Chemical Surface Modification and Characterization of Carbon Nanostructures Without Shape Damage

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Carbon nanostructures have been extensively studied due to combination of properties they present. With different geometries and reactivities, carbon nanotubes, graphene and fullerene were oxidized and modified with octadecylamine (ODA) in order to decrease van der Waals's interaction and consequently improve the polymer-carbon nanostructures affinity for use in nanocomposites. Nanostructures were characterized as morphology, chemical structure, molecular conformation and thermal properties. All nanostructures showed results that confirm the modification with ODA, without geometry being altered. Modified nanostructures showed different percentages of ODA: graphene 86%, carbon nanotubes 83% and fullerene 63%. It was attributed to distinct reactivities, shapes and specific surface area available, due to different amounts of reactive terminals obtained before oxidation reactions. However, they showed a lower interfacial interaction, which is highly favorable for use in polymer nanocomposites.

Keywords: *fullerene, carbon nanotubes, graphene, octadecylamine.*

1. Introduction

Carbon is a remarkable element in its ability to combine itself and other chemical elements in different ways and thus form the basis of organic chemistry and life. Carbon nanostructures are made up of carbon only and have different geometries and dimensions. However, these structures have distinct reactivities, which can be justified due different tensions between its curvatures. Graphene shows sp^2 hybridization, whereas carbon nanotube and fullerene have same type of hybridization, but only deformed because of their geometries[1].

Tension in nonplanar conjugated molecules results from two main sources: pyramidalization of conjugated carbon atoms and misalignment of π-orbital between adjacent pairs of conjugated carbon atoms. Pyramidalization angle (θ_p) is between an σ-orbital and a π-orbital on the same carbon atom[1,2]. Therefore, carbon nanostructures present different pyramidalization angles, which are directly related to the distinct reactivity for each nanostructure.

Chemical reactions that saturate carbon atoms are highly favored due to relief of tension. In this way, the reactivity is favored according to geometry of nanostructure, varying according to increase of pyramidalization angle and misalignment of π-orbitals. Carbon nanotubes have a lower influence of curvature, but they present misalignment of π-orbitals that also favor reactivity. Thus, modifications in case of fullerene are more susceptible, since it presents the greatest tension between carbon bonds, when compared to nanotubes and later to graphene[1,3].

Carbon nanostructures are constantly functionalized in search of compatibility with other materials, for example

with polymers to produce nanocomposites with polymer matrix[4-6]. These types of nanostructures tend to agglomerate due to intermolecular interaction of van der Waals, which hinders their dispersion when incorporated into a polymeric matrix. Functionalization is an alternative to avoid the agglomeration of nanostructures and increase interaction with polymer, usually through functional groups inserted by superficial modification[7]. However, changes in the chemical structure of the carbon nanoparticles may alter its properties. If this occurs, the nanocomposite does not show the desired properties. So, it is important to understand how superficial modification takes place and if the alteration in its properties is due to this modification or its geometry.

Fullerene was discover in 1985 by Kroto et al.[8], and is a highly unsaturated spheroidal molecule, which may be composed of distinct amounts and pairs of carbon. C_{60} and C_{70} fullerene are the most abundant and representative[9], but there are many already discovered fullerenes and the large range of fullerenes can be represented by C_n, where n = 30 - 190[9]. C_{60} presents a combination of optical and electrical properties[10]. Arriagada and co-works studied the types of interaction between graphene and fullerene complexes with and without surface modifications. They showed that fullerenes are physisorbed on graphene while the chemisorption is reached on Fe-doped graphene nanosheets (cycloadditions)[11].

Carbon nanotubes (CNT) have the combination of low density, high surface area and high aspect ratio[12-15]. Carbon nanotubes are allotropes formed by long cylinders of covalent bonds between carbon atoms, those are entirely of sp^2 character. Moreover, the end of these nanotubes may or

may not be closed by hemi-fullerenes. There are two types of structure in terms of number of layers: single-wall carbon nanotube (SWCNT), which consists of a single "seamless" rolled sheet of graphene and multi-wall carbon nanotube (MWCNT), which are composed of graphene cylinders aligned coaxially around a central hollow core with a layer spacing of approximately 0.34-0.36 nm[7,14-16].

