Localized surface grafting reactions on carbon nanofibers induced by gamma and e-beam irradiation

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ABSTRACT

Electron beam and gamma-ray irradiation have potential application to modify the carbon fiber nano-structures in order to produce useful defects in the graphitic structure and create reactive sites. In this study, the methodology to functionalize carbon nanofiber (CNF), via a radiation process and using acrylic acid as a source of oxygen functional groups, was investigated. The samples were submitted to a direct grafting radiation process with electron beam and gamma-ray source. Several parameters were changed such as: acrylic acid concentration, radiation dose and percentage of inhibitor necessary to achieve functionalization, with higher percentage of oxygen functional groups on CNF surface, and better dispersion. The better results achieved were when mixing CNF in a solution of acrylic acid with 6% of inhibitor (FeSO$_4$·7H$_2$O) and irradiated at 100 kGy. The samples were characterized by X-ray photoelectron spectroscopy and the surface composition (atomic%) showed a significant increase of oxygen content for the samples after irradiation. Also, the dispersion of the functionalized CNF in water was stable during months which may be a good indication that the functionalization process of CNF via ionizing radiation was successful.

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1. Introduction

Carbon nanofibers (CNFs) are being thoroughly investigated for application in structural composites for the aerospace industry. This requires careful control of their surfaces to promote properties required for end use because CNFs are not compatible with most polymers.

CNFs are cylindrical nanostructures composed of graphene layers that may take one of the several arrangements such as stacked cones. CNFs have also attracted attention in the last 10 years because they offer somewhat comparable electrical, mechanical, and thermal properties, at a lower production cost than SWCNTs and MWCNTs [1]. CNFs differ from SWCNTs and MWCNTs in the following respects: carbon nanofibers have an average diameter of 60–200 nm while carbon nanotubes have an average diameter of 10–20 nm, they are longer (30–100 μm) and they have a different surface morphology [2,3].

Advanced CNF–polymer nanocomposites can be obtained combining two specific properties: uniform dispersion of CNFs in the polymeric matrix and strong interfacial adhesion for efficient tension transfer from the polymeric matrix to the CNFs [4,5]. Likewise, CNFs without any surface treatment may have a weak interfacial adhesion with a polymeric matrix. Therefore, it is necessary to modify their surfaces through chemical or physical techniques to produce optimized polymer nanocomposites from a mechanical property view.

There are several methods to functionalize carbon-based materials and these modifications may promote changes in the (nanostructure) surface [6–12]. Some works investigate the impact of the process conditions on nanostructures and, consequently, on the technological applications of the final product. The main effects investigated are: composition of monomers and solvents employed in the functionalization [12–14], reaction temperature [12,15], additives [15], and dispersion of carbon materials in solvents and water [16–18].

Radiation process, with the aim to modify carbon-based materials, has been used for a long time and is a subject that still has plenty to be explored [19–26]. Ionizing radiation has high-enough energy to convert at least one neutral atom or a molecule into

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Sample name	Samples PR-25-PS-XT	Dose (kGy)		FeSO₄·7H₂O (%)
GA-1	Pristine	0	—	None
Blank-1	Pristine	0	—	1
Blank-2	Pristine	0	—	6
GA-11	Pristine	50	E-beam	6
GA-12	Pristine	100	E-beam	6
GA-13	Pristine	100	Gamma	6
GA-14	Pristine	100	Gamma	10
GA-16	Pristine	90	Gamma	6
GA-17	Pristine	90	E-beam	6
GA-18	E-beam pre-irradiated at 1000 kGy	90	E-beam	6

an ion pair. The energy employed by this radiation is localized in individual atoms or molecules, and it is sufficiently high to break and induce chemical reactions in a short period of time. This is the basic principle of using ionizing radiation to chemically modify materials. Therefore, radiation grafting polymerization may be an alternative way to induce surface modification, and it is a uniform, effective, and environment-friendly method. It can be conducted at room temperature and in gas, liquid, and solid-state phases. To date, there are some published papers related to radiation grafting polymerization to functionalize graphitic nanostructures [2,9,11] but this subject still draws some attention because several structural transformations may occur in carbon nanostructures under the irradiation process. Characterization, control, and reproducibility are still a challenge when particle size is in the nanometer range and it is not an easy task to compare methods of characterization which are usually not in agreement with each other.

The aim of this work was to investigate and to propose a methodology for functionalization of CNFs and compare two different methods to promote grafting reactions: gamma-ray and electron beam irradiation. Different parameters, such as inhibitor concentration in acrylic acid solution, were applied to the samples during the process to establish this methodology. X-ray photoelectron spectroscopy (XPS) was used to evaluate the functionalization degree and the rearrangement of the Csp^2 hybridization of the CNFs after irradiation processes, comparing the two methods tested. Raman spectroscopy was used to investigate the nanostructure of carbon samples after irradiation and is a usual nondestructive tool for structural characterization of carbon materials.

