

## COMPOSITE POLYMERIC MATRIX MODIFIED WITH MICROWAVED TREATED MULTI WALLED CARBON NANOTUBES.

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**Abstract.** The stability of carbon nanotubes discourages their use as reinforcement agents for polymer composites production. However, once functionalized it shows interesting new properties. A multi-walled carbon nanotubes (MWCNT) were initially treated by a mixture of concentrated H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> in a microwave oven and were functionalized, with coupling agent, 3-aminopropyltriethoxysilane (3-APTES). This process is fast and produces a MWCNT solution clean of fragments. A FT-IR spectroscopy of MWCNT showed specific peaks that indicate its oxidation and functionalization. Mechanical tests of the obtained nanocomposites with phenol / epoxy resin and MWCNT, were prepared showing improved mechanical properties such as flexural strength and impact resistance.

### 1. Introduction

The carbon nanotubes uses have been a great source of researches due to its unique mechanical, electrical and thermal proprieties, which can be extremely applicable to engineering development [1]. However, while carbon nanotubes discovery represents a opportunity in reinforced polymers, there is a some impediments that must be overcome, by the nanotubes high stability, which is similar to graphene [2]. Technical application of MWCNT for composites formulation can only be realized by solving two main problems: (i) the dispersion of the carbon nanotubes in the polymer matrix; (ii) the interfacial adhesion between the carbon nanotubes and the matrix [1].

Studies showed that there is, at least, two ways to increase carbon nanotubes compatibility with an epoxy matrix. One is by non-covalent functionalization, which Van der Waals forces interact with polymers and nanotubes [3]. Apart from this, there is covalent functionalization,

which consists on modifying MWCNT surface inserting functional groups or coupling agents. The second option has shown more compatible with matrix resins composite [4]. Dispersion techniques, like heat, mixers and ultrasound were employed separately or together, to achieve good level of dispersion.

In the present work a route was proposed to functionalize carbon nanotubes by microwave enhanced oxidation process followed by an addition of 3-APTES. Although sulfonitric oxidation treatment can easily modify the MWCNT surface, it also grinds the MWCNT. To minimize this effect, it was introduced the microwave enhanced oxidation. With the microwave irradiation it was observed a less intense grinding of the nanotubes. In fact, it was observed a reintegration of fragments in its main structure [5]. This oxidation led to the appearing of carboxyl and hydroxyl groups that may be connected to 3-APTES, which in turn enable interactions between nanotubes and resins by amine and ethoxy group linkage. The presence of bonded 3-APTES transforms the non-reactive surface of carbon nanotubes into an organophilic behavior.

## 1.1 Experimental

The (MWCNT) used in this experiment were obtained from the Physics Institute of Universidade Federal de Minas Gerais (UFMG). They were produced via chemical vapor deposition and have diameters between 10 nm and 30 nm, 200 nm lengths and purity above 95% [6].

### 1.1.1 Oxidation

A sample with 0.25 g of unmodified MWCNT (U-MWCNT) was dispersed in 5 mL of H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> 3:1 (v/v) and placed in a polytetrafluorethylene (PTFE) and polyetheretherketone (PEEK) microwave oven vessel of 100 mL capacity (Microwave Labstation Milestone Model ML 1200). The mixture had reacted under a microwave power of 150 W during 10 minutes, faster than 10 h of sulfonitric oxidation bath [7