Graphene is obtained by exfoliation of graphite, presenting a single layer of carbons bound by sp^2 hybridization. Novoselov and collaborators isolated the first sheet of graphene in 2004, with the aid of an adhesive tape, thus performing a mechanical exfoliation. This nanostructure presents a combination of electrical, thermal and mechanical properties[17,18].

The isolation of graphene sheets can be performed by chemical and mechanical exfoliation. Chemical exfoliation by oxidation is the most common, this modification generates chemical bonds in graphene sheets, thus facilitating unpacking of sheets. However, this exfoliation generally promotes defects in the structure of graphene, which can be detrimental in some properties of graphene, such as electric.

The aim of this study is to modify surface of different carbon nanostructures (multi-walled carbon nanotubes, graphene and C_{60} fullerene) with octadecylamine and to characterize the modified nanostructures regarding morphology, chemical structure, molecular conformation and thermal properties.

2. Experimental

Fullerene C_{60} 98% was purchased from Sigma Aldrich; multi-walled carbon nanotubes from Laboratory of Nanomaterials – Physics Department - ICEX – UFMG and graphite HC 30 from *Grafmax* were modified in this work. Octadecylamine 99.0%, nitric acid 65% PA, sulfuric acid 95-99% PA and phosphoric acid 85% were supplied from Sigma Aldrich and used as received. Chloroform, ethanol 99.5% and potassium permanganate PA from Merck S.A. were used as received.

Fullerene C_{60} were treated with sulfuric acid (H_2SO_4) and nitric acid (HNO_3), as received. The system was refluxed, stirred and heated at 100 °C for 24 hours. After, product was washed with water, filtrated until pH was equal to that of pure water, and dried for 48 hours at 50 °C. This oxidation was adapted from literature[19-21].

Oxidized fullerene and octadecylamine (1:10) were heated at 65 °C and stirred for 24 h. This procedure were adapted[19,22], but presents a differential that is not use a solvent. After this, to the system was added ethanol (50 mL) and subjected on ultrasound bath for 30 minutes. The solution was vacuum filtered through a 0.22 µm membrane, washed with ethanol to remove excess of octadecylamine, and dried at 50 °C for 48 hours. The same treatment was used to carbon nanotubes[19,22].

Graphite (0.75 g) was treated with a solution of sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4) (90:10 mL) and potassium permanganate (4.5 g $KMnO_4$), that was subjected on ultrasound bath for 30 minutes. After that, the system was refluxed, stirred and heated at 80 °C for 24 hours. At the end of reaction, hydrogen peroxide (2 mL H_2O_2) and 200 mL of ice were put in the reaction, and final solution was vacuum filtered through a 0.22 µm membrane and washed with water.

It was filtrated until the pH was equal to that of pure water and after these; the product was dried for 48 hours at 50 °C[23,24].

Graphene oxide were treated with octadecylamine (1:10), heated at 130 °C and stirred for 48 hours. After this, to the system was added ethanol (50 mL) and subjected on ultrasound bath for 30 minutes. The solution was vacuum filtered through a 0.22 µm membrane and washed with ethanol to remove excess of octadecylamine. At the end, modified graphene was dried at 50 °C for 48 hours.

2.1 X-ray diffraction measurements (XRD)

XRD was used to determine structural changes in carbon nanostructures caused by modification steps. Bragg's Law was applied in order to relate 2θ values of reflection peaks and interplanar spacing (d). XRD patterns were obtained by using a Rigaku Ultima IV x-ray diffractometer with CuKα radiation source (λ = 0.1541 nm) operated at 40 kV, 30 mA, 0.05° s⁻¹ at room temperature and interval degree 2θ = 2 to 50°.

2.2 Fourier transform infrared spectroscopy measurements (FTIR)

FTIR analysis were performed in range 4000-400 cm⁻¹, analyzed at 25 °C in a Perkin Elmer Spectrum release device:10.4.2 and Frontier model FT-IR/FIR zinc selenite crystal using KBr to analyses nanostructures.

