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SURFACE MODIFICATION OF MWCNTS BY DIFFERENT METHODS TO IMPROVE FABRICATION WITH POLYMER COMPOSITES

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***Abstract**. Multiwalled carbon nanotubes (MWCNTs) consist on orderly materials, with C-C and C=C sp² chemical bonds. In order to improve the chemical interaction between MWCNTs and polymeric matrix, oxidative chemical treatments can generate polar groups on it surface. Different oxidation processes like liquid oxidation in hydrogen peroxide and AC plasma were investigated. The untreated and treated MWCNTs were analyzed by Raman spectroscopy and by chemical affinity tests based in solvent dispersion/sedimentation. Raman spectra provide characteristics about changes in structural order confirming the existence of modifications in treated MWCNTs. Dispersion/sedimentation tests showed information about the affinity of MWCNTs with solvents presenting different polarity, what provide previous information about dispersion in polymer matrix. The MWCNTs were used in fabrication process, like a selective laser sintering, injection mould material and casting of thermoset resin. Polar groups become interesting to polyamide and epoxy composite systems.*

***Keywords**: MWCNTs, surface treatment, fabrication process*

1. INTRODUCTION

Initial studies focused as on understanding the structure and physical properties of the pristine nanotubes. Recent efforts are dedicated to chemical modification (Li, 2005). There are two main kinds of functionalization (covalent and noncovalent). In the first, functional groups are directly attached to the nanotube´s surface.

Oxidation treatment become interest because the insertion of –COOH groups, aiding the interaction with polar polymers. Many routes have been conducted using mixture of acids on reflux method, mainly HNO_3 and H_2SO_4 with different times and temperatures of the process (Hong, 2007 e Kim, 2007). Peroxide treatments consist on an oxidation method not much used and investigated, but can get good results (Montoro, 2006). This method consist on a less critical reaction compared with others and by the way, can achieve greater sensitivity to obtaining more sensible surface oxidations. Oxidation using an AC plasma discharge is an efficient method of oxidation treatment presenting short run times to treatment. Unfortunately, there is few information about the effect of AC plasma oxidation in carbon and polymeric materials.

In this work, the oxidation treatment of MWCNTs by reflux and plasma techniques was investigated. The treated MWCNTs were analyzed by Raman scattering spectroscopy that identifies the graphitic carbons and by dispersion/sedimentation tests in solvents with different polarities.

2. MATERIALS AND METHODS

2.1. Materials

The multiwalled carbon nanotubes were purchased from MER Corp.. These nanotubes were obtained from the chemical vapor deposition and have, according to manufacturer, an average diameter of 140 + / - 30nm and length of 7 + / - 2 µm, with level of purity greater than 90%.

2.2. Reflux oxidation

Intending a surface treatment of oxidation in carbon nanotubes acquired, there was a treatment with hydrogen peroxide as an agent of oxidation. 300mg of MWNTs were dispersed in a solution of H_2O_2 (10%) under stirring ultrasonic during 1h. The suspension was taken to a 500ml flask of being coupled to an equipment for the realization of reflux at a temperature of 100 °C for 5, 10 and 15 hours. Samples taken from the balloon were filtered under vacuum and washed with deionized water and acetone in abundance. After, the powder was dry in oven at 100 °C for 8h.

2.3 AC plasma oxidation

The treatments were performed in a vacuum chamber, under pressure from 4.10^{-4} Torr, and then fed with a flow of oxygen (White Martins 2.8) to stabilize the pressure in 6.10^{-3} Torr. Inside the chamber, two cylindrical aluminum electrodes (13mm in diameter and 400mm in length) were positioned separated by 270 mm. Among the electrodes was applied a voltage of 2000 V (AC, 60 Hz), by forming a discharge plasma. The samples were positioned between the electrodes and subjected to different times of treatment: 0.5, 1.0, 3.0, 8.0 and 16 minutes. The times of treatment were determined without a thorough knowledge of possible answers, so it was decided to initially use small time, with the initial 1 minute and 3 minutes later as. A major change with time (8 minutes) was selected to test most significant changes. After preliminary tests were decided to use two more times of extreme treatment (0.5 and 16 minutes) to confirm possible changes in the early stages of operation and in times longer.

