Polyaniline/Graphite Nanocomposites: Synthesis and Characterization

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Summary: Graphite nanosheet (GNS) was prepared by physical/chemical method. The polyaniline (PANI)/graphite nanocomposites were synthesized by *in situ* polymerization of aniline monomer using different amounts (1 to 5 wt%) of graphite nanosheets. The formation of graphite nanosheets was confirmed by Transmission Electron Microscope (TEM) and X-ray Diffraction (XRD). The surface morphology of exfoliated graphite and PANI/GNS nanocomposites were studied by the Scanning Electronic Microscopy (SEM). A device for electrical conductivity measurements was developed in this work and the results show that the conductivity of PANI/GNS is dependent of the GNS contents.

Keywords: conducting polymers; nanocompósitos; polyaniline; TEM; XRD

Introduction

The field of nanotechnology is one the most important areas for current research and development in basically all technical disciplines.[1] Polymeric nanocomposites are defined as composite materials where nanometric dimensions inorganic fillers are dispersed in an polymeric matrix.[2] Conducting polymers have been intensively studied because potential applications in various devices as evidenced by different authors in light emitting diodes and electrochromic displays,[3] chemical and bio sensors,[4] storage batteries,[5] etc. The understanding of the nature of these polymers is of primordial importance for developing electrochemical devices. Polyaniline is one of the most versatile materials that has attracted much attention in recent years due easy synthesis,[6] good environmental stability,[7] controllable electrical conductivity,[8] reparation with a high yield by polymerization[9] it is cheap and versatile applications.[10,11] In recent years polymeric nanocomposites reinforced with graphite nanosheets are considered as highly prospective filler materials for future polymer composites, and have shown substantial improvements in the lack of mechanical and electrical properties against the unmodified polymer.[12] Graphite is a flake naturally abundant material and is well known to be a layered material with highly conductivity, 10^4 S/cm at ambient temperature. It is constituted by thousand of layers graphene sheets, where the carbon atoms tightly packed into a two-dimensional successive hexagons.[13] Some chemical (intercalation and expansion) and physical (ultrasonic bath) treatments are needed in order to intercalate polymers into graphite layered materials.[14] The graphite intercalation are commonly made using acids baths, and the expansion of intercalated graphite becomes possible at high temperature, which destroys their regular layered structure.[15]

Exfoliated graphite consists of a large number of delaminated graphite sheets. The good uniform dispersion of graphite nanosheets in polymer matrices is generally attributed to the excellent exfoliation character of graphite. Therefore, monomers and polymers can be intercalated into the pores and galleries of the graphite

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sheets in exfoliated graphite to produce polymer/graphite nanocomposites.[9,16,17]

The aim of this work is to prepare graphite nanosheets with a well defined structure in order to permit the growing of polyaniline among their galleries and obtain a well dispersed nanocomposite. A new device for electrical conductivity characterization is also described in this work.

Experimental Part

Preparation of Graphite Nanosheets

Natural graphite was supplied from Sigma-Aldrich with an average diameter of 500 μm. The aniline monomer supplied from Nuclear was previously distilled before use. All chemical reagents used in this work were of analytical grade.

The GNS samples were prepared using a three step procedure: (a) intercalation with a H_2SO_4/HNO_3 concentrated acid bath; (b) expansion by thermal shock; and (c) exfoliation using an ultrasonic bath at 25 kHz.

Expandable graphite powders were prepared using chemical method with intercalation of HNO_3-H_2SO_4. A mixture of concentrated sulfuric acid and nitric acid (4:1) was mixed with graphite flakes at ambient temperature and stirred for 24 h. The obtained graphite intercalation compound (GIC) was washed and filtrated with deionized water until the neutral pH (6-7) and then it was dried at 100 °C for 4 h to remove the remaining water by evaporation. The resulting dry GIC was heated up to 1000 °C for 30 seconds, in order to obtain the expanded graphite (EG)[14]. The graphite nanosheets (GNS) were obtained by immersing in 70% aqueous alcohol solution in an ultrasonic bath for 9 h, the dispersed solution were filtered and dry in a furnace for 3 hours at 100 °C.