2.3 Thermal Gravimetric Analysis (TGA)

Measurements were obtained through of Thermogravimetric Analyzer TGA Q-500 (TA Instruments). Samples were heat from 40 to 700 °C, at heating rate of 5°C/min and under nitrogen atmosphere (flow rate = 100 mL/min).

2.4 Scanning Electron Microscope analysis (SEM)

SEM analysis were carried out to identify morphology of carbon nanostructures modified and unmodified. The samples in powder form were fixed on surface of metal stubs with the aid of a carbon ribbon. These stubs were taken to Sputter Coater equipment BAL-TEC, SDC 005 and covered with a layer of gold. Analyses of carbon nanostructures were held in scanning electron microscope FEI Quanta 400. For fullerene modified with octadecylamine and oxidized carbon nanotubes were used the scanning electron microscope HITACHI, model TM3000.

3. Results and Discussion

By X-ray diffraction, it was observed that Fullerene features eight narrow crystalline peaks centered at 2θ = 10.5°; 17.3°; 20.4°; 21.3°; 27.0°; 27.7°; 30.5°; 32.4°. Oxidized fullerene exhibits the same eight peaks but all with reduced light intensity and smooth extension of their bases (Figure 1a). The same phenomenon was observed by Oh et al.[25] which indicates a lower degree of organization after oxidation.

Fullerene modified with octadecylamine has only two broad-based peaks which are centered 2θ = 3° and 21.2°. This result shows that organization of the particles of fullerene before modification with octadecylamine had a regularity and uniformity, while with modifier in the structure this
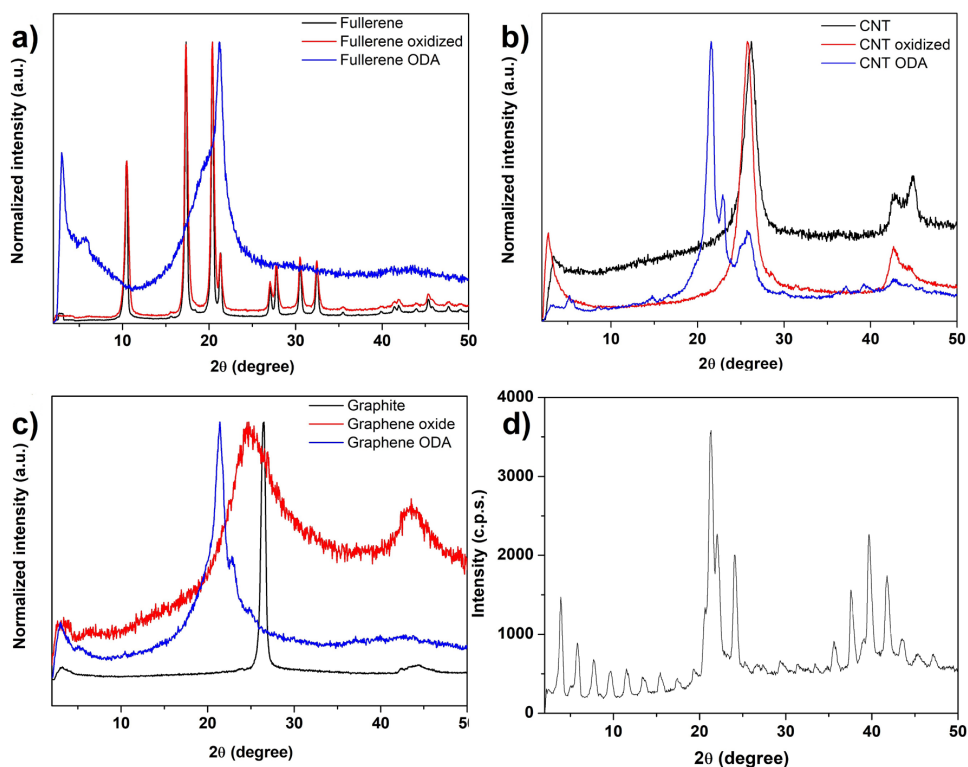
Figure 1. (a) XRD of fullerene, oxidized and modified with octadecylamine; (b) XRD of carbon nanotubes, oxidized and modified with octadecylamine; (c) XRD of graphite, graphene oxide and graphene ODA; (d) XRD of octadecylamine.

organization has been modified and has irregular and larger interplanar distances.