2.4 Raman spectroscopy

The samples obtained were then taken to a Raman spectrometer, Renishaw inVia Raman Microscope, equipped with an argon laser (514nm). The acquisition of the data was obtained with 100% of the laser power, using three accumulations for construction of the curves. The range of scanning has spread from 100 to 3500cm^{-1}, and all curves were obtained with an increase of 20X, for standardization of results and better analysis of the peaks. Three different samples were analyzed in order to obtain the best curve.

2.5 Solvent tests

To the dispersion/sedimentation tests, the methodology used for initial preparation it was the selection of chemical solvents that with different characteristics in terms of polarity and dielectric permissivity. Eight different solvents and their physical-chemical properties are listed in Tab.1. Ten images were registered in the dispersion/sedimentation tests using glass flask and microscopy sample supports for each mixture solvent-MWCNTs in order to select the better visualization.

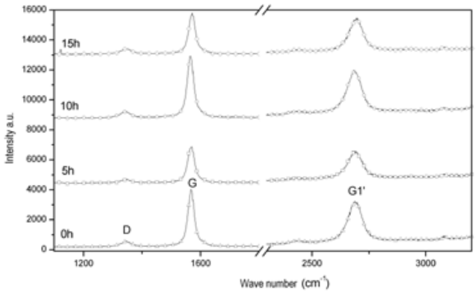
Table 1. Physical-chemical properties of solvents

Solvents	*Chemical formule*	*Dielectric permissivity (25ºC)*	*Density (g/cm³)*	*Solubility parameter g [(cal/cm³)½]*
Hydrogen peroxide	H_2O_2	82,00	1,128	-
Distilled water	H_2O	78,54	1,000	23,50
DMSO	C_2H_6OS	45,00	1,100	12,90
DMF	C_3H_7O	37,00	0,949	12,14
Acetone	$C_{16}H_{21}O$	20,70	0,788	9,75
Isopropyl alcohol	C_3HO	20,10	0,785	11,97
THF	C_4HO	7,52	0,886	9,49
Chloroform	$CHCl_3$	4,80	1,480	9,21

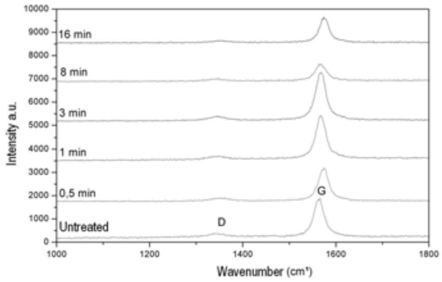
3. RESULTS AND DISCUSSION

3.1. Raman spectroscopy

Figure 1 shows the Raman spectra for untreated and treated MWCNTs by reflux and plasma treatment. Table 2 presents the ratio of intensity peaks obtained by analyzes of graphics. The peaks intensity variation (%) describes the effect of treatment in the MWCNTs structure (Delhaes, 2006). Raman spectra provided characteristics about changes in structural order confirming the existence of modifications in treated MWCNTs as indicated in the peaks intensity variation at Tab. 2.



(a)



(b)

Figure 1. Raman spectra for reflux treatment (a) and plasma treatment (b).

Table 2. Ratio between Raman peaks and its intensity variation. Reflux (a) and plasma (b).

	Ratio I_D/I_G	*Intensity variation (%)*
Untreated material	0,145	--
5 hours treated	0,159	9
10 hours treated	0,149	3
15 hours treated	0,183	21

(a)

	Ratio I_D/I_G	*Intensity variation (%)*
Untreated material	0,16	--
0,5 minute treated	0,158	1,4
1 minute treated	0,18	12
3 minutes treated	0,185	15
8 minutes treated	0,199	41
16 minutes treated	0,2	41

(b)

