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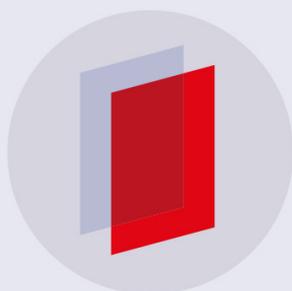
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Carbon nanofibers obtained from electrospinning process

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Abstract

In recent years, reinforcements consisting of carbon nanostructures, such as carbon nanotubes, fullerenes, graphenes, and carbon nanofibers have received significant attention due mainly to their chemical inertness and good mechanical, electrical and thermal properties. Since carbon nanofibers comprise a continuous reinforcing with high specific surface area, associated with the fact that they can be obtained at a low cost and in a large amount, they have shown to be advantageous compared to traditional carbon nanotubes. The main objective of this work is the processing of carbon nanofibers, using polyacrylonitrile (PAN) as a precursor, obtained by the electrospinning process via polymer solution, with subsequent use for airspace applications as reinforcement in polymer composites. In this work, firstly PAN nanofibers were produced by electrospinning with diameters in the range of (375 ± 85) nm, using a dimethylformamide solution. Using a furnace, the PAN nanofiber was converted into carbon nanofiber. Morphologies and structures of PAN and carbon nanofibers were investigated by scanning electron microscopy, Raman Spectroscopy, thermogravimetric analyses and differential scanning calorimeter. The resulting residual weight after carbonization was approximately 38% in weight, with a diameters reduction of 50%, and the same showed a carbon yield of 25%. From the analysis of the crystalline structure of the carbonized material, it was found that the material presented a disordered structure.

1. Introduction

Carbon materials present scientific and technological interests, due to their wide applicability in different areas of knowledge. These materials are mostly applied in airspace, automotive, marine, medical and electrochemical fields as well as in the nuclear industry [1, 2].

Carbon materials present advantageous properties, such as, chemical inertia, resistance to the most of common corrosive reagents and stability in a broad range temperatures under inert atmosphere (sublimating at 3900 K under atmospheric conditions and melting temperature at 4800 K). Furthermore, the carbon has a low density in comparison with metals and alloys, making it appropriate for compact and lightweight applications. Thus, among the carbon materials nowadays available can be cited carbon foam, carbon nanofibers, carbon nanotubes and carbon matrix composites [3–5].

As result of their excellent multifunctional properties and various technological applications, especially in airspace and biomedical fields, the processing of polymeric materials on micrometric and nanometric dimensions come lately, attracting more attention to specific purposes. Examples in this area are the carbon micro and nanofibers, which have been widely studied, because they present excellent thermal, electrical and mechanical properties. These fibers have good mechanical strength, good electrical and thermal conductivities, high temperature resistance, great chemical stability and wide surface area, and yet can be manufactured easily and in large quantities. The carbon micro and nanofibers also have the advantage of having low cost compared

with carbon nanotubes. Thus, these materials may be applied in several areas, including reinforcing materials, catalyst supports, high temperature filter, in orthopedic implants and others [6–9].

Still in the field of nanotechnology, which has shown an accelerated development in experimental area, we highlight contributions involving nanocomposites, cosmetics, flame resistant materials, materials with electro-optical and antibacterial properties, among others. Basically, the nanoscale is a transition zone between the macro and molecular levels. Nanocomposite materials appear as suitable alternatives to overcome the limitations of microcomposites. It is found that the interactions at the interfaces of composites are improved when there is the use of nanomaterials in the matrix of composites, with the consequent improving of their properties [10–13].

Inside in this context, the electrospinning via polymer solution has been considered an effective alternative to produce uniform and continuous micrometric and nanometric fibers. This technique highlights due to its easily of using and experimental condition control. In this process the polymer solution is in a capillary tube which is connected to an electrode and the same is coupled to a source of high voltage that can be positive or negative. At first, the solution displays a format of a drop at the end of the capillary. Then, the drop surface extends to produce a cone (called Taylor cone) as result of the increased voltage. Subsequently, a jet of solution is ejected. In this step, the solvent evaporates and the polymer solidifies, producing a fiber mat that is deposited on a metallic collector under grounding. During this process, some factors may influence the morphology and structure of micro and nanofibers produced. Among these the main processing parameter are: the applied voltage, the solution flow in the capillary, the concentration of polymer solution, and the working distance. The working distance is defined as the distance between the exit of solution and the collector [14–17].

Among the polymeric precursors used to manufacture carbon nanofibers through the electrospinning process may be considered the polyacrylonitrile (PAN), because it present a high carbon yield in the carbonization heat treatment and simple preparation process [6, 18].

This work has as objective the production of carbon nanofibers based on carbonization of PAN mat precursor, obtained by electrospinning process of polymer solution. In order to obtain the PAN nanofiber mat, a study concerning the main variables related to the electrospinning process to obtain micrometers and nanometers with homogeneous distribution and free of defects was done. The characterization of PAN mats considered the thermal behavior (by thermogravimetric and differential scanning calorimetry (DSC) analyses), morphological aspects (by scanning electron microscopy, SEM) and crystalline structure (by Raman spectroscopy).

2. Materials and methods

2.1. Materials
The PAN used in this work was supplied by Radici company in powder form. The dimethylformamide solvent (DMF), with concentration $\geqslant$99%, was supplied by Mallinckrodt Chemicals company.

2.2. The solution preparation
A solution containing 4%, 5% and 6% (wt/wt) of PAN in DMF was prepared. The homogenization of this solution was guaranteed by constant agitation for 3 h, at room temperature.

2.3. Electrospinning
The electrospinning system used in this work (figure 1) consists of a high voltage source (0–30 kV) the Faísca brand, a cylinder underground (collector) that is rotated by a gear motor the Tekno brand, MRT910 model (0–300 rpm) and a Tekno brand CVET2002 model controller, a glass syringe with 20 ml that has a stainless steel fitting and a stainless needle Hamilton type. To control the humidity during this process was used a dehumidifier Thermomatic brand, Desidrat Plus model and thermohygrometer watch Minipa brand MT-241 model. To quantify the cylinder speed was used a tachometer Minipa brand and MDT2238A model.