Through XRD, it is possible to calculate interplanar spacing and in the case of multiwall carbon nanotubes, the values can be found from distance between inner layers of nanotubes and the distance between carbon nanotubes, which tend to be agglomerated due to van der Waals interactions.

The peaks are found centered at 2θ equal to 26.2°; 42.8° and 45° (Figure 1b) with values for distance between nanotubes and between layers of 0.34 nm; 0.21 nm and 0.20 nm, respectively. According to Moniruzzaman and Winey (2006), the distance between walls for this type of carbon nanotube is about 0.34 nm, even spacing between graphene sheets in graphite.

XRD results for oxidized carbon nanotube also exhibit a peak centered at 2θ equal to 25.8° with a distance between walls of 0.34 nm nanotubes. The permanence of this distance shows that even with acid treatment for oxidation, the structural integrity of nanotubes was maintained. For carbon nanotubes modified with octadecylamine, peaks are centered at 21.6°; 22.9° and 25.9° with values for d-spacing around 0.41; 0.39 and 0.34 nm, respectively (Figure 1b). The peak shift at 21.6 ° shows that after modification with ODA nanotubes presented an organization with a greater distance between walls, but more organized than to oxidized nanotubes, which may be related to the interaction between ODA and nanotubes. The increase in distance between layers of nanotubes indicates that ODA chains have been inserted

between walls of nanotubes causing distancing or opening of these layers.

Diffractogram obtained for graphite has a single peak crystalline, narrow and centered at 2θ = 26.5° (Figure 1c). Through this value was calculated interplanar spacing of graphene sheets using Bragg's Law, which is 0.34 nm. The narrow peak characteristic indicates that graphite has a uniform distance between sheets[21]. After oxidation, were obtained graphene oxide, which presents two peaks with an extremely broad base, which denote a strong organizational change due to structural modification of carbon nanostructure[26].

XRD for graphene oxide shows an increase of interplanar distances after oxidation, which is due to the presence of carboxyl groups and hydroxyls of graphene surfaces and broadening of peaks, indicates heterogeneity of distances between crystalline planes. When modified with octadecylamine, interplanar spacing was increased due to appearing of two peaks, because both are on lower 2θ values when compared with other structures. The first centered at 2θ = 3 ° and second 2θ = 21.4°. Through calculations by Bragg's Law, these peaks indicate interplanar spacing of 5.89 nm and 0.83 nm, respectively.

The narrowing of peaks in sample Graphene ODA expresses minor variations for values of distances between planes, when compared with results for graphene oxide[27]. Therefore, indicating that in addition to increasing spacing, the modification method was also efficient in relation to periodicity with which interplanar distances were repeated.

In order to understand the appearance of a peak at 21° for all samples, an octadecylamine diffractogram was performed (Figure 1d) and this showed an intense peak centered at approximately 21°. Xu et al.[19] for carbon nanotubes modified with octadecylamine also report this phenomenon. According to authors, the most intense diffraction peak corresponds to crystallinity of octadecylamine.

FTIR analysis of modified nanostructures had as main intention to investigate the occurrence of chemical bonding between octadecylamine and the three carbon nanostructures evaluated. According to results obtained (Figure 2) was determined that modification occurred similarly for all nanostructured due to the appearance of bands related to bonding's vibrations -CH$_2$ and -CN, which are characteristic from octadecylamine.

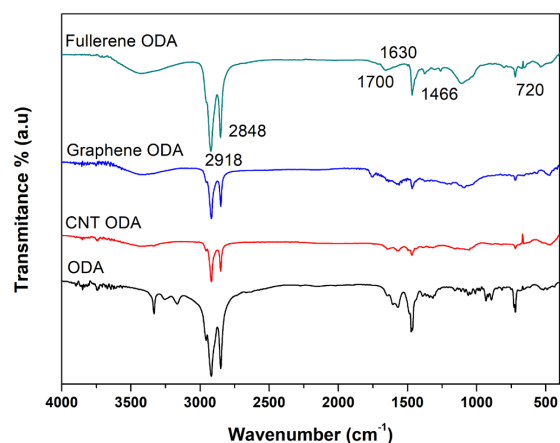Absorption bands at 2918 and 2848 cm^{-1} correspond to symmetric and asymmetric stretching vibrations and the rocking vibration at 720 cm^{-1} of aliphatic hydrocarbon groups[20,22,28-31]. As well as the stretching vibration at 1466 cm^{-1} regarding C-N amide bond between octadecylamine and the carbon nanostructures[22,31,32].