3.2. Dispersion analysis

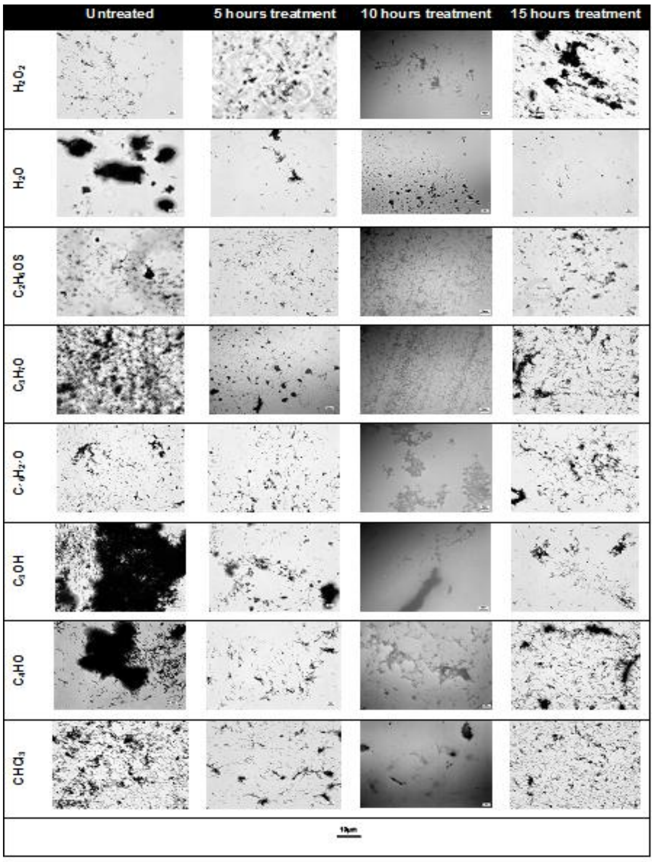


Figure 2. Microscopy images of the dispersion of MWCNTs in solvents at different treatment time (500X).

Figure 2 shows microscopy images of the dispersion of MWCNTs in solvents at different treatment time by reflux in hydrogen peroxide. An analysis of these images shows a significant improvement in the dispersion in isopropyl alcohol, distilled water and THF as function of treatment time. The hydrogen peroxide suspension showed a significant reduction in dispersion distribution. The best improvement in dispersion was observed for treated MWCNTs in DMF, DMSO and chloroform, i.e. intermediate polarity solvents.

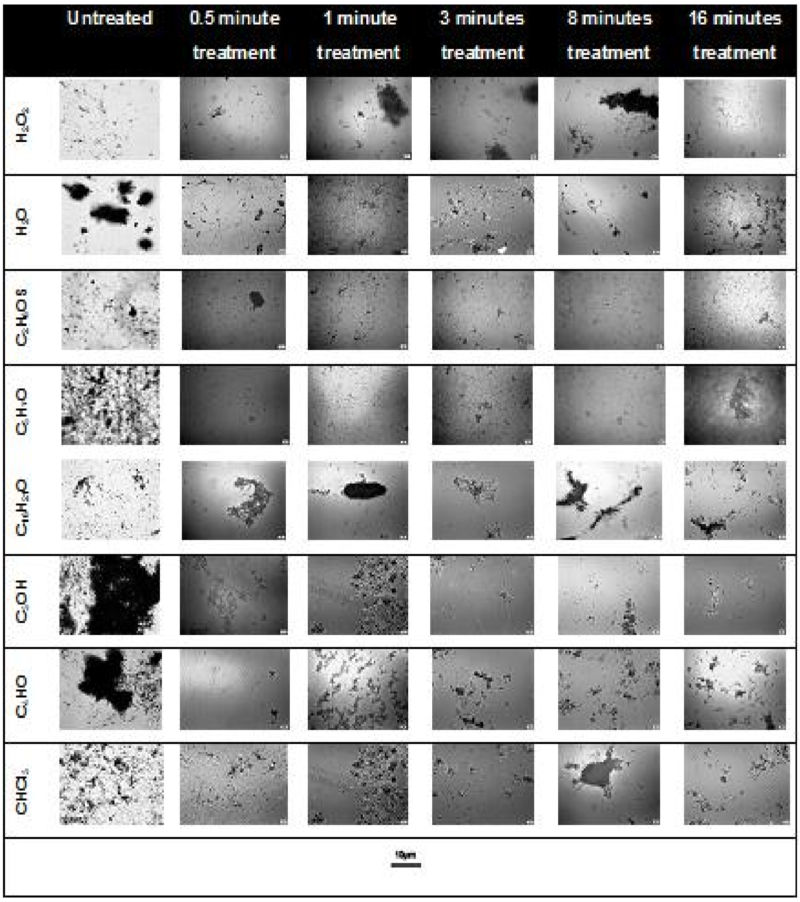


Figure 3. Comparative of dispersion between solvents to "glow" treatment (500X).

