MICROWAVE ASSIST FUNCTIONALIZATION OF MULTI WALLED CARBON NANOTUBES

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Abstract
There are many technique to increase reactivity of carbon nanotubes, this article study a improvement in oxidation and silanization procedures. Two oxidation methods are frequently used in carbon nanotubes: the conventional acid treatment, and the microwave treatment. The nanotubes oxidation was studied using microwaves and varying power and time of exposure. Compared to conventional acid treatment, the use of microwave provides benefits in speeding the reaction time, lowest amount of acids required and agitation is not needed. The present procedure was successful in the functionalization of carbon nanotubes with 3-aminopropyltriethoxysilane, which is a coupling agents that have a unique feature, bound organic to inorganic molecules.

1 Introduction
1.1 Carbon nanotubes

The carbon nanotubes (CNT) have been of great R & D interest since it provides mechanical, electrical and thermal unique properties, which may have wide use in engineering applications [1]. Conceptually a carbon nanotube is made of a graphene sheet rolled into a cylinder (see Fig. 1). These characteristics are similar to the graphite in terms of reactivity, that is, the covalent bonds between carbons are as stable as the structure of graphite [2]. There are two structures of CNT a single walled carbon nanotubes (SWCNT) and a multi walled carbon nanotubes (MWCNT). The option for using MWCNT is based on the fact that will remain internal walls even if the oxidation partially destroys external ones.

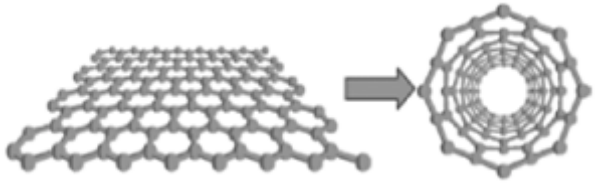

Figure 1 - Carbon nanotube look like a tube formed from a graphene sheet [3].

Therefore treatments are needed in order to changes the surface of the nanotube allowing their interaction with another material, e.g., for example, by oxidation and silanization. Oxidation creates carboxyl, hydroxyl bonds groups or sulfonic acids on the surface, depending on reaction conditions and reagents. These changes are 'defects' in the outer layer, which can directly interact with a polymer [4, 5]. Or even, after oxidation, a coupling agent a material, such as a silane, can functionalize the nanotube. In present work it was studied the accelerated oxidation using a microwaves compared to conventional acids treatment.

1.2 Accelerated microwave oxidation

Microwaves are electromagnetic waves or radiation whose spectrum ranges from 300 MHz to 300 GHz; these frequencies are lower than the ionizing radiation. Ionizing radiations are those able to ionize biological material, with serious potential consequences to human exposure. Examples include the short ultraviolet, X-rays and gamma rays. So, the microwaves are classified as non-ionizing radiation, and do not cause this kind of danger. The microwaves may be used for material heating and in this case the phenomenon takes place in different ways, depending on whether it is conductive or has thermal insulation.

If the material is conductive, the magnetic field will cause the movement of electrons in this conductor producing electric current. If the material offers some resistance, the electric current causes the heating. This phenomenon is known as resistive heating.

In insulating materials there is no movement of electrons, in this case, the orientation of molecules electric dipoles occurs due to electromagnetic induction. This orientation is varied continuously, since the high frequency electromagnetic waves will cause a rapid and constant change of the magnetic field. This variation of the dipoles is the cause of the heating in insulating material.

The heating characteristics of a material exposed to microwaves are dependent on their dielectric properties. The ability of a substance to convert electromagnetic energy into heat, at a given temperature and frequency, is determined by the dissipation factor (tan δ) where δ is called loss angle and is the angle between the current and the resultant capacitance between the capacitive current and resistive current in phase with the voltage as a sinusoidal voltage is applied [6].

The dissipation factor is provided by the ratio between the dielectric loss (ε ") $\tan\delta = \frac{\varepsilon'}{\varepsilon'}$ and the material dielectric constant (ε '). Some values of dielectric constant are found in Table 1.

	Dielectric constant (ε')
Nitric acid	40
Sulphuric acid	100
Teflon (PTFE)	2.1

Table 1 - Values of dielectric constant [7].

The dielectric loss indicates how efficiently electromagnetic radiation is converted into heat. And the dielectric constant describes the ability of the molecules being polarized by the magnetic field. The larger the dissipation factor, more the substance will absorb radiation and consequently faster the heating.

The microwave heating method has already been used in some organic syntheses and, besides being faster, it is still advantageous in another way. As the heat supplied to the system is traditionally an external source, a water bath for example, it has to penetrate various materials layers to heat the reaction medium. As a result, the recipient temperature is greater than the reaction one. Comparatively it is a slow, inefficient, and energy transfer loss method [8,9,10].

