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Effect of Different Carbonization Heat Treatment on Textile PAN-based Carbon Fiber Functional Chemical Surface

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Abstract. *Textile PAN-based carbon fibers have been achieved great interest in the scientific community due to their attractive properties and variety of applications. The manufacturing process, consisting of three main steps: oxidation/stabilization, carbonization, and graphitization/activation, is already well known, however, there are other types of surface treatments being studied. Heat and chemical treatments can significantly improve and prepare the surface for other materials. Therefore, this work is the beginning of in-depth research on the surface treatments of the textile PAN-based carbon fiber and its influence on the capacitive processes of supercapacitor electrodes. It was identified that a simple variation of time and temperature significantly alters the surface chemical groups of the material.*

Keywords: Carbon fiber; Heat-treatment; Surface chemistry; Functional groups.

1. Introduction

Carbon fibers are filamentary materials that content more than 90% fix carbon. They have a planar atomic arrangement distributed in a hexagonal shape [JAMES, 1983; RAHAMAN; ISMAIL; MUSTAFA, 2007]. The performance of carbon fiber depends directly on its raw material. There are several raw material, but the main and most studied today are the PAN-based carbon fibers because of their properties [KHAYYAM et al., 2020; KOPEĆ et al., 2019; MAO et al., 2020]. In addition to the applications already known as reinforcement for composites, PAN-based (polyacrylonitrile based) fibers have been extensively studied in other areas such as filter antimicrobial [SIM et al., 2014], gas adsorption [FOURNEL et al., 2005], supercapacitor electrodes [RODRIGUES et al., 2019], biosensors [WANG; LI; RU, 2010], shielding electromagnetic radiation [DO AMARAL JUNIOR et al., 2019],

photocatalytic degradation of contaminants [GONG et al., 2016], and water treatment [LI et al., 2015].

To obtain a PAN-based carbon fiber or an activated carbon fiber, some steps are necessary. These steps consist of three main heat treatments, called are oxidation or stabilization, carbonization, and graphitization or activation [YUSOF; ISMAIL, 2012]. Each treatment is responsible for part of the transformation of the polymer into carbonaceous material: oxidation/stabilization, is to cross-link PAN chains and prepares the structure for the next step; carbonization, is the transformation of the linear chain into an aromatic chain; graphitization, is the ordering of the carbon structure making a graphite structure; activation, it can be employed instead of the graphitization, is a treatment used to improve the surface to create a microporous structure [YUSOF; ISMAIL, 2012].

In addition to heat treatments, there are chemical treatments used to chemically modify the surface of carbon fibers. The surface characteristics, such as chemical surface, surface area, and surface energy, influences the performance of the carbon fiber [PAMULA; ROUXHET, 2003]. Especially in supercapacitor applications, the chemical surface, and the chemical functional groups (nitrogenous groups) have a great contribution to the performance of the devices [RODRIGUES et al., 2019].

Therefore, in this work, we study the effect of different carbonization temperatures on the surface chemistry of textile PAN-based carbon fiber.

2. Methodology

A textile PAN-based fiber felt 5.0 dtex and 200 g/m^2 of grammage was used and was oxidized at 250 °C for 50 min, named the starting sample (0 ox). Part of the PAN fiber felt was oxidized at 250 °C for another 90 min, named 90 ox. The samples were carbonized in an argon atmosphere for 20 min at 700, 800, 900, and 1000 °C.

The samples were characterized by Raman spectrum to analyze carbonic structures after thermal processes, using a Horiba Scientific, model Labram Hr Evolution, 515 nm laser. The X-ray photoelectron spectra (XPS) were performed on a Kratos Axis Ultra XPS spectrometer, using monochromatic radiation (Al-Kα 1486.6 eV), realized in a high vacuum (7 x 10^{-9}). XPS analysis gives all the information about the superficial chemical surface characteristics and functional groups of the samples.

3. Results and Discussion

Figure 1 presents the Raman shift of the samples treated at different times of the oxidation process and carbonization temperature. Both, Figure 1a and 1b, shows the characteristics of carbon bands, about 1350 and 1660 cm^{-1}. These bands are associated with the degree of structure disorder (band D), or defects, and to the degree of ordering (band G), or graffiti, respectively. All samples behave as classical amorphous structure material [SHIMODAIRA; MASUI, 2002].