Figure 3 show dispersion of MWCNTs after oxygen plasma treatment. The indication of augmentation in polarity of MWCNTs surface as function of time treatment was the improvement in the distribution of MWCNTs in water even after only 3 minutes. The dispersion in water was comparable to the dispersion distribution in DMSO and DMF after 16 minutes of plasma treatment. The oxygen plasma treatment reduced the dispersion distribution of MWCNTs in chloroform, as expected once chloroform is a less polar solvent.

3.3. Sedimentation Analyses

Figure 4 shows images of sedimentation tests to MWCNTs in solvents as function of time treatment under reflux. In Fig. 4, it is possible to observe the modification in sedimentation behavior of MWCNTs in different solvents caused by the surface oxidation. The untreated MWCNTs showed no sedimentation in DMSO, DMF and chloroform. The Treated MWCNTs showed no sedimentation in isopropyl alcohol, DMF, THF and chloroform confirming an indicative of oxidation in MWCNTs surfaces. It's important to relate that a change in the interaction of MWCNTs with isopropyl and THF is desired. These two solvent showed intermediated polarity, similar to epoxy, polyester and polyamide groups.

Figure 5 shows images of sedimentation tests to MWCNTs in solvents as function of time treatment under oxygen AC plasma. In Fig. 5, it is possible to observe the modification in sedimentation behavior of MWCNTs in different solvents caused by the surface oxidation. The untreated MWCNTs showed no sedimentation in DMSO, DMF and chloroform as previous reported. The Treated MWCNTs showed no sedimentation in isopropyl alcohol, DMF, THF and chloroform confirming an indicative of oxidation in MWCNTs surfaces at only 0.5 minutes of treatment. Such effect was also obtained in reflux process after 15 hours of treatment, indicating that the oxygen plasma is a powerfully oxidant medium. The MWCNTs treated during 16 minutes showed low degree of sedimentation in water and acetone indicating strong modifications in the MWCNTs structure/properties caused un aggressive oxidation under oxygen AC plasma.

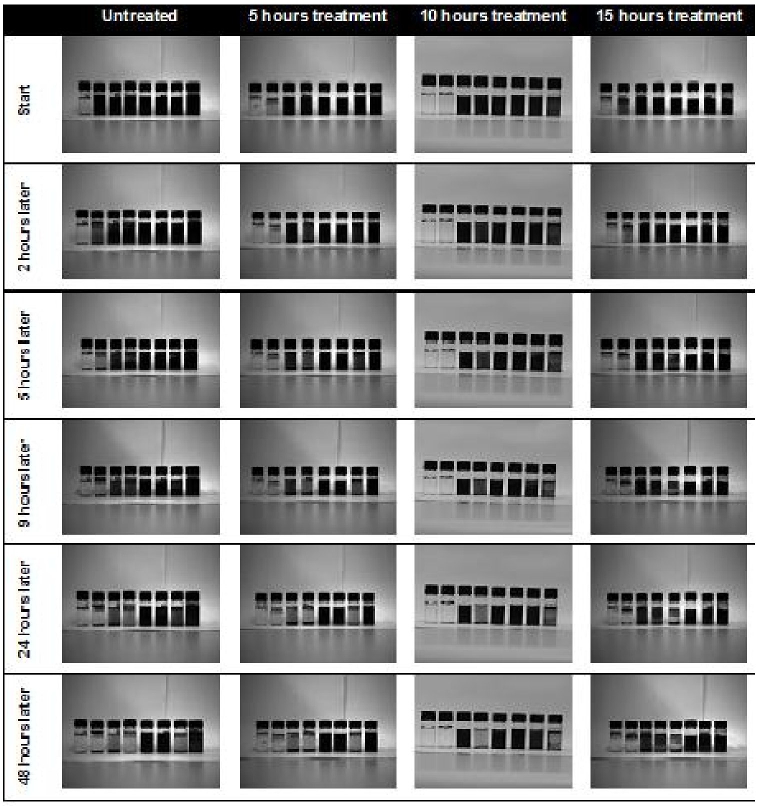


Figure 4. Images of sedimentation behavior tests to MWCNTs in solvents as function of time treatment under reflux. The solvent order from left to right is: water, hydrogen peroxide, isopropyl alcohol, acetone, DMSO, DMF, THF and chloroform.

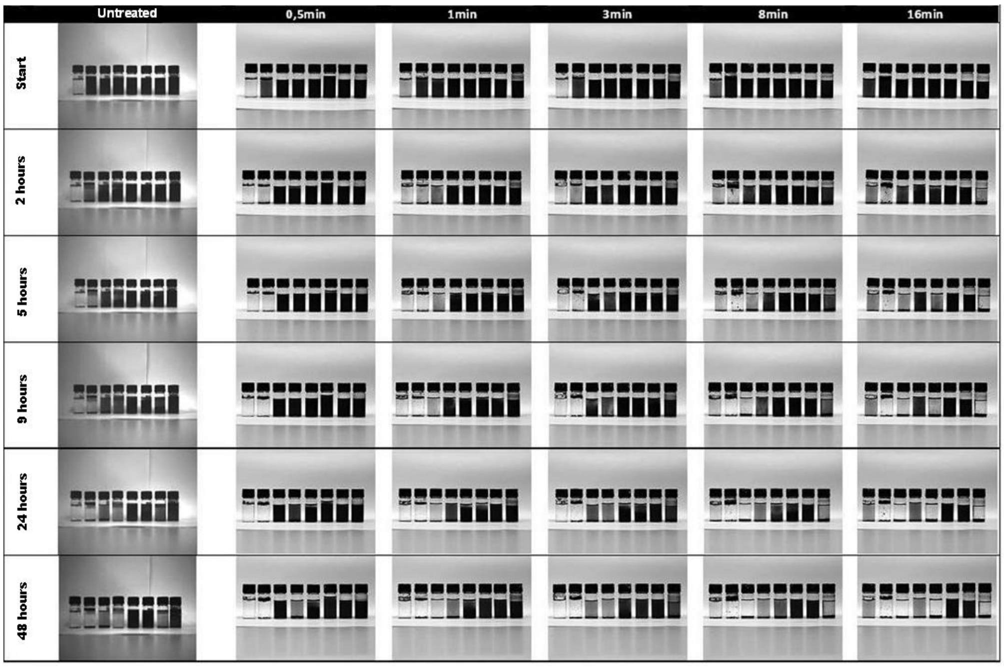


Figure 5. Images of sedimentation behavior tests to MWCNTs in solvents as function of time treatment under oxygen plasma. The solvent order from left to right is: water, hydrogen peroxide, isopropyl alcohol, acetone, DMSO, DMF, THF and chloroform.

4. CONCLUSIONS

Raman spectra provide characteristics about changes in structural order confirming the existence of modifications in treated MWCNTs. The peaks intensity variation (%) describes the effect of treatment in the MWCNTs structure confirming the existence of modifications in treated MWCNTs by reflux and AC plasma process. The microscopy images of the dispersion of MWCNTs in solvents at different treatment time by reflux in hydrogen peroxide showed a significant improvement in the dispersion in isopropyl alcohol, distilled water and THF as function of treatment time. The best improvement in dispersion was observed for treated MWCNTs in DMF, DMSO and chloroform, i.e. intermediate polarity solvents.

The images of the dispersion of MWCNTs after oxygen plasma treatment in microscopy demonstrated an indication of augmentation in polarity of MWCNts surface as function of time treatment. It was observed an improvement in the distribution of MWCNTs in water even after only 3 minutes. The dispersion in water was comparable to the dispersion distribution in DMSO and DMF after 16 minutes of plasma treatment. To the dispersion/sedimentation tests based in a methodology using the affinity with chemical solvents of different polarity showed interesting results. The images analyses of the dispersion/sedimentation tests using glass flask and microscopy sample supports for each mixture solvent-MWCNTs showed information about the affinity of MWCNTs with solvents presenting different polarity, what provide a oxidation process control and previous information about dispersion in polymer matrix.

The images of sedimentation tests in flasks of MWCNTs in solvents as function of time treatment under reflux reveled modification in sedimentation behavior of MWCNTs in different solvents caused by the surface oxidation. The treated MWCNTs by reflux showed no sedimentation in isopropyl alcohol and THF, what is important once these two solvent showed intermediated polarity, similar to epoxy, polyester and polyamide groups. The Treated MWCNTs by plasma showed no sedimentation in isopropyl alcohol and THF confirming an indicative of oxidation in MWCNTs surfaces at only 0.5 minutes of treatment. Such effect indicate that the oxygen plasma is a powerfully oxidant medium. The treated MWCNTs were used in fabrication process such as selective laser sintering, injection mould and casting of thermoset resin.

5. ACKNOWLEDGEMENTS

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