The microwave heating, on the other hand, produces efficient heating of the internal container, or, heating the reaction medium. This happens because the microwaves excite the own molecules of the reaction (solvents, reagents, catalysts). Fig. 2 shows the comparison between the temperatures of the vessels.

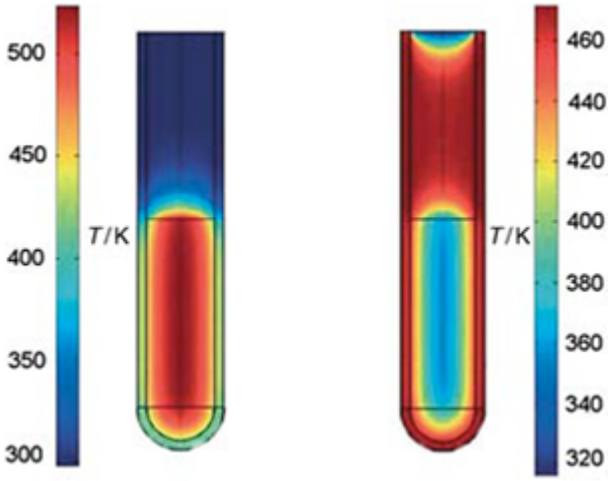

Figure 2- Inversion of the temperature gradient between the microwave heating for 1 min (left) and the conventional heat treatment (right). The microwaves simultaneously increase the temperature in the whole volume while the first bath causes the heating of the mixture just in contact with the container [11].

The oxidation process is accelerated when exposed to electromagnetic radiation. The microwaves are used for heating the acid solution, although there are researches on the non-thermal microwave effect in organic synthesis [12, 13, 6, 7].

1.3 Funcionalization

The functionalization was carried out with an organosilane compound, 3-aminopropyltriethoxysilane. These coupling agents have a unique feature, functional groups which react with organic materials and other groups which reacts inorganic materials. In other words it provides the interaction between organic and inorganic materials.

The organic group (R) may vary including epoxy groups, amino, vinyl, mercapto, and polisulfido among other organic groups. There are also different hydrolysable groups (X) as chlorine, methoxy and ethoxy. Figure 3 shows the general organosilane structure.

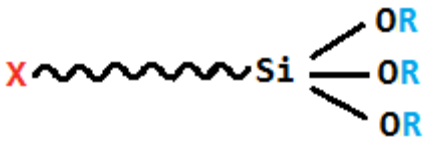

Figure 3 - General organosilane structure

The interaction occurs with inorganic materials to hydrolysis and subsequent dehydration and condensation of silane. As a result multiple hydrogen bonds between the inorganic and organic surface

Some properties of the silane, 3-amine propyltriethoxysilane, used in the study are shown in Table 2.

Functional group	Name	Formula	Molecular Weight	Specific Weight (25°C)	Ebullition point (°C)	CAS No.
Amine	3-amine propil triethoxysilane	$(C_2H_5O)SiC_3H_6NH_2$	221,4	98	217	919-30-2

Table 2 - Silane properties

According to the manufacturer the amount of silane should be 0.5 to 2.0% by mass of the inorganic material [14, 15].

2 Materials and testing methods

The multiwalled carbon nanotubes (MWCNT) used in this experiment were obtained from the Physics Institute of Universidade Federal de Minas Gerais (UFMG). Were produced via chemical vapor deposition, have diameters between 10-30 nm, length of 200 nm and a purity above 95%.

The following reagents were used without further purification: sulfuric acid, nitric acid, acetone and ethanol.

2.1 Microwave Oxidation

A sample with 0.25 g of MWCNT were dispersed in 5 mL of H2SO4/HNO3 3:1 (v / v) and placed in a microwave oven (Microwave Labstation, Milestone Model ML 1200 mega; vessel of 100 mL teflon PEEK (Microwave Laboratories of Instituto Mauá de Tecnologia – IMT Brazil) for different reaction times and power. We will call M10-150 reaction of the sample 10 minutes and 150 W. The sample time of 20 minutes 150 W will call M20-150. The sample with power of 300 W and 10 minutes of reaction called M10-300. All samples were cooled for 30 minutes. Then the solution was filtered and washed with 10 mL of water / acetone 1:1 (v / v). The filtrate was dried in an oven for 9 hours at 100 °C.

2.2 Conventional heat treatment oxidation

A sample with 0.5 g of MWCNT were dispersed in 50 mL of H_2SO_4/HNO_3 3:1 (v / v) at 55 °C for 9 hours. Then the solution was vacuum filtered and washed with 10 mL of water / acetone 1:1 (v / v). The filtrate was dried in an oven for 9 hours at 100 °C. This sample was identified as c-MWCNT.

