilization, oxidation and carbonization. After the carbonization, post-treatments including surface oxidation treatment and sizing are applied, and they can be specifically designed for the type of matrix the fibers will be impregnated with. The oxidative surface treatment aims at removing low cohesion pyrolytic carbon produced during the carbonization step that could generate some defects at the interface with the matrix, thus damaging the mechanical properties of the corresponding composite. It also aims at generating oxygen (and eventually nitrogen)-containing surface functionalities in order to optimize the density of interactions at the interface (physical and chemical interactions), which can increase the wetting of the carbon fiber surface by the matrix and the interfacial adhesion, thus potentially improving the mechanical properties of the resulting composite. Different processes have been developed for the surface oxidation of carbon fibers: treatment at high temperature in an oxidative gas phase (air [1], oxygen [2], ozone [3]) or in an inert gas after impregnation of the fiber with an oxidizing solution [4], or treatment in an oxidizing solution like strong acids, hydrogen peroxide, potassium dichromate, potassium permanganate or sodium hypochlorite [5]. The use for electrochemistry is still widely used, especially for the industrial production of carbon fibers. That is why an impressive number of electrolytes have been tested: phosphoric acid [6], sulfuric acid [7], alkaline solutions [8], ammonium salts [9], dichromate salts [10], nitrate salts [11], etc. When salts are used, a thorough rinse with distilled water has to be performed to avoid remaining surface contamination with carbonate, sodium, chlorate and calcium ions [12].

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Oxidation by plasma treatment was also investigated with different gas like air [13], oxygen [14], carbon dioxide [15]. Finally, radiation techniques generating radicals at the fiber surface that react with the surrounding atmosphere gave interesting results in the case of UV–ozone [16], γ radiation [17], and electron [18] and ion beams [19]. One important rule about the design of carbon fiber surface treatments is that it should not lead to a severe decrease of the mechanical properties because of the generation of surface defects. In this study, the surfaces generated by different types of fiber oxidative surface treatment (electrochemical, boiling nitric acid, oxygen plasma) are characterized by atomic force microscopy (AFM), gas adsorption and BET analysis, Raman spectroscopy and the measurement of the active surface area (ASA). The mechanical properties of the fibers are assessed by the measurement of the tensile strength of single fibers at different gauge lengths and a correlation between the tensile strength of the fibers and the type of defects created at their surface is proposed. This study also highlights the fact that plasma surface treatments are potentially more effective in generating surfaces with a high density of functionalization and without the loss of tensile strength.

2. Materials and methods

2.1. Oxidation of carbon fiber surfaces by different processes

2.1.1. Carbon fibers

The intermediate modulus PAN-based Tenax® IMS 5000 (12 k) carbon fibers used in this study were produced by Toho Tenax Europe GmbH. These fibers were not surface treated and not sized.

2.1.2. Oxidation processes

In order to generate sharp differences in terms of surface chemistry (density of oxygen-containing functional groups) and topography, IMS 5000 fibers were surface treated by different types of oxidative treatments.

IMS 5001 fibers were IMS 5000 fibers surface treated by the manufacturer's electrochemical process, which details are not revealed here for proprietary reasons. A full description of the surface properties, including properties that will not be given in this study (surface chemistry and surface energy) can be found elsewhere [20].

IMS 5000 fibers were oxidized in concentrated boiling nitric acid (70%) for times ranging from 10 min to 2 h, rinsed and extracted in distilled water with a Soxhlet extractor. The complete description of the preparation of those samples and their surface properties including surface chemistry and surface energy was given in a previous study [21].

IMS 5000 were also surface treated by oxygen plasma for 1 min with different incident powers from 1 W to 120 W. The complete description of the preparation, the surface chemistry, and the surface energy of those fibers was also reported previously [22].