The parameters used in the processing of PAN blankets by electrospinning were: a stainless steel needle of 10 mm^{-1} long and 1.5 mm diameter, a cylinder rotation around 24 rpm, applied voltage range of 18.8–27.1 kV, working distance of 10 cm, humidity range of 35%–48%, room temperature range of 29.4–37.5 °C and collection time of 1, 2, 6 and 12 h. These parameters were stablished in a previous work of the research group [19]. The equipment used in the treatment of the mats does not have a control of solution flow. The exit of the solution of the needle tip is controlled by gravity (9.8 m s^{-2}).
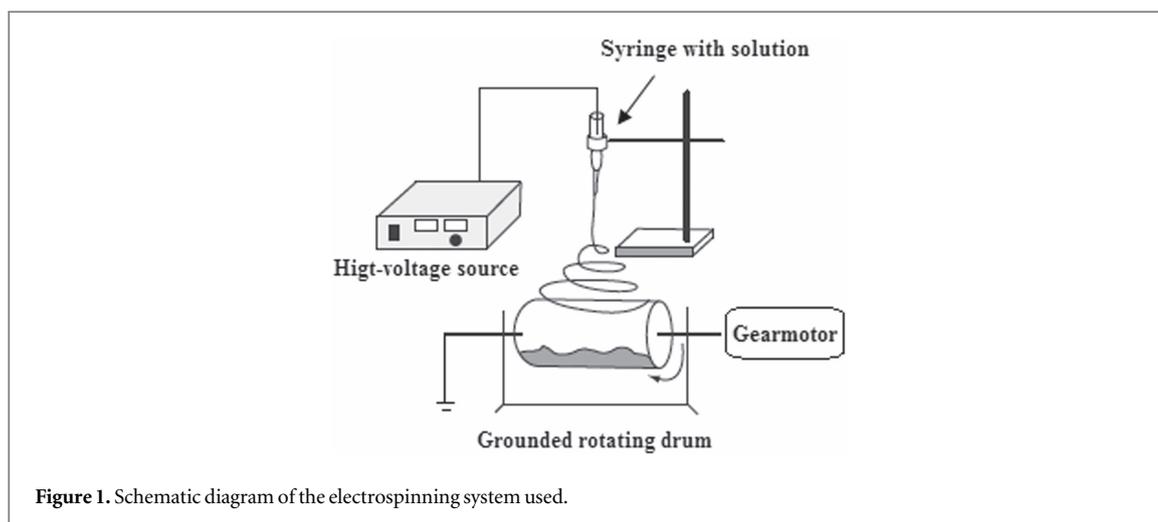
Figure 1. Schematic diagram of the electrospinning system used.

2.3.1. PAN characterization

The thermogravimetric analyses (TGA) were conducted in a SEIKO SII Nanotechnology equipment, EXSTAR 6000 (TG/DTG6200) model, using about 8 mg of PAN mat in a platinum pan, at a heating rate of 15 °C min^{-1}, under a nitrogen flow of 100 ml min^{-1}, in the temperature range of 30–1000 °C.

The DSC analyses were performed in a TA Instruments equipment, Q20 series, with controlled nitrogen flow of 40 ml min^{-1}, using approximately 5.7 mg of PAN mat, and the heating rate of 10 °C min^{-1}, in the temperature range of 25–400 °C.

The morphological analyses of nanofibers were performed in a scanning electron microscope of ZEISS, EVO|LS15 model, equipped with OXFORD link for microanalysis and tungsten filament. The analysis conditions were electron beam with a resolution of 20 μm, 10 kV and vacuum of 10^{-3} Pa. The mats were cut, pasted into a double-sided tape of carbon and metallized with gold. The Image J program was used for the image analyses.

2.4. Carbonization and characterization of carbon fibers

The PAN fibers obtained from the electrospinning process were carbonized in an electric furnace with cylindrical chamber of quartz, under constant flow of nitrogen. During this step, it was used the heating rate of 1 °C min^{-1}, starting from ambient temperature up to 1000 °C, remaining 1 h at the maximum temperature. A stainless steel screen 304 of 100 mesh, diameter of wire of 0.10 and 0.154 mm opening was used to wrap and protect the nanofibers to avoid that they do not flew during the carbonization process.

2.4.1. Characterization method of the carbonized material

Morphological analyses of carbon nanofibers was held in a scanning electron microscope of ZEISS, model EVO| LS15 with tungsten filament. Just the same was used in the PAN mats characterization. The carbon mats were glued on a double-sided tape of carbon and metallized with gold. The image analyses were also performed using the Image J program.

In this research work, analyses of the carbon mats by Raman spectroscopy was also performed on an optical microscope Renishaw 2000, with laser at 514.5 nm. Calibration was previously performed with diamond.
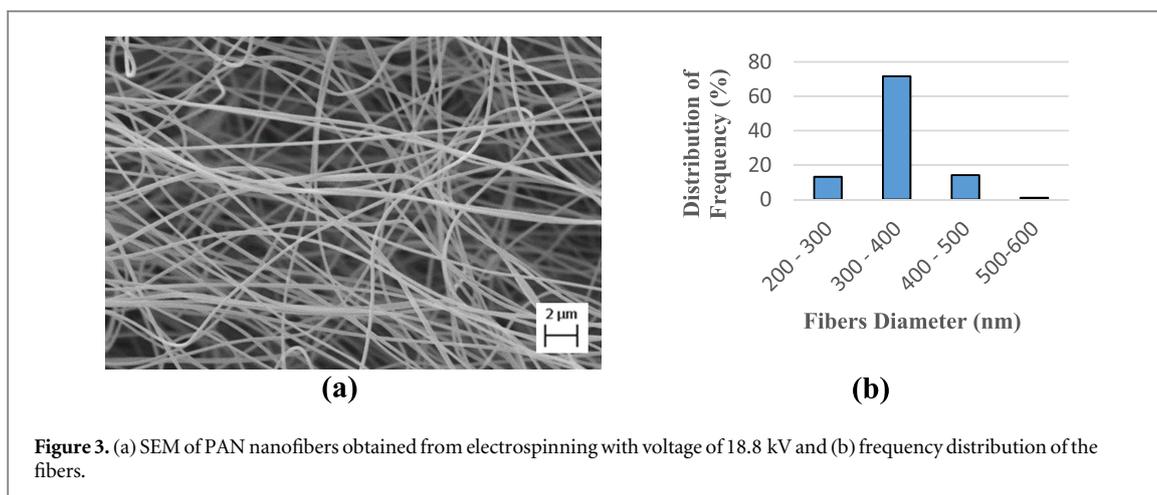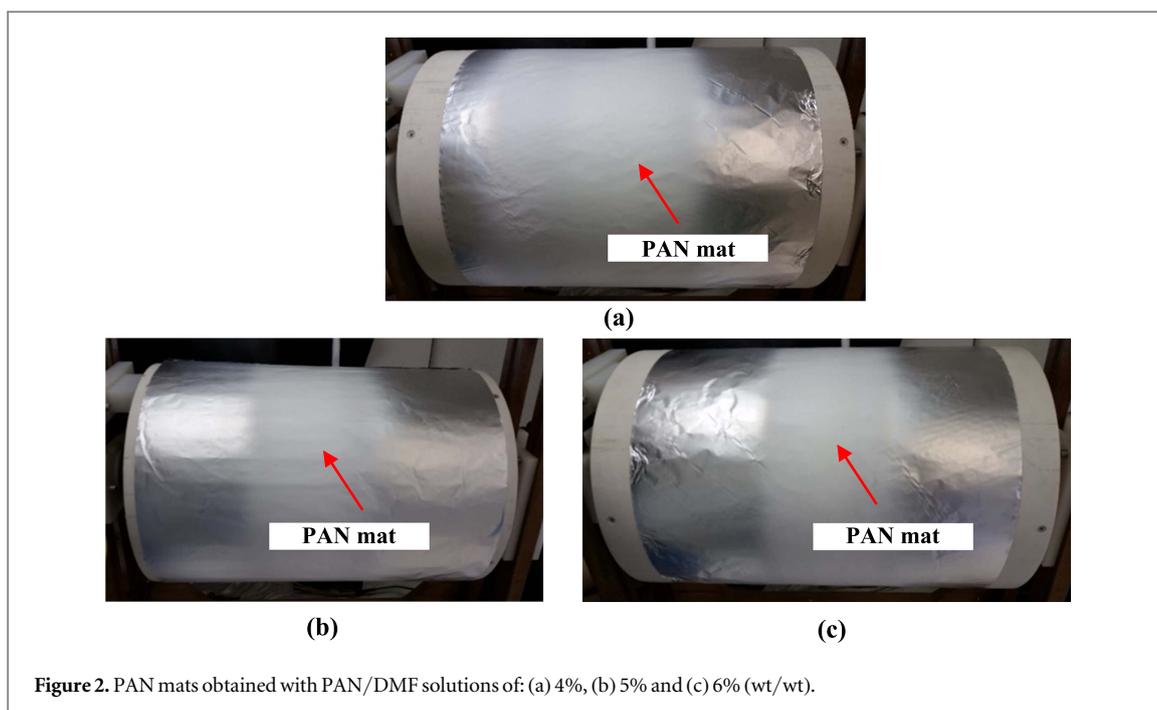
3. Results and discussion