2. Material and methods

2.1. Sample preparation

CNFs used in this study were obtained from Applied Sciences Inc. Cedarville Ohio (under licenses from General Motors Corp. and Applied Science Inc.) and they are manufactured in a continuous vapor phase growth process that contributes to a significantly lower cost compared to most carbon nanotubes, and they are readily available in large quantities and in several grades.

CNFs (PR-25-PS grade) were selected for the investigation in this work because, in a previous work, they showed to be less resistant under an electron beam process and it was possible to promote surface oxidation [26]. CNF has a chemically vapor deposited (CVD) layer of carbon on the surface of a graphitic tubular core fiber. CNFs are available in different grades. The PS grade is produced at 1100 °C by pyrolytically cleaning of the as-produced CNF, and to remove polyaromatic hydrocarbons from the surface.

Table 1 enrolls the samples submitted to the direct radiation grafting process. As-received PR-25-PS-XT samples were

weighted, and then immersed in solutions of 10% of acrylic acid (MERK/stabilized with 200 ppm of hydroquinone) with 1, 6 or 10% of inhibitor metal salt (FeSO₄·7H₂O). One part of the sample was poured into Petri dishes and irradiated with a direct accelerator operated by the Instituto de Pesquisas Energéticas e Nucleares (IPEN- São Paulo/Brazil). These samples were irradiated with an industrial electron accelerator Dynamitron, from Radiation Dynamics Inc., model DC 1500/25-JOB 188 operating with the following parameters: beam energy 1.5 MeV, pulse current 5.62 mA, 5 kGy/pass with a dose rate of 22.42 kGy/s. The other part of the sample, with the same amount of acrylic acid and FeSO₄·7H₂O, was irradiated by the gamma radiation process in a Cobalt-60 irradiator, Gammacell model 220, series 142, manufactured by Atomic Energy of Canada Limited whose activity is 64.946 TBq (1755.1 Ci)—06/2012. The Gammacell design provides uniform gamma field and the samples were irradiated at a dose rate of 1.48 kGy/h. The mixtures were purged with dry nitrogen for 10 min to remove dissolved oxygen and then sealed.

2.2. Characterization

The surface oxygen content of the nanofibers was characterized by X-ray Photoelectron Spectroscopy (XPS) analysis. The XPS analyses of GA-1, Blank-1, GA-12, GA-13, and GA-14 samples were conducted in a K-Alpha XPS equipment from Thermo Fisher Scientific, with a 400 μm X-ray spot size and with the low energy electron gun for charge neutralization system turned on. XPS survey spectra (0–1350 eV) were collected for all samples to provide qualitative and quantitative surface analysis information. XPS measurements of GA-1, Blank-2, GA-16, GA-17, and GA-18 samples were carried out at National Institute of Metrology, Quality and Technology (Inmetro). X-ray photoelectron spectroscopy (ESCAplus P System; Omicron Nanotechnology; Taunusstein, Germany) was used in order to study the chemical composition and chemical groups in carbon nanofibers before and after an irradiation process. The XPS analyses were performed using an Al Kα=1486.7 eV X-ray source, 10^{-10} mbar base pressure and 10^{-8} mbar during the analysis, with a 20 mA emission at a voltage of 13.5 kV. Survey spectra were acquired in the range of 1350–0 eV, step of–0.8 eV, dwell time of 0.2 s, and analyzer pass energy of 70 eV. For carbon, the high-resolution spectra were obtained with analyzer pass energy of 30 eV. No charging effects were observed (C 1s binding energy peak ~284.4 eV). The peak fitting was performed using the CasaXPS software. Before the peak fitting, the background was subtracted using a Shirley function. This software introduces the classical parameters (intensity, binding energy, line-width, Gaussian/Lorentzian mixing ratio) for symmetrical lines and the exponential tail parameters for asymmetrical ones. X-ray-excited Auger electron spectroscopy (X-AES) C KLL peaks were acquired in the kinetic range of 180–300 eV and using a step of −0.1 eV.

Raman analyses were carried out in a Renishaw InVia Reflex spectrometer equipped with a peltier cooled CCD and using an 1800 gr/mm grating. The samples were deposited onto a glass slide, and the spectra were collected using a 20x (NA 0.40) objective in a backscattering configuration. The excitation energy was 2.41 eV from the 514.5 nm line of an argon laser. Spot size was approximately 2 μm and low power (below 100 μW) was used in order to avoid sample graphitization. For each sample, a set of 10 spectra were collected at different points in the interval of 1050 to 1950 cm^{-1}. All the spectra were treated to subtract the background and the peaks were fitted using Lorentzian curves.

3. Results and discussion

Fig. 1 shows the results of the dispersion of the samples Blank-2, GA-16, GA-17, and GA-18. The samples were dispersed in water