2.3 Silanization

A sample with 0.20 g of MWCNT were dispersed in 50 mL of ethanol via ultrasound for 30 minutes. Then it was added the 3-aminopropyltriethoxysilane maintaining agitation for 4 hours at 55-60 ° C. The product was centrifuged and washed with water, four times, and them followed by acetone and dried in oven for 20 h at 80 ° C. This sample was identified as Si-MWCNT.

3. Results and discussion

3.1 Infrared

The infrared spectrum (FTIR) of the carbon nanotube sample pure oxidized and silanized tablets were made with 1 mass% of the sample and KBr. All samples oxidized show the same profile in the spectrum.

The Fig. 4 shows the infrared spectra (IR) that corresponds to an unmodified sample (identified here as p-MWCNT). According to literature, the bands at 1600 cm -1 and 1550 cm-1 represent the connection between carbons.

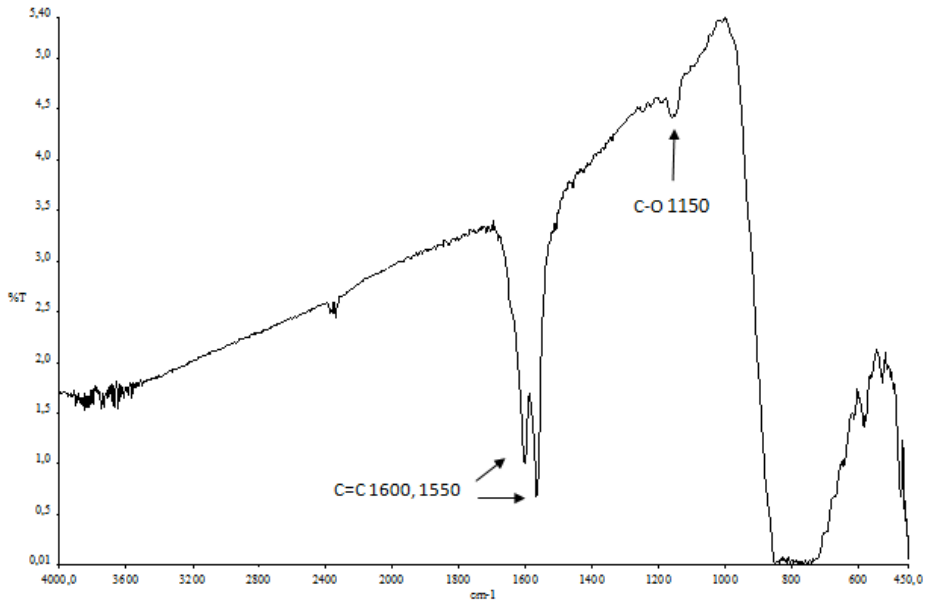

Figure 4 – FTIR spectrum IV of p-MWCNT sample showing the presence of the bands at 1600 cm^{-1} and 1550 cm^{-1} representing the connection between carbons.

The Fig. 5 shows the FTIR spectrum of the sample m-MWCNT. It can be observed, despite the interference, the band corresponding to the presence of hydroxyl groups, which characterizes the oxidation.

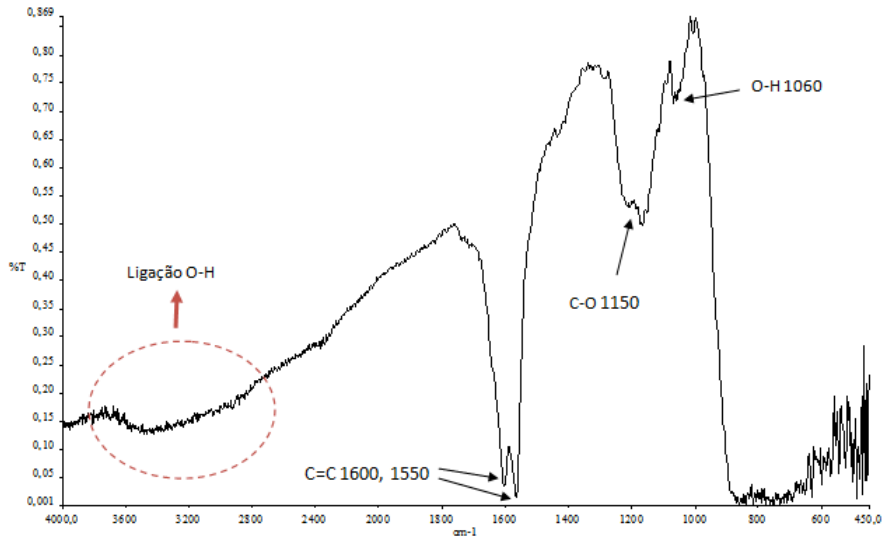

Figure 5 - Spectrum IV of m-MWCNT sample showing the presence of the bands at 1060 cm^{-1} representing the O-H groups.