3.1. PAN nanofibers produced by eletrospinning

In this work 3 processing parameters of the electrospinning process were evaluated for production of the nanofibers: solution concentration, voltage and processing time.

3.1.1. Solution concentration

The solution concentration used to produce nanofibers were 4%, 5% and 6% (wt/wt). Figure 2 shows the mats based on PAN fibers produced by electrospinning process, using PAN concentrations of 4%, 5% and 6% (wt/ wt), processed under the conditions described in item 2.3.
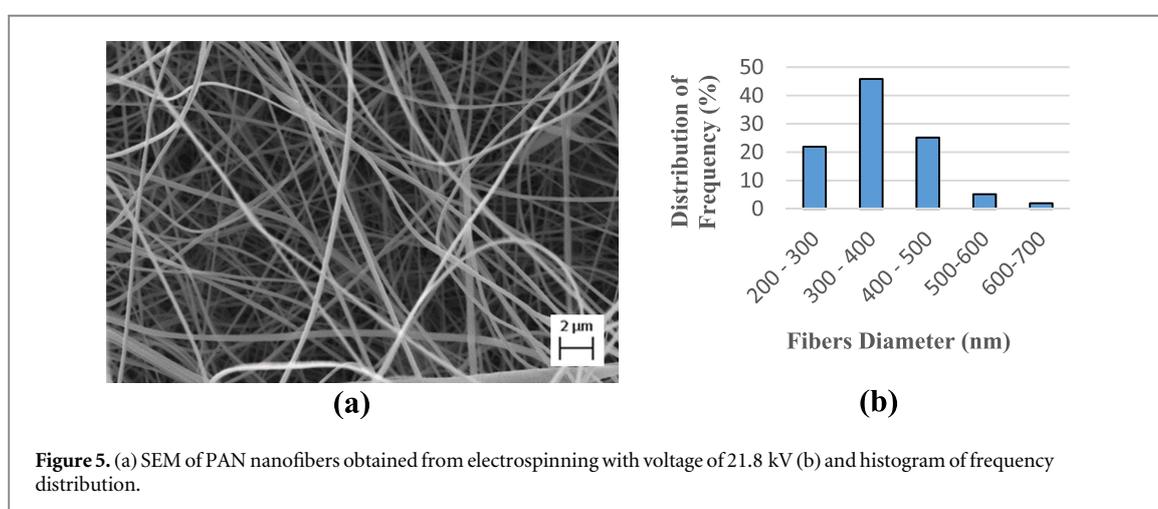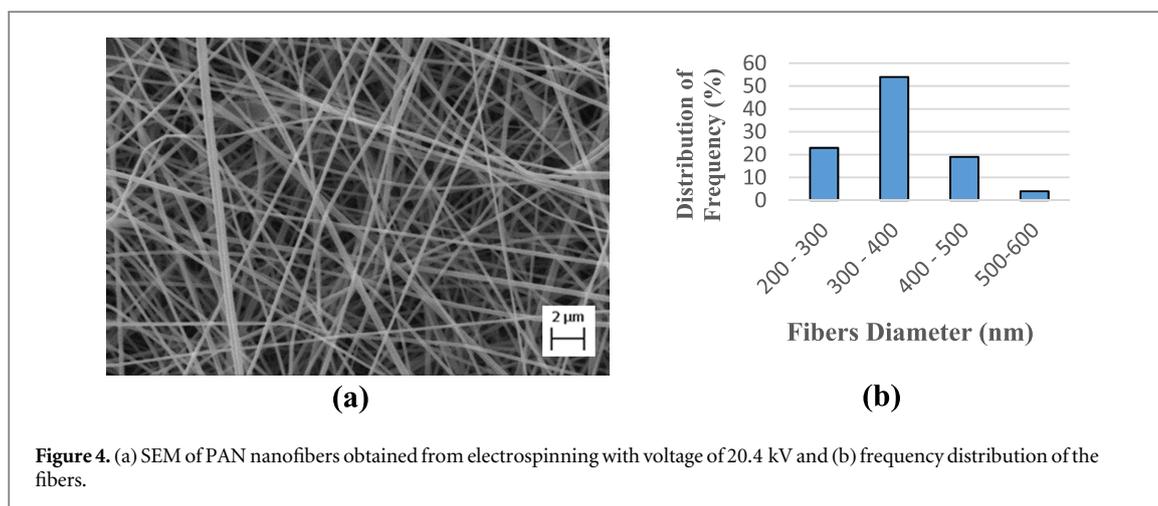
Concerning about the use of 4% wt/wt PAN/DMF contents was necessary to raise the solution voltage to 27.1 kV for the production of PAN fiber jet in the needle. This problem occurs due to the low concentration of polymer in solution and consequently its low viscosity.

Figure 2. PAN mats obtained with PAN/DMF solutions of: (a) 4%, (b) 5% and (c) 6% (wt/wt).

Figure 3. (a) SEM of PAN nanofibers obtained from electrospinning with voltage of 18.8 kV and (b) frequency distribution of the fibers.