Analyzing the Raman spectra, it is possible to identify that the samples carbonized at higher temperatures have a thinner D band. This is due to the greater degree of graphitization caused by the higher temperatures. On the other hand, samples with lower carbonization temperatures have a thicker D band. This was already expected, since heat

treatment at high temperatures is applied to carbon materials to eliminate heteroatoms from the structure and consequently improve the graphitic structure of the material [RAHAMAN; ISMAIL; MUSTAFA, 2007; WANG et al., 2006].

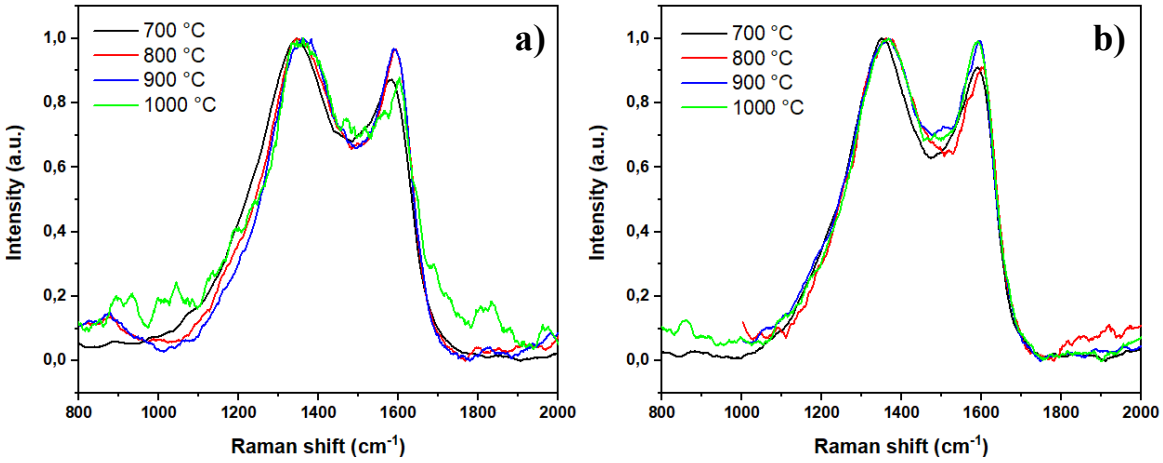

Figure 1. Raman spectra of samples (a) 0 ox, and (b) 90 ox.

To analyze possible variations or changes in the surface chemistry of the samples, an analysis of X-ray photoelectron spectra (XPS) spectra was performed. The XPS analysis was able to identify the main elements and their respective concentrations, present on the surface of each sample, such as C1s, O1s, and N1s. Figure 2 shows the concentration of each element under the carbonization temperature, in each oxidation time.

Through the XPS technique, it was possible to identify the main chemical bonds and the main functional groups for each element. The C-C bond (Figure 2a and 2b) is related to the graphitic carbon. As presented in Raman (Figure 1), the increase in temperature carbonization process increased the concentration of C-C bonds, therefore, the graphitization of the material increased [WANG et al., 2006]. The other groups are related to common bonds found in carbon fibers [RODRIGUES et al., 2019; WANG et al., 2006]. The O1s spectra (Figure 2c and 2d) presents the oxygen groups accordantly with the literature [PAMULA; ROUXHET, 2003]. In all cases, C1s, O1s, and N1s, there was variation in the concentration of the elements with the increase in the carbonization temperature. However, the variation is small in most cases, and in other cases, some groups do not appear at higher temperatures. This is the case with pyridine oxide, which only appears in the 700 °C sample, in both oxidation times. There is also a tendency to decrease the concentration of the pyridine group and increase the quaternary group. Pyridine and quaternary groups are related to pseudocapacitive processes in supercapacitor electrodes that is, better performance of the supercapacitors [RODRIGUES et al., 2019].