2.2. Characterization of surface topography, surface graphitic structure and surface defects

2.2.1. Characterization of the topography at a nanometric scale

Atomic force microscopy (AFM) imaging was performed using a Veeco D3000 atomic force microscope in tapping mode and controlled by the software Nanoscope III. AFM tips with an aluminum reflex coating Tap300Al-G from Budget Sensors were used. Single fibers were deposited on some double-side adhesive tape that was covering the sample holder. Images of 1 μm × 1 μm were obtained.

2.2.2. Investigation of the graphitic structure of the carbon fiber surface by Raman spectroscopy

Raman analysis was conducted with an Olympus BX40 confocal Raman spectrometer equipped a motorized three-axis *XYZ* mapping stage and controlled by the software Labspec. The wavelength of the laser was 632.81 nm and the power was fixed at 2.7 mW. The laser was focused with a 50× magnification objective, giving a spot which diameter was 1 μm. Confocal spectra were accumulated in the 500–3000 cm^{-1} range. The characterization of each sample involved the analysis of 20 different single fibers. The analysis of each single fiber was the result of the average of three spectra corresponding to different areas of the fiber surface. For each spectrum, the accumulation time was 30 s. The depth of analysis in the material was estimated to be 100 nm. Before analysis, the spectral calibration was done with the 520.5 cm^{-1} transverse optical phonon–phonon mode peak of a Si wafer reference.

The fitting of the spectrum between 800 cm^{-1} and 1800 cm^{-1} involved four components: a peak located at 1600 cm^{-1} (G peak) due to graphitic in plane vibrations with E2g symmetry, a peak located at 1350 cm^{-1} (D peak) due to a vibration with A1g symmetry and existing only because of the disorder existing in the graphitic lattice (increase of the ratio edge plans/basal plans, decrease of the size of the crystallites, grain boundaries, amorphous carbon, doping), a peak located at 1200 cm^{-1} corresponding to C–H covalent bonds (referred as C–H peak in the following) and a peak located at 1500 cm^{-1} due to heteroatoms and sp^2 carbon atoms located in defects and in amorphous phase (D″ peak). A straight line was used as the base line and all four components of the spectra were mixes of Gaussian and Lorentzian curves. The location of the peaks was not fixed, so that the fitting could be as close as possible to the experimental spectra.

Raman spectroscopy is a widely used technique for the assessment of the disorder existing in the structure of carbon materials, whatever their origin and their level of graphitization [23]. Bessac et al. [24] listed all the precautions that have to be taken in order to use that technology for a quantitative analysis of the disorder existing in the structure of the surface of carbon fibers, especially the necessity of using a low power for the laser (less than 5 mW), because carbon fibers can be very sensitive to the heat generated by the laser. Otherwise, the location of the peaks can be affected.

2.2.3. Measurement of the active surface area (ASA)

The method was developed by Walker and al. [25] and is based on oxygen gas chemisorption. The analysis was performed with a vacuum system linked to a mass spectrometer. The fibers were hold in a fused silica tube and heated up to 950 °C with a linear heating rate of 10 °C min^{-1} and kept at 950 °C for 2 h and in vacuum (10^{-4} Pa) in order to clean the surface. Then, oxygen was chemisorbed at 300 °C during 10 h, with an initial pressure of 66.5 Pa, leading to the creation of oxygen-containing surface functionalities. Then, the functionalized fibers were heated up to 950 °C with a linear heating rate of 5 °C min^{-1}. The gas phase was continuously analyzed quantitatively by the mass spectrometer during the experiment. The amount of oxygen complexes formed was determined by measuring the amount of CO and CO_2 resulting from their decomposition. Considering that the area of an edge carbon site that chemisorbed an oxygen atom is 0.083 nm^2, it was possible to calculate the surface area occupied by chemisorbed oxygen.

2.3. Assessment of the mechanical properties by tensile testing on single fibers

The tensile strength of single fibers was measured according to ASTM C1557. The fiber was mounted on a slotted testing tab with the fiber aligned along the center of the tab. The fiber was secured at opposite ends of the slot with cyano-acrylate based glue. Care was