After performing the electrospinning process, it was measured the thickness of mats, using a micrometer device. The mats based on 4%, 5% and 6% (wt/wt) solutions presented, respectively, the following average thickness values: (0.069 ± 0.004) mm; (0.050 ± 0.002) mm and (0.066 ± 0.004) mm. It was observed that the thickness of mats produced with the 5% (wt/wt) PAN/DMF solution presented lower values when compared with the others, but all values are similar. However, it was verified that the process that used 4% (wt/wt) solution consumed twice more than the mat obtained from electrospinning process using 6% (wt/wt) PAN solution, keeping the same final thickness. Thus, in order to promote the PAN mat production with the solution containing 4% (wt/wt) of PAN, high voltages and more solution were required, being a disadvantage. Considering these arguments, in this work the mats based on PAN fibers were produced with 6% (wt/wt) PAN/ DMF solution.

3.1.2. Voltage variation in the electrospinning process
In order to produce PAN fibers with smaller diameters, in the electrospinning process were tested the voltages of 18.8, 20.4 and 21.8 kV. Applying the voltages previously cited and keeping constant the other parameters (concentration of solution in 6% (wt/wt); drum rotation of 24 rpm, work distance of 10 cm and time collection in 2 h, humidity of 35%; and temperature of 37.5 °C it was possible to obtain PAN nanofibers as depicted in figures 3–5. These figures show the morphologies of fibers and histograms of distribution of frequency as a function of fiber diameter.

Figure 4. (a) SEM of PAN nanofibers obtained from electrospinning with voltage of 20.4 kV and (b) frequency distribution of the fibers.

Figure 5. (a) SEM of PAN nanofibers obtained from electrospinning with voltage of 21.8 kV (b) and histogram of frequency distribution.

Figures 3(b), 4(b) and 5(b) show the highest frequency of diameters in the range of 300–400 nm for the three different voltages used. According to figures 3(a), 4(a) and 5(a), the morphologies of the fibers are similar, without defects. The average diameters measured were (359 ± 49) nm, (359 ± 73) nm and (373 ± 82) nm for fibers obtained at 18.8 kV, 20.4 kV and 21.8 kV, respectively. Comparing the diameters of the fibers obtained with different voltages no significant variation is observed. Since the voltage of 21.8 kV remained more stable for a longer period of processing time, this value was used in this work.

3.1.3. Processing time
The variation of processing time is extremely important because this parameter determines the amount of fibers obtained for the subsequent carbonization heat treatment. Thus, with this purpose in this work was first used PAN/DMF solution with concentration of (6% wt/wt) for 1 h, and the parameters used in the electrospinning process were: stainless steel needle of 10 mm length and 1.5 mm diameter; drum rotation of 24.1 rpm; applied voltage of 21.8 kV and the working distance of 10 cm; humidity 32% and temperature 33.5 °C. However, when the PAN mat with thickness of (0.041 ± 0.002) mm was carbonized it was verified no carbon yield in the end of the heat treatment. The same behavior happened with the mat electrospinned for 2 h, using the same processing parameters cited. Despite greater thickness $((0.066 \pm 0.004)$ mm) when compared to the mat electrospinned for 1 h, this thicker sample was not proper for the carbonization yet due probably to the insufficient mass of PAN mat exposed to the heat treatment.

Due to this difficulty, it was carried out the electrospinning of PAN/DMF solution of 6% (wt/wt) for 6 h. In this case the thickness reached the value of (0.082 ± 0.003) mm, using the following parameters: applied voltage of 22.2 kV, humidity of 48% and temperature of 31.6 °C.

The PAN nanofiber mat obtained in 6 h of electrospinning, after carbonization, presented a good carbon yield. In order to increase the PAN mat production it was used 12 h of electrospinning. In this case, using the applied voltage of 21.8 kV; humidity of 43% and 29.4 °C. In this condition, the thickness of the mat produced increased for (0.103 ± 0.003) mm. The increased time of electrospinning process also resulted in an increase in
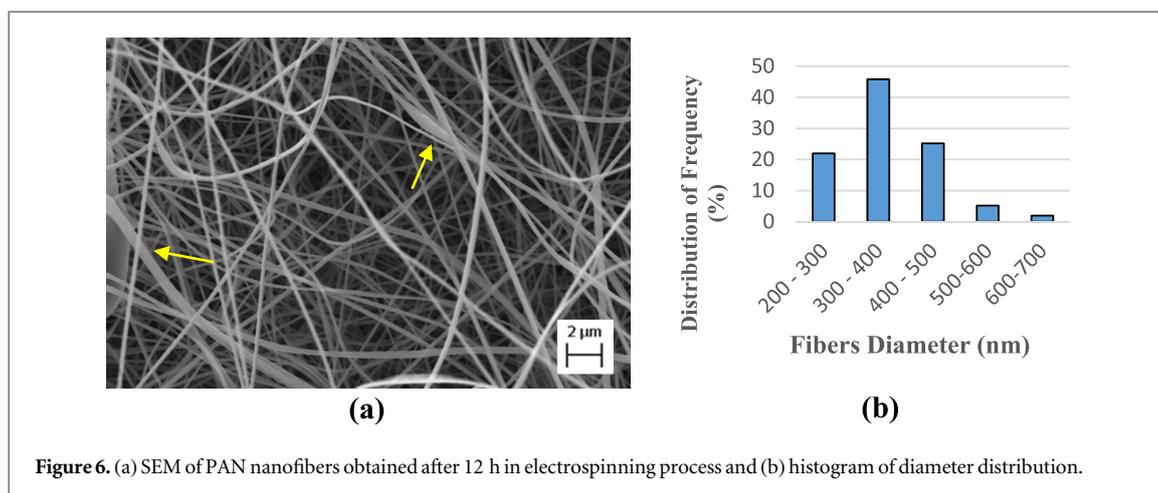
Figure 6. (a) SEM of PAN nanofibers obtained after 12 h in electrospinning process and (b) histogram of diameter distribution.
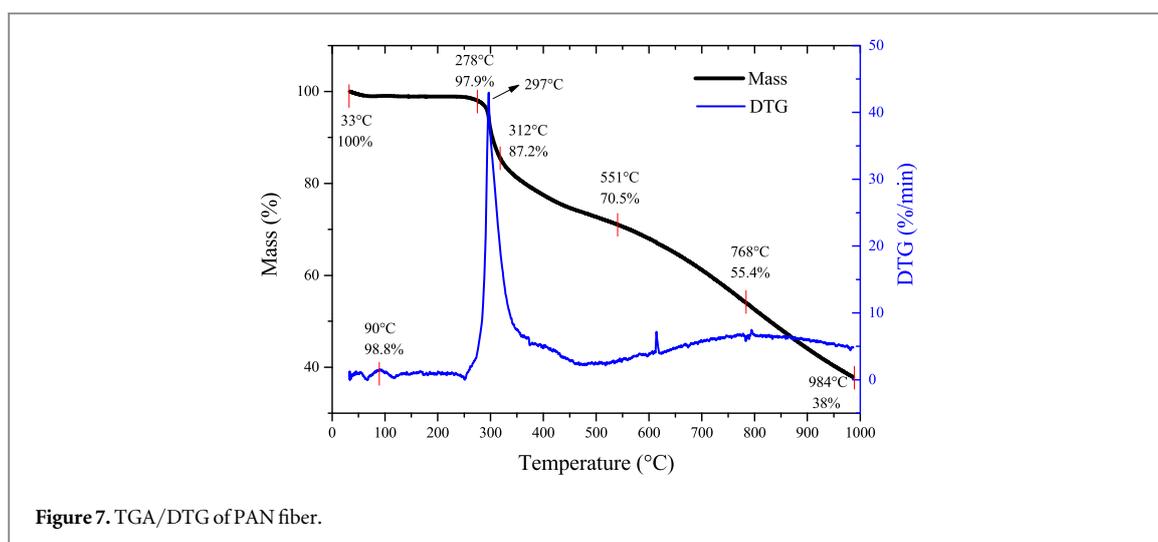

Figure 7. TGA/DTG of PAN fiber.

the scattering of PAN nanofibers on the aluminum foil, used as a collector, hindering a significant increase in the final material thickness. Nevertheless, the fibers produced by this process, after carbonization, resulted in carbon mats.