Finally, in Fig. 6 the FTIR spectrum of silanized sample (Si-MWCNT) shows that the characteristic of presence of silicon according to the peak 795 cm -1, and the other peaks of oxidation.

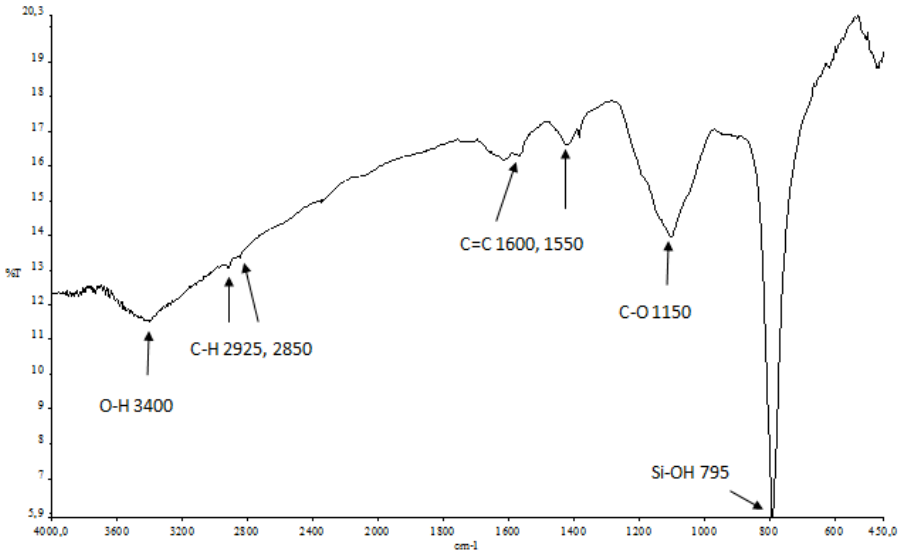

Figure 6 - Spectrum IV of Si-MWCNT sample showing the presence of the bands at 795 cm^{-1} representing the presence of silicon.

The FTIR showed in Fig.6 spectrum confirms that the method was successful in both oxidizing and in silanizing the carbon nanotube.

3.2 EDS analysis

The energy dispersive spectroscopy (EDS) technique was used to study the influence of time exposure to microwave radiation and the power thereof. Tab. 3 shows the percentage in mass

of each element in the samples oxidized and silanized. It is possible to observe that the increase in power does not benefit oxidation, therefore tests with 300 W and 20 minutes have not been made. It should be noted that even longer periods of exposure to microwave radiation power does not increase the amount of oxidized sample.

	Samples			
	150 W/10 min	150 W/20 min	300 W/10 min	Silanized
Element	*Wt%*	*Wt%*	*Wt%*	*Wt%*
CK	79.96	84.45	92.34	81.27
OK	15.50	12.65	6.02	11.72
SK	4.53	01.13	1.63	0.62
SiK	-	-	-	6.38

Table 3 - Mass percent of each element of the samples after the microwave treatment measured using EDS. (-not mesured)

Studies demonstrated that microwave reaction time determines how oxidized the nanotube is[6,10]. When it is exposed for long time, the reaction takes opposite direction and disfuncionalizate the molecule. In this case the microwave radiation itself begins to act as catalysts, forcing the reaction equilibrium to the other side. Therefore, the present study and under the present conditions it is shown that 150 W and 10 minutes are the best conditions for the input power and time, respectively.

Conventional treatment promote the oxidation by increasing the temperature, reaction times and quantity and concentration of the involved acids. While oxidation promoted by microwaves has benefits as removing impurities such as amorphous carbon and catalysts waste. This happens because the HNO3 can quickly absorb the heat and microwave energy and dissolve impurities, like metals or amorphous carbon found in nanotubes, without causing damage.

The microwave accelerated oxidation does not require stirring, considerably decreases the reaction time and requires a smaller amount of acid solution as compared to conventional thermal oxidation. For silanization it was used the convention heat treatment to functionalizes carbon nanotubes with 3-aminopropyltriethoxysilane.

4. Conclusions

The microwave accelerated NTC oxidation and do not require stirring witch considerably decreases the reaction time and requires a smaller amount of acid solution as compared to conventional thermal oxidation. Microwave treatment obtained a clear solution differently of the conventional acid witch produced a lot off amorphous carbon by degradation of external walls.

The method employed functionalizes carbon nanotubes with 3-aminopropyltriethoxysilane efficiently.

This great absorption that the carbon has over microwaves allows numerous applications where the carbon would assist in many procedure, like resin cure or catalysis.

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