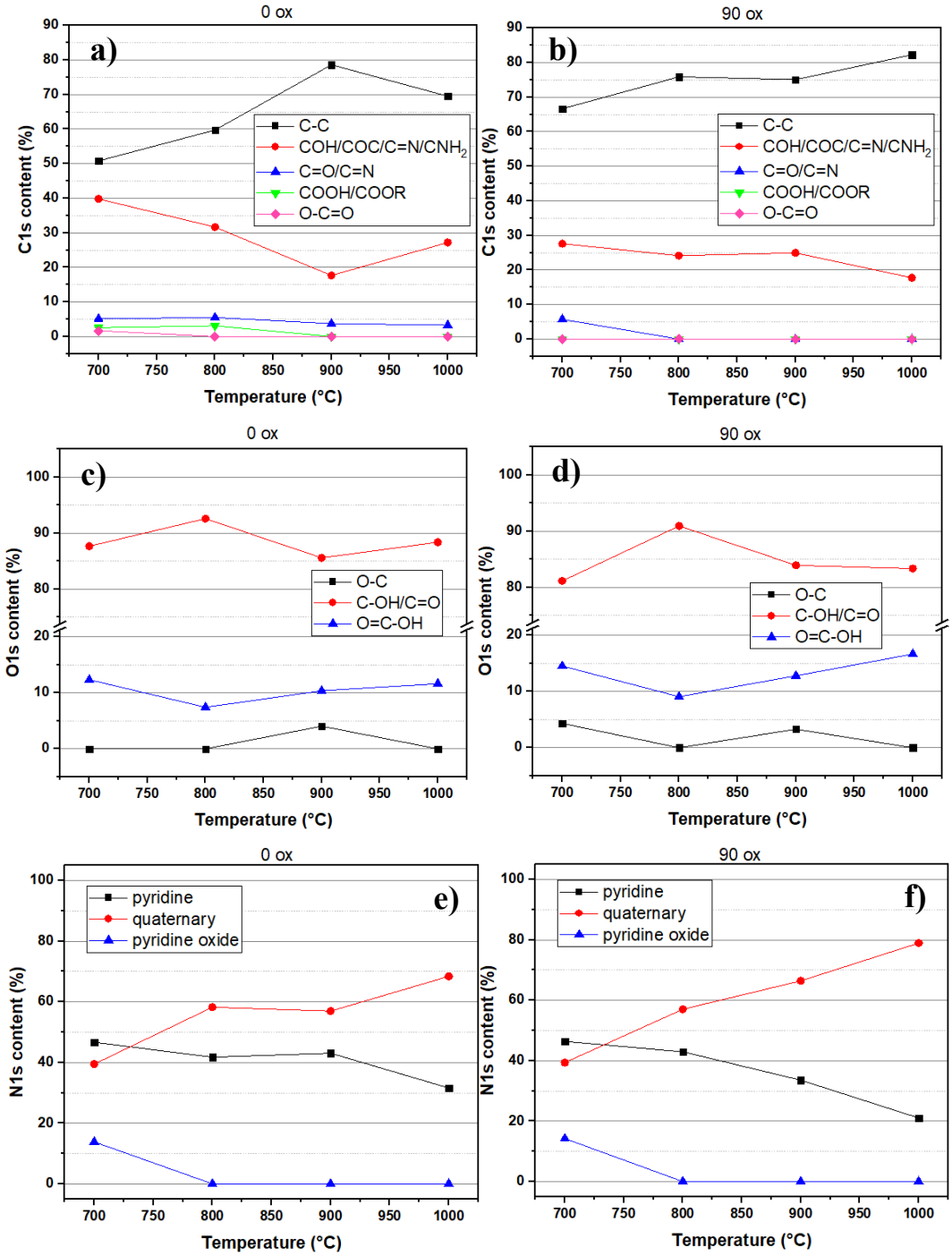

Figure 2. XPS element content: (a) C1s, (c) O1s, and (e) N1s of the 0 ox samples, and (b) C1s, (d) O1s, and (f) N1s of the 90 ox samples.

4. Conclusion

Textile PAN-based carbon fiber was used and the thermal oxidation times and carbonization temperatures were varied. The purpose of these heat treatments was to study changes in the

surface of the samples. The Raman analyzes, as expected, showed that there was an increase in the degree of graphitization with the increase in temperature, which was confirmed by the XPS analyzes. Both, the oxidation time and the carbonization temperature variations, changed the surface groups of the materials. Such information is valuable for the studies that will follow, so it will be possible to manufacture a carbon fiber that best responds to the application as a supercapacitor electrode.

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