Figure 6 depict, respectively, the morphologies obtained by SEM and the histograms of the distribution frequency of the fibers obtained in the electrospinning of 12 h. As can be observed in figure 6(a), the fiber structure presents few defects such as junctions (indicated by arrows). These defects may occur when the nanofibers are deposited on the collector, and these one get in contact with each other under the influence of solvent still present, join or coalesce each other. However, it was verified that this fiber generates mats almost no defects like drops.

According to the results observed in figure 6(b), it is seen that the highest frequency of diameters is in the range of 300–400 nm (with average diameters equal to (375 ± 85) nm). According to the literature [20, 21], the distribution of diameters of PAN nanofibers, produced by electrospinning, is in the range of 0–2000 nm, with an average diameter between 100 and 280 nm.

3.1.4. Thermal behavior of PAN blankets produced by electrospinning process

Figure 7 presents the thermal decomposition obtained by TGA for PAN fibers processed from the temperature range of 30–1000 °C, at a heating rate of 15 °C min^{-1}, under a nitrogen flow of 100 ml min^{-1}.

According to the TGA, the thermal degradation of PAN fiber occurs in at least 4 different stages: 1st stage— presence of moisture; 2nd stage—presence of solvent; 3rd stage—degradation of the PAN fiber and 4th stage— gases that are volatilized, as identified in accordance with the DTG results. Initially, there is a weight loss of 1.2% in the TGA curve, as shown in the derivative curve. This variation occurs at 90 °C, possibly, due to the presence of moisture or low molecular weight fractions in the mat. Then, it is observed a second weight loss of around 0.9%, that occurs between the temperatures of 150 and 230 °C, which may be related to the presence of DMF (solvent used in the electrospinning process). According to the literature, the boiling temperature of DMF is
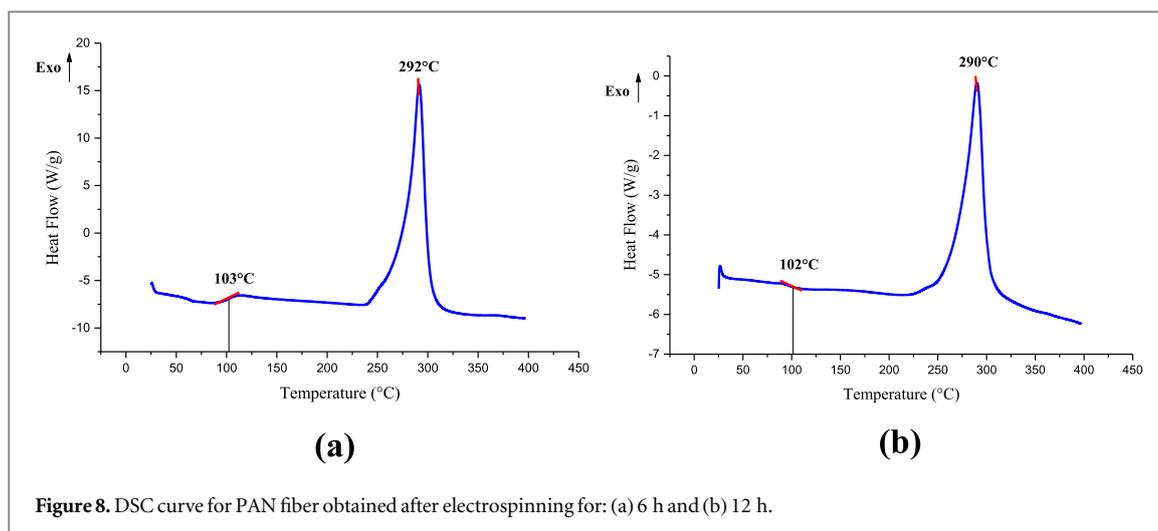
Figure 8. DSC curve for PAN fiber obtained after electrospinning for: (a) 6 h and (b) 12 h.

equal to 153 °C [22]. In the temperature of 278 °C, begins the degradation of PAN fibers; the DTG curve shows that this step finalizes at 312 °C. The weight loss of PAN starts at 278 °C, and goes until about 1000 °C, where is consumed 59.9% of the PAN weight. These losses are attributed to different gases that are volatilized during the decomposition of PAN, such as H_2O, CO_2, CO, CH_4, NH_3 and HCN [23, 24]. According to Xue *et al* [25], the formation of NH_3 and HCN is originated from the terminal amino groups of the cyclized structure of the PAN copolymer. In accordance with the literature, the onset of PAN degradation occurs around 160 °C [26]. Other authors, such as Brito Jr *et al* [27], reported that was not observed by TGA technique a significant weight loss below 280 °C.

The DSC curves of PAN fibers produced by electrospinning are presented in figure 8. Figure 8(a) shows the thermal behavior of PAN fiber obtained from solution of 6% (wt/wt) processed for 6 h. Figure 8(b) presents the results of PAN fiber with concentration of 6% (wt/wt) electrospinned for 12 h. According to these curves, the PAN presents a glass transition temperature value (Tg) well defined. The Tg of PAN fiber, obtained from electrospinning process of 6 h, is 103 °C. This value is very close to the Tg value obtained for the PAN fibers from electrospinning process of 12 h, which is 102 °C. This Tg values are found slightly lower than that presented in the literature, i.e., around 125 °C [28].

Both curves observed (figure 8) present a peak of degradation (exotherm) with a maximum temperature of 292 °C (starting in 238 °C and ending in 329 °C) to the mat after electrospinning for 6 h and a peak with a maximum temperature of 290 °C (with onset in 222 °C and endset in 323 °C) for the mat after electrospinning for 12 h. The degradation values presented in both graphs are close. These values are in accordance with the literature for PAN [29], which reports value of 293 °C and also the value of PAN degradation temperature found in figure 7, which is 297 °C. The enthalpy of degradation reaction for PAN obtained from the area contained under the exothermic peak is 827.4 J g^{-1} (figures 8(a)), and 629.1 J g^{-1} (figure 8(b)), considering PAN fibers obtained after 6 h and 12 h, respectively, being found in the work of Santos [29] a value lower but closed than verified in this study, equal to 515 J g^{-1}.