FTIR spectrum also shows an axial deformation at 1700 to 1630 cm^{-1}. The occurrence of this vibration demonstrates that octadecylamine is covalently bonded to each carbon nanostructures, since the reaction between carbonyl carbon (generated in the oxidation) and octadecylamine forms an amide function.

Another important point in the spectra of nanostructures is the absence of bands in range of 3400 to 3250 which corresponded to NH stretching and also of the range 1650 to 1580 of NH vibration bending, as both are characteristic of aliphatic primary amine (in all spectra of modified nanoparticles). Through this, it is possible to state that any unreacted amine has been successfully eliminated.

Thermal degradation curves of evaluated nanostructures allow us to observe its high thermal resistance in its modified state not denoted by reduced mass loss of these samples up to 700°C (Figure 3). Such behavior is already known in literature and is justified based on the high stability and structural rigidity of these particles[30,33,34]. After the oxidation process, it is possible to observe a slight reduction in thermal resistance thereof. This behavior reflects the structural defects created by the oxidation process, which reduces the stability of its structure and hence its rigidity, as previously observed by XRD.

The octadecylamine used in the modification of carbon nanostructures has a thermal resistance much lower than the
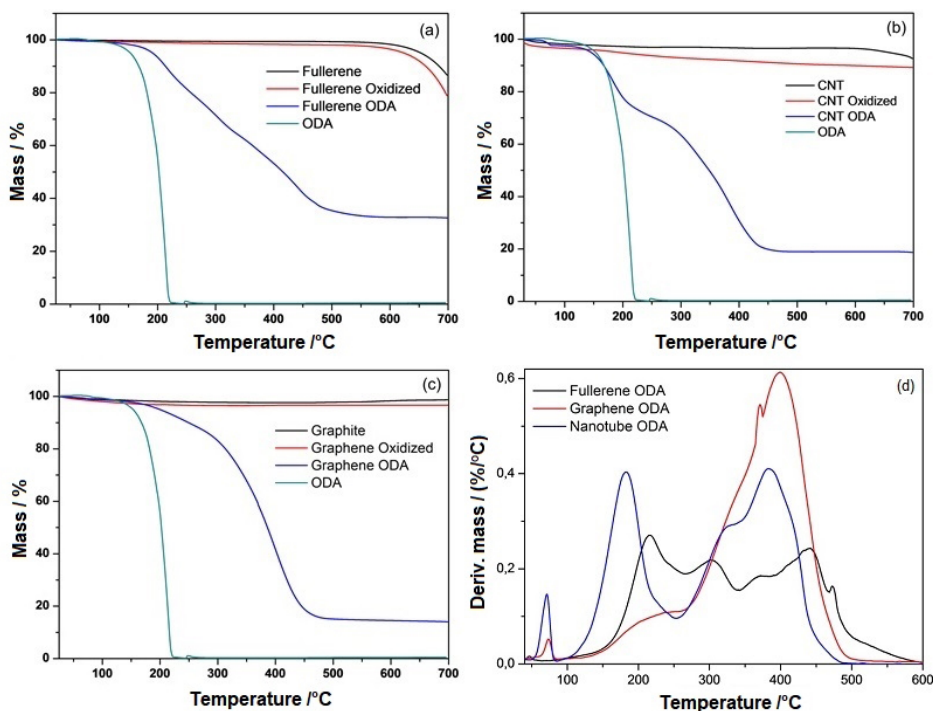

Figure 2. FTIR of octadecylamine and modified nanostructures.