In Situ Polymerization of Polyaniline (PANI)

Polyaniline was chemically synthesized by the oxidative polymerization of aniline in 1 M aqueous HCl solution with $(NH_4)_2S_2O_8$ as oxidant. To obtain the nanocompositie samples to this work, a mixture of 1 mL pure aniline with 1 wt%, 2 wt%, 3 wt%, 4 wt% and 5 wt% GNS were added to 10 mL of ethanol and dissolved in 30 mL 1 M HCl. The mixture was ultrasonicated for 2 hours to randomly disperse the inclusions. Afterwards the ammonium persulfate acid solution was added to the becker containing aniline to initiate the polymerization. The polymerization was allowed to proceed for 24 hours at controlled room temperature (21 to 22 °C). The product obtained was filtered and washed with deionized water, and the resulting green nanocomposites were dried at 100 °C for 4 hours.

Characterization

The exfoliated graphite and PANI/GNS nanocomposites morphology were performed by using Philips XL30 Scanning Electron Microscope (SEM). Prior to SEM examination, the specimens were coated with a very thin layer of gold. Transmission Electron Microscopy (TEM) investigations were performed using a JEOL JEM-1200 microscope. Thermogravimetric analysis (TGA) were made under N_2 flow at a heating rate of 10 °C/min from 45 to 800 °C, with Ta Instruments. The addition of GNS content was monitored by X-ray diffraction (XRD) on a Shimadzu XRD-7000 diffractometer.

The electrical conductivity measurements were carried out by a method developed according Celzard *et al.*[18] and adjusted by authors. Samples of PANI and PANI\GNS were compressed using Perkin Elmer equipment with 100 kN loads until pellets of 13 mm in diameter were formed. The device used to measure the electric conductivity of the sample is schematized in Figure 1. The electrical impedance was measured using a two silver electrode device built in a thick-walled glass tube. The silver contacts were fixed on copper pistons to transport the electrical current from the sample to an analytical multimeter. The measurements are converted

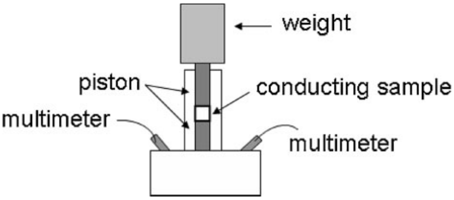

Figure 1.
Representative scheme of development device to analyze electrical conductivity.

to electrical conductivity by means the equation (1):

$$G = \frac{1}{\rho} = \frac{l}{R \cdot A} \qquad (1)$$

where **R** is a measured electrical impedance, ***ρ*** is the material resistivity, **l** is the sample height and **A** is the sample area and **G** is the conductivity.

Results and Discussion

The morphology of the graphite nanosheets and nanocomposites was studied using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) which confirmed the exfoliation structure of the graphite nanosheets.

Figure 2 shows SEM micrographs of natural graphite flakes and intercalated one. The distances between the layers are showed in figure 2 (b) indicating an increase about three times in volume.

The thermal annealing at 1000 °C decomposes the acids trapped between graphite layers and forces them to separate randomly. Figure 3 (a) shows that the exfoliation occurs preferentially along the normal to basal plane in graphite flakes, resulting in worm-like particles. When the graphite worms were sonicated in an

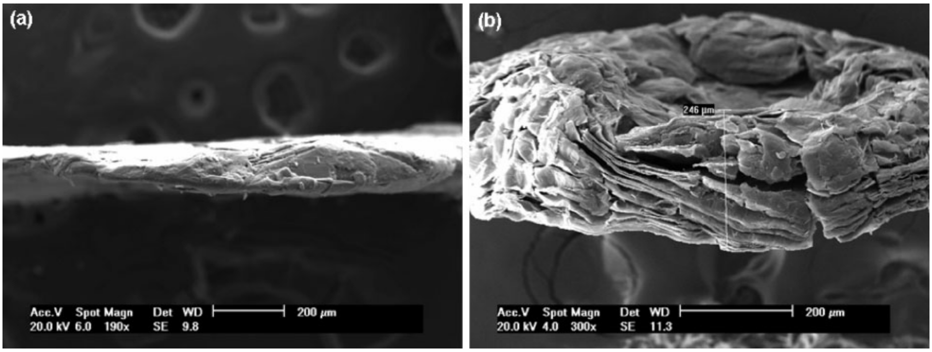

Figure 2.
SEM micrographs in SE mode: (a) natural graphite flakes and (b) intercalated graphite.

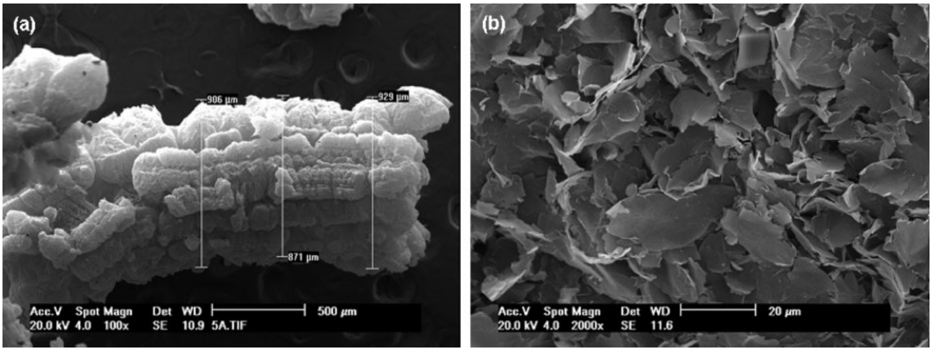

Figure 3.
SEM micrographs in SE mode: (a) expanded graphite and (b) graphite nanosheets.

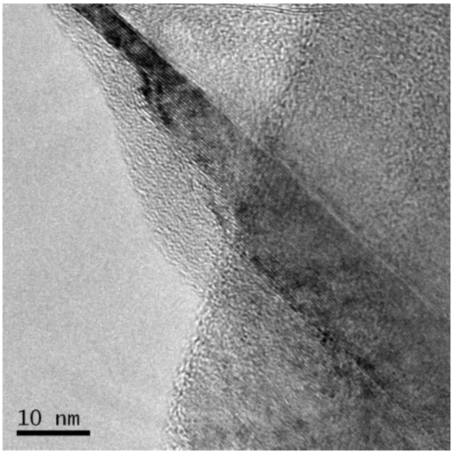

Figure 4.
TEM micrographs of graphite nanosheets.

alcohol solution, nanosheets with thickness of around 50 nm were formed as is showed in Figure 3 (b).

It was reported the presence of –OH and –COOH functional groups in the graphite nanosheets after acid and annealing treatments. These functional groups are assumed to promote both physical and mechanical interactions between the polymer and graphite nanosheets. The crystalline structure of the GNS samples was characterized by TEM and XRD analyses.

Figure 4 shows the high resolution transmission electron microscopy (HR-TEM) micrograph of the GNS sample where one nanosheet with thickness about 13 nm is presented. The parallel lines showed in the micrograph correspond to the cross-sections of the graphene inter-layers with a distance of about 0.34 nm that agree which the XRD data. Furthermore, the uniform distribution of the nanosheets confirms that the graphite layer structure is retained after intercalation with strong acids (H_2SO_4/HNO_3) and the expansion at high temperatures.[7,19]

The structural properties of GNS were characterized using the XRD analysis, as shown in Figure 5. The strong peak at $2\theta = 26.45^\circ$ is the results of the diffraction of the GNS (002) planes and correspond to the typical d-spacing between the carbon layers in graphite. They indicate a highly organized crystal structure. The neat PANI present broad peaks characteristic of amorphous structures.[20] The peaks centered at $2\theta = 19^\circ$ and $2\theta = 25^\circ$ are ascribed to the parallel and perpendicular periodicity to the polymer chains respectively.[21,22] With the GNS addition in the PANI matrix the GNS peak appear with intensity proportional to their concentration in the nanocomposite, indicating a good dispersion of the fillers.

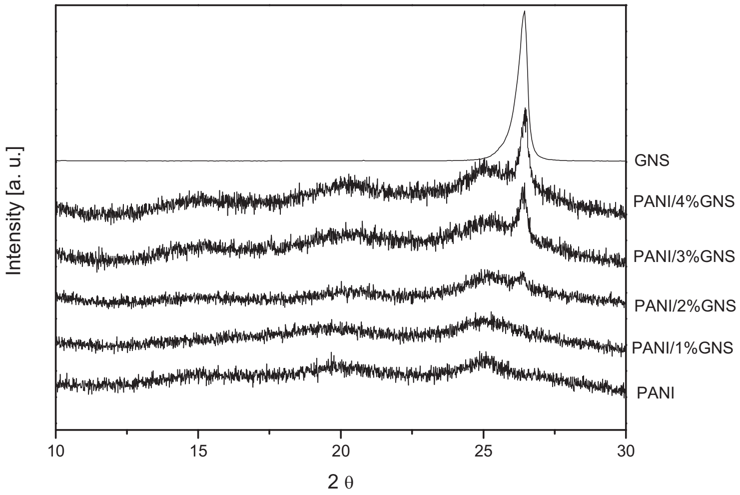

Figure 5.
X ray diffraction patterns of GNS, neat PANI and PANI/GNS nanocomposites.

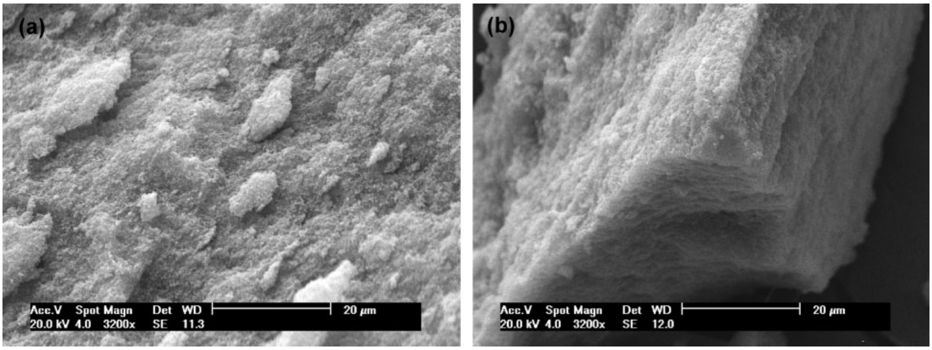

Figure 6.
SEM image in SE mode: (a) neat PANI and (b) PANI/GNS nanocomposite.

Figure 6 shows polyaniline and nanocomposite images SEM. The neat PANI morphology is compact, while the nanocomposite has a structure looking almost as exfoliated graphite, suggesting that the polymer has been grown among the graphene sheets.

The TGA curves illustrate the results of thermogravimetric analysis of pure polyaniline and nanocomposites, Figure 7. These TGA plots show that weight loss occurs in several systematic steps each corresponds to the loss of particular species. It can be seen that the mass of the PANI starts to decrease at a relatively low temperature region under 50 °C. Neat PANI is completely oxidized at about 730 °C. The first weight loss period of all the samples (50–130 °C) may be attributed to the loss of sorbed water molecules by evaporation. The second loss step begins at around 130–320 °C owing to the loss of dopant molecules from the polymer structure in the form of HCl gas and lower molecular weight oligomers along surface of the samples.[23,24,25] The third step (320–500 °C) for neat PANI involves a typical weight loss curve of low molecular weight fragments, cross linking of chains and onset of degradation of polymer.[225,26] PANI/GNS 1 wt% nanocomposites shows step at 574 °C, while the PANI/GNS 2 wt%

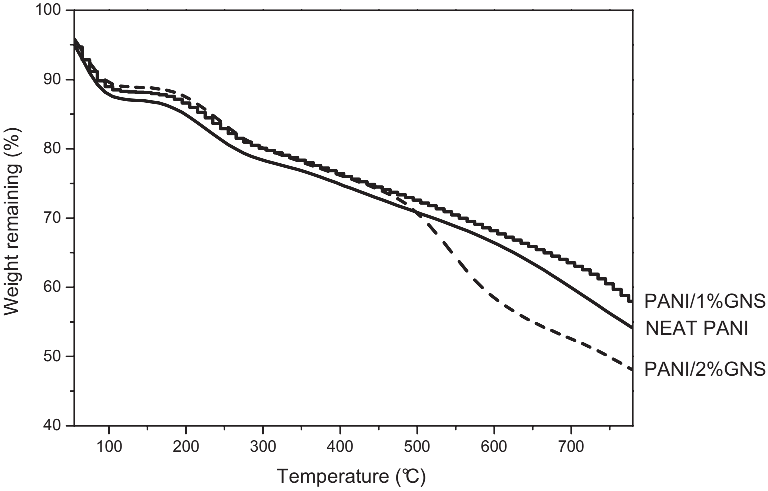

Figure 7.
TGA curves of neat PANI and PANI/GNS nanocomposites.

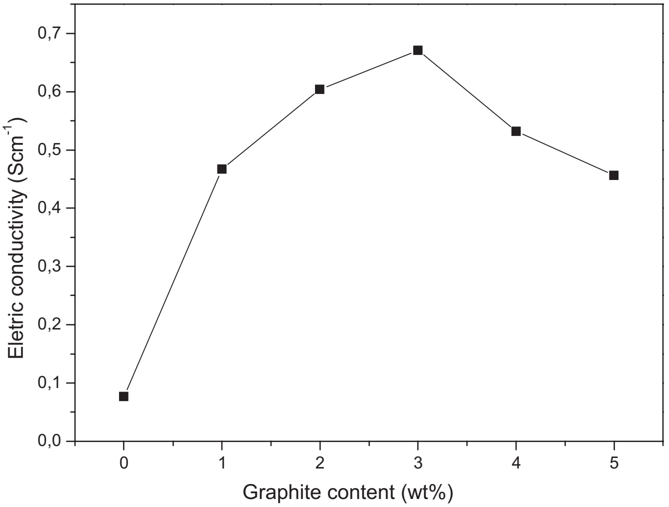

Figure 8.
Electrical conductivity of neat PANI and PANI/GNS nanocomposites versus graphite content.

nanocomposites shows peaks at 549 °C which can be ascribed to the degradation of polymer into heavier fragments. The last step of weight around 750 °C corresponds to the complete breakdown of the polymer linkages as well as heavier fragments into still smaller fractions and gaseous products. The residues (remaining at 800 °C) are inert materials like pure graphite and carbonized polymeric fragments. The addition of GNS, increases the corresponding residue in nanocomposites indicating incorporation of graphite inside the PANI matrix. Figure 7 show that the incorporation of graphite in PANI increased the thermo stability of nanocomposites. There is a variation of percentage weight loss in each step when adding graphite nanosheets into polymer matrix. The nanocomposites are completely oxidized at a higher temperature (774 and 769 °C) to neat PANI (735 °C). The TGA results suggest that there is a good interaction between PANI and GNS and support the SEM observation as shown in Figure 6.

The electrical conductivity measurements were made by an easy method according to Celzard *et al.* [18] Considering that the problem associated with the utilization of PANI is its poor solubility in all available solvents, the advantage of this method is the easy sample preparation for conductivity measurements. Figure 8 shows the conductivity of the pure polyaniline and PANI/GNS nanocomposites. It can be see that the conductivity of nanocomposites increased with increasing graphite content. The conductivity found for neat polyaniline was 0.0768 Scm^{-1}. However after addition of 1, 2 and 3 wt% of GNS the electrical conductivity of nanocomposites increased significantly, showing a maximum rate conductivity of 0.671 Scm^{-1} for PANI/GNS 3 wt% sample as shown in Figure 8, indicating that, for the electrical properties, the PANI/GNS 3 wt% present the better compromise between filler and polymeric matrix.

Conclusion

In SEM images changes can be observed in morphologic structure from the graphite flake to the nanosheets, while the TEM analysis confirmed the nanometric dimensions. XRD analysis indicated a good dispersion of the filler and the nanocomposites morphology observed by SEM images suggesting that the monomer grows between the GNS. The addition of GNS to the PANI increases the thermo stability of nanocomposite and improves the electrical conductivity.

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