Based on figure 8 it was not possible to detect a peak related to the melting of PAN, only the peaks relating to degradation. This is possibly as a consequence of the final degradation reaction occurs at temperatures near to the melting temperature (320–326 °C), as mentioned in the literature [30].

3.2. Carbon nanofiber

The PAN mats produced by electrospinning for 6 and 12 h were carbonized in an electric furnace. After carbonization process, these blankets exhibit black color, and fragile behavior (brittle) and weight loss of approximately 75%. The high weight loss exhibited by carbon nanofiber blanket is justified probably by the non-execution of the thermal stabilization step of PAN. Thermal stabilization typically occurs between the temperature range of 200–300 °C, with the main purpose to make the PAN precursor fibers stable for the subsequent heat treatment process, preventing the melting of PAN during the carbonization process, as reported in the literature [31].

Figure 9(a) shows the morphology of PAN fiber after electrospinning for 12 h and figure 9(b) presents the same mat after carbonization process originating carbon nanofibers, both assessed by SEM. As can be seen from figure 9(a), PAN mat has a constitution of well defined and spaced fibers, overlapped in a random arrangement, forming different planes. However, figure 9(b) depicts a more homogeneous structure generated after the carbonization of the PAN fibers into carbon fibers. In other words, in his case it is observed a more compact
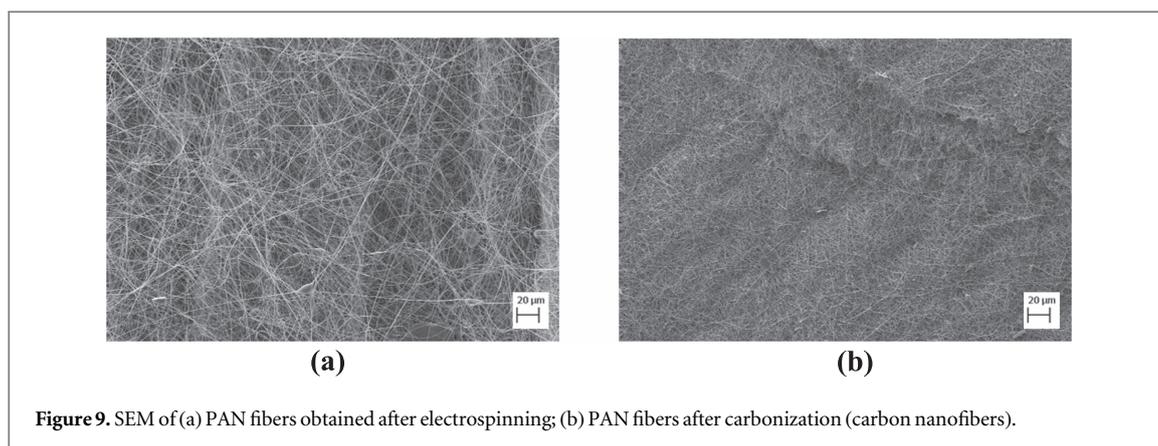
Figure 9. SEM of (a) PAN fibers obtained after electrospinning; (b) PAN fibers after carbonization (carbon nanofibers).
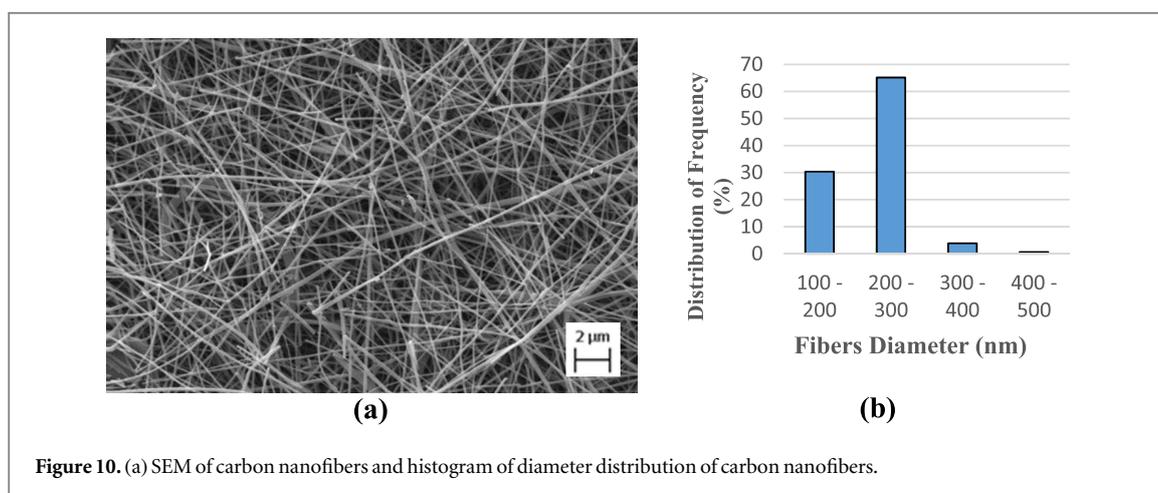

Figure 10. (a) SEM of carbon nanofibers and histogram of diameter distribution of carbon nanofibers.

material, not being possible to distinguish one fiber from the other. Figure 10(a) presents the same carbon nanofiber, analyzed in higher magnification. This figure shows the presence of fibers separated and well defined, superposed in several planes. It may also be seen that occurred the breakage of some fibers after carbonization and that they presented, visibly, a reduction in their diameters. This break probably happened due to the release of volatile materials of low molar mass. This reduction in diameter is expected due to volumetric shrinkage that the polymeric materials may suffer when they are converted in carbonaceous materials, often this shrinkage is of approximately 30% by volume [32]. This change can also be observed in the histogram of diameter distribution of the fibers, according to figure 10(b).

According to figure 10(b), it was observed that the carbon nanofibers obtained from PAN fibers exhibit more homogeneous dimensions, with 65% of the fibers presenting diameters values in the range of 200–300 nm. The average diameter of these fibers is equal to (186 ± 45) nm. This figure shows also that the carbonized fibers present a decrease of approximately 50% in their diameters. According to the literature this reduction may be attributed to the heat treatment which provides the weight loss with the release of volatiles such as ammonia, hydrocyanic acid and water, reducing, thus, the diameter of fibers [21]. According to Adabi [21], it is possible to use nanofibers that were processed by electrospinning and subsequently carbonized, such as nanoelectrodes, but to function as a nanoelectrode, the fiber diameters have to be between 75 and 80 nm, because below or above these values there is a decrease in the conductivity of the carbon fiber, not serving the function in question. t has been the application for composite reinforcement area requires that the blanket has made a suitable size so it can be, for example, used in a press with a composite. The carbonized blankets had small dimensions, since the tubular furnace used for the procedure had a diameter of approximately 60 mm.