Figure 3. (a) TGA curves of octadecylamine and fullerenes; (b) TGA curves of octadecylamine and CNTs; (c) TGA curves of octadecylamine and modified graphenes; (d) DTG curves of nanostructures with ODA.

particles and the degradation starts on temperatures below those observed for nanostructures (T_{onset} approximately 165°C). Thus, the incorporation of amine reduces the thermal resistance of nanostructures.

T_{onset} of modified nanostructures is concerning the start of the incorporated surface modifier degradation. In this perspective, although all particles exhibit a reduction of its heat resistance, it is remarkable that the beginning of the modifier loss is different for each geometry of evaluated particles.

According to previous studies, this behavior stems from the degree of thermal protection provided to amine by the greater or lesser intensity of interfacial interactions throughout their chain can establish with each of these nanostructures, giving the modifier chain a greater or lesser stiffness so influencing their resistance thermal[35].

In the initial mass loss, one can observe a distinct profile of degradation curves of modified nanostructures. It was indicated by XRD that the octadecylamine chain was possibly inserted between nanotube layers. The thermal degradation profile of these particles corroborates this possibility, since are observed two instances well-defined mass loss, where both located at higher temperatures possibly correspond to degradation of octadecylamine chains with different thermal protection levels conferred by its position more superficial or more internal areas of carbon nanotubes.

TGA results of modified fullerene and graphene (Figure 3a and 3c, respectively) showed the existence of more than one loss event but in this case, is not possible to separate loss levels as observed for nanotube-ODA. The other data that can be extracted from thermograms are final residue and the slope on the main event mass loss. Although fullerene presents a T_{onset} at temperatures below those observed for graphene, the loss event is slower leading to an offset temperature higher than that observed for graphene.

Analysis of residues on modified nanostructures may indicate which one has a higher amount of amine on their surface. Given that, the carbon nanostructures in their oxidized state have little mass loss until 600°C[36], one may define the losses observed until this temperature corresponding to inserted modifier its surface. Thus, the largest insertion amine was in graphene, followed by nanotube and fullerene[30].

The difference in insertion of amine in each nanostructure occurs possibly because of their different geometries correlated with the extension of chain amine used in the modification process. Graphene and nanotubes showed very close mass loss of values among themselves, which included a loss of 86% and 83%, respectively.

Fullerene lost just 63% indicating the presence of a minor amount of amine incorporated. In this case, it should be considered that its spherical shape formed by only 60 carbons when oxidized leads the formation of terminals really close which may be limited to the bonding of amine due to higher steric hindrance. While graphene and nanotube, due to the high aspect ratio, have these more distant terminals. Moreover, the difference in oxidation processes may have originated a greater number of reactive terminals on the surface of these nanostructures increasing its modification.

DTG curves denote the complex pattern of weight loss of the modified nanostructures (Figure 3d). In all these samples, it can notice an initial loss between 60 and 80°C, although this loss can be observed in DTG available in the literature, there are no reports about their origin. However, after the modification of the nanostructures it is possible that these will have absorbed moisture after the drying. This is possible due to the presence of hydrophilic terminals, which may have absorbed moisture on the surface.

Images of SEM were captured in order to know geometry and morphology of carbon nanostructures before and after chemical surface modification. In Figure 4a and 4b it is possible to note the decrease in size of the clusters with fullerene oxidation process, as well as increased surface roughness, thus evidencing oxidation. Image 4c shows
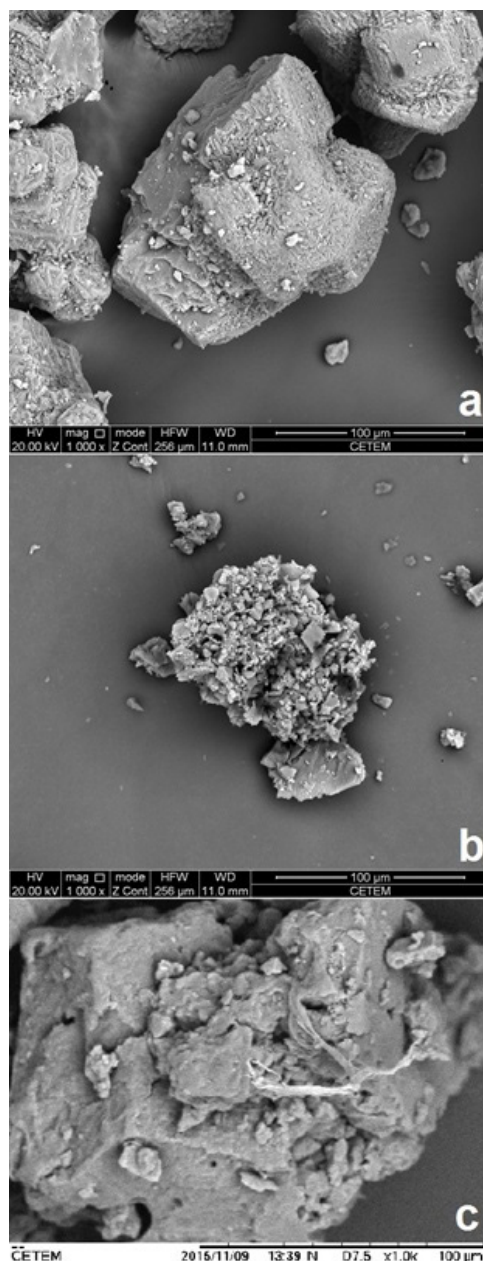

Figure 4. Images of SEM (a) fullerene C_{60}; (b) oxidized fullerene and (c) fullerene modified with octadecylamine.

change of surface with the chemical surface modification with octadecylamine as well as an increase of agglomerate, reinforcing the results revealed by FTIR, XRD and SEM.

Figure 5a shows multiwall carbon nanotubes as received. It is possible to see the high aspect ratio of the nanotubes. Figure 5b shows nanotubes after oxidation and it is apparent that acid treatment did not affect the geometry of nanostructure, thus retaining its tubular form. However, it is observed that there was some structural disorganization, because there was the appearance of some clumps of tangled nanotubes, suggesting that there was surface oxidation[37].

Figure 5c shows the modified carbon nanotubes with octadecylamine. In this image is still possible to view the morphology of tubes, but the presence of a mass, which

is possibly the modifier between the nanotubes strongly entangled indicating that they actually suffered some superficial chemical modification, as previously observed by FTIR. The presence of multiwall on carbon nanotubes cannot be visualized by SEM, but were confirmed by distance found between nanotube walls in XRD analysis.

Figure 6a shows graphite as received, which graphene sheets packaged with a distance between sheets that is not noticeable form. After the oxidation, graphene oxide was obtained in order to separate graphene sheets[38]. Figure 6b shows graphene oxide on a level of disorganization of material and a greater distance between sheets that indicates there was an expansion of graphite due to the aspect crumpled and exfoliated[39]. Figure 6c shows graphene modified with
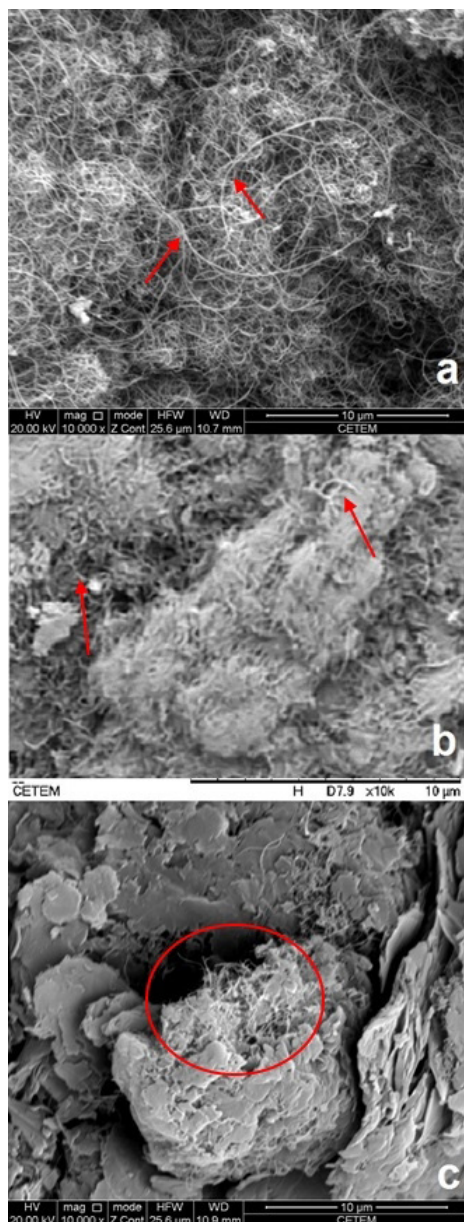

Figure 5. Images of SEM (a) CNT; (b) oxidized CNT and (c) CNT modified with octadecylamine.
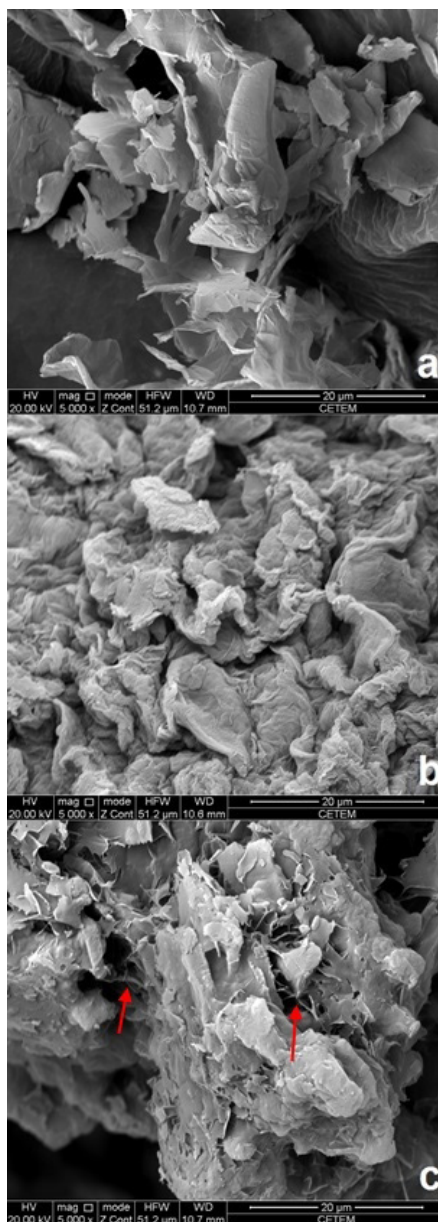

Figure 6. Images of SEM (a) graphite; (b) graphene oxide and (c) graphene modified with octadecylamine.

octadecylamine. SEM images confirm the increase in distance between sheets already seen by XRD, when compared to packaged sheets of graphite. In addition, it is possible to observe the presence of a mass, which indicates the presence of a modifier on the surface of graphene sheets, which is in accordance with the results of TGA. This modification was designed to increase interfacial interaction with a polymer in a nanocomposite on a future study.

4. Conclusions

Surface modifications of different carbon nanostructures (multi-walled carbon nanotubes, graphene, and C_{60} fullerene) with octadecylamine were performed. The modified nanostructures were characterized in terms of morphology, chemical structure, molecular conformation and thermal properties. Routes of oxidation for each carbon nanostructure were successfully performed and verified by X-ray diffraction, FTIR and SEM measurements. Surface chemical modification of all carbon nanostructures with ODA were confirmed by XRD, FTIR, and SEM and demonstrated not to have altered the geometry of the nanoparticles. Thermogravimetric analysis revealed not only the success of surface oxidation of all carbon nanostructures, but showed us a very interesting trend too. Even if the reactivity order of the nanostructures is fullerene > nanotubes > graphene, the latter was the one that had the largest amount of ODA. That is the species of lower reactivity had the highest degree of modification, evidencing that the effect of specific surface area was greater than reactivity, and both oxidation and chemical modification method was very successful. In this way, we demonstrate that it is possible to perform chemical surface modification of carbon nanostructures without shape damage, making possible the maintenance of the properties inherent to each of the structures and allowing their use in polymer nanocomposites.

5. Acknowledgements

6. References

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