3.2.1. Raman spectroscopy analysis of carbon nanofiber

The carbon element can present different crystalline and morphological structures with different characteristics and Raman spectroscopy is usually used for qualitative evaluation of the crystallographic ordering concerning about carbonaceous materials or to evaluate the effect of heat treatment on cokes or organic precursors. The D band at ~1360 cm^{-1} is related to defects such as edge effects, impurities and finite size, corresponding to disordered structure of carbon and reflecting the sp^2 vibration of the ring. The G band at ~1590 cm^{-1}, reflects
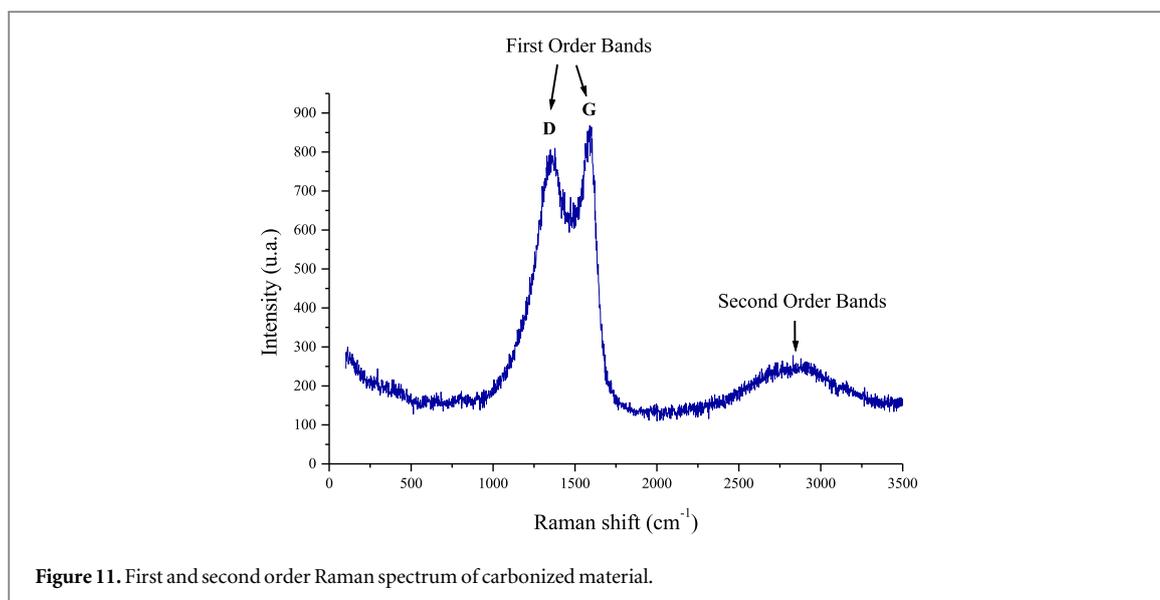
Figure 11. First and second order Raman spectrum of carbonized material.

Table 1. D and G bands positions and I_D/I_G intensity ratio of the carbonized nanofiber (measured in three different places).

Measure	D band (cm^{-1})	G band (cm^{-1})	I_D/I_G
1	1361.1	1587.2	0.918
2	1359.5	1590.3	0.930
3	1358.1	1590.3	0.914
Average	1359.6 $\pm$ 1.5	1589.3 $\pm$ 1.8	0.921 $\pm$ 0.009

the degree of graphitization of the studied material (crystalline and atomic arrangements) [33–35]. The most important parameter calculated with this technique is the I_D/I_G intensity ratio which is useful to estimate the degree of ordering in carbonaceous material [36]. The second order Raman is related to the stacking disorder along the crystallographic *c*-axis [37].

Figure 11 shows the first and second order Raman spectrum of the carbonized material which displays two broad D and G bands characteristic of disordered carbon. In addition, the second order region does not show any band development which indicates the heat treatment temperature used (1000 °C) is not enough to improve crystallographic ordering of carbon nanofiber.

Table 1 contains the positions of D and G bands and I_D/I_G intensity ratio obtained from the Raman spectra of the sample measured in three different places.

According to the data presented in table 1, D and G bands positions correspond to a graphitic disordered system [38] due to the bands around 1360 cm^{-1} and 1590 cm^{-1}, respectively. The I_D/I_G intensity ratio is 0.921 $\pm$ 0.009, slightly smaller than for carbon nanofibers produced by catalytic thermal chemical vapor deposition (CVD) ($I_D/I_G = 1.35$) [36]. Since I_D/I_G ratio decreases as sample disorder decreases, then, the produced nanofibers are more ordered than the as-produced nanofibers by CVD method. According to Ren *et al* [39], the microstructure of carbon fibers changes along the axial direction indicating the surface heterogeneity. Moreover, the amount of amorphous carbon varied significantly in different regions. In this work, the low standard deviation shows the nanofibers are quite homogeneous, probably related to the reduced diameter of the fibers.

4. Final conclusions

The polyacrylonitrile mat was produced by electrospinning generating nanofiber with an average diameter of (375 $\pm$ 85) nm. The more appropriate processing conditions were: applied voltage of 21.8 kV, distance working of 10 cm and rotation of the cylinder of 24.7 rpm, PAN/DMF concentration solution of 6% m/m and time of material collection of 6 and 12 h.

The thermal degradation of the PAN nanofibers obtained from electrospinning process occurred in four steps and the residual mass that remained after this degradation was 38%, when analyzed in an inert atmosphere.

In DSC analysis were found the glass transition temperature de values of 103 and 102 °C respectively for the PAN nanofibers obtained by electrospinning considering 6 and 12 h.

The carbon nanofiber mat with a diameter of (186 ± 45) nm was successfully obtained from the carbonization of the PAN nanofiber produced by electrospinning process. After carbonization, there occurred a reduction of 50% in the carbon nanofiber diameter in relation to the diameters of the mat before carbonization. The aspect of the mat observed was brittle and with black color, and the same presented a mass yield of 25% when compared with the no carbonized mat. The more appropriate conditions obtained in the carbonization process were: heating rate of 1 °C min^{-1}, starting from room temperature up to 1000 °C, remaining 1 h at the final temperature selected under a constant flow of nitrogen;

Raman spectroscopy analysis showed the material can be classified as disordered carbon and is quite homogeneous due to the low standard deviation for I_D/I_G ratio which indicated the good structural quality of the carbon nanofibers.

Acknowledgments

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References

[1] Strelko V V, Stavitskaya S S and Gorlov Y I 2014 Proton catalysis with active carbons and partially pyrolyzed carbonaceous materials *Chin. J. Catalysis* **35** 815–23

[2] Trung T S B *et al* 2015 Carbonaceous materials as catalyst supports for the enantioselective hydrogenation of (e)-α-phenylcinnamic acid: effect of the support acidity *Appl. Catalysis* A **503** 1–25

[3] Joshi V S *et al* 2010 Fabrication, characterization and electrochemical performance of single strand carbon fiber prepared by catalytic chemical vapor decomposition method *Electrochim. Acta* **55** 2022–8

[4] Wang Q *et al* 2012 A review on application of carbonaceous materials and carbon matrix composites for heat exchangers and heat sinks *Int. J. Refrig.* **35** 7–26

[5] Tsai H Y and Tseng P T 2015 Field emission characteristics of diamond nano-tip array fabricated by anodic aluminum oxide template with nano-conical holes *Appl. Surf. Sci.* **351** 1004–10

[6] Liu C K *et al* 2015 Effect of carbonization temperature on properties of aligned electrospun polyacrylonitrile carbon nanofibers *Mater. Des.* **85** 483–6

[7] ZHU X *et al* 2015 Application of nanomaterials in the bioanalytical detection of disease-related genes *Biosens. Bioelectron.* **74** 113–33

[8] Wei G *et al* 2016 Effect of the graphitization degree for electrospun carbon nanofibers on their electrochemical activity towards VO^{2+}/VO_2^+ redox couple *Electrochim. Acta* **199** 147–53

[9] Zhang X *et al* 2016 An electrochemical non-enzymatic immunosensor for ultrasensitive detection of microcystin-lr using carbon nanofibers as the matrix *Sensors Actuators* B **233** 624–32

[10] Paul D R and Robeson L M 2008 Polymer nanotechnology: nanocomposites *Polymer* **49** 33187–204

[11] Camargo P H C, Satyanarayana K G and Wypych F 2009 Nanocomposites: synthesis, structure, properties and new application opportunities *Mater. Res.* **12** 1–39

[12] Chen C *et al* 2009 The influence of surface morphology and rigidity of the substrata on cell motility *Mater. Lett.* **63** 1872–5

[13] Zare Y and Shabani I 2016 Polymer/metal nanocomposites for biomedical applications *Mater. Sci. Eng.* C **60** 195–203

[14] Bhardwaj N and Kundu S C 2010 Electrospinning: a fascinating fiber fabrication technique *Biotechnol. Adv.* **28** 325–47

[15] Li W 2015 Hybrid gel polymer electrolyte fabricated by electrospinning technology for polymer lithium-ion battery *Eur. Polym. J.* **67** 365–72

[16] Guo J *et al* 2016 Characterization and application of chondroitin sulfate/polyvinyl alcohol nanofibres prepared by electrospinning *Carbohydrate Polym.* **143** 239–45

[17] Kim M *et al* 2016 Electrochemical improvement due to alignment of carbon nanofibers fabricated by electrospinning as an electrode for supercapacitor *Carbon* **99** 607–18

[18] Low L W *et al* 2015 Carbonization of elaeis guineensis frond fiber: effect of heating rate and nitrogen gas flow rate for adsorbent properties enhancement *J. Ind. Eng. Chem.* **28** 37–44

[19] Guerrini L M *et al* 2006 Eletrofiação do poli (álcool vinílico) via solução aquosa *Polímeros: Ciência e Tecnol.* **16** 286–93

[20] Bourourou M *et al* 2015 Chemically reduced electrospun polyacrilonitrile–carbon nanotube nanofibers hydrogels as electrode material for bioelectrochemical applications *Carbon* **87** 233–8

[21] Adabi M *et al* 2015 Performance of electrodes synthesized with polyacrylonitrile-based carbon nanofibers for application in electrochemical sensors and biosensors *Mater. Sci. Eng.* C **48** 673–8

[22] Brquim 2010 http://brquim.com.br/fispq/10547.pdf(Accessed: 07 August 2016)

[23] Wu G P *et al* 2009 Comparative investigation on the thermal degradation and stabilization of carbon fiber precursors *Polym. Bull.* **62** 667–78

[24] Ribeiro R F 2010 *Caracterização de fibras e filmes de poliacrilonitrila extrudada* Program of Pos-Graduation in Aeronautical and Mechanical Engineering in area of Physics and Chemistry of Aerospace MaterialsSão José dos Campos

[25] Xue T J, Mckinney M A and Wilkie C A 1997 The thermal degradation of polyacrylonitrile *Polym. Degrad. Stab.* **58** 193–202

[26] Peeples L H *et al* 1990 Carbon fibers: formation, structure and properties *Carbon* **28** 707

[27] Brito C A R Jr *et al* 2011 Estudo termogravimétrico da poliacrilonitrila com o plastificante glicerol *In Annals of the 11th Brazilian Congress of Polymers (Campos do Jordão)*

[28] Gazard M 1986 *Handbook of Conducting Polymers. v.1* (New York: Marcel Dekker Inc.)

[29] Santos V M 2009 Estudo dos filmes de poliacrilonitrila modificados pela adição de clorofilas, citocromo C, Fe (II) E Fe (III) *Dissertation —Program of Pos-Graduation in Chemistry* Universidade Federal do Espírito Santo. Vitória

[30] Brandrup J, Immergut E H and Grulke E A 2003 *Polymer Handbook* vol 2 4th edn (New York: Wiley-Interscience)

[31] Shin H K *et al* 2014 Preparation and characterization of polyacrylonitrile-based carbon fibers produced by electron beam irradiation pretreatment *J. Ind. Eng Chem.* **20** 3789–92

[32] Rezende M C, Costa M L and Botelho E C 2011 *Compósitos Estruturais: Tecnologia e Prática* (São Paulo: Artliber) pp 34–7

[33] Lobo A O *et al* 2005 Caracterização de materiais carbonosos por espectroscopia raman *Rev. Bras. Aplicações Vácuo* **24** 98–103

[34] Jauris I *et al* 2011 Produção de nanotubos de carbono via técnica de deposição química de vapor *Disc. Scientia. Série: Ciências Naturais e Tecnológicas, S. Maria.* **12** 125–37 https://www.periodicos.unifra.br/index.php/disciplinarumNT/article/view/1285/1217

[35] Oishi S S 2013 Produção e Caracterização de Carbono Vítreo Monolítico a Partir das Resinas Poliarilacetileno e Furfurílica *Thesis— Program of Pos-Graduation in Mechanical Engineering in area of Materials* Universidade Estadual Paulista, Faculdade de Engenharia de Guaratinguetá. Guaratinguetá

[36] Ramos A, Cameán I and García A B 2013 Graphitization thermal treatment of carbon nanofibers *Carbon* **59** 2–32

[37] Baldan M R *et al* 2007 Raman validity for crystallite size La determination on reticulated vitreous carbon with different graphitization index *Appl. Surf. Sci.* **254** 600–3

[38] Takai K *et al* 2003 Structure and electronic properties of a nongraphitic disordered carbon system and its heat-treatment effects *Phys. Rev.* B **67** 1–11

[39] Ren G Z *et al* 2015 Microstructural heterogeneity on the cylindrical surface of carbon fibers analyzed by Raman spectroscopy *Xinxing Tan Cailiao/New Carbon Mater.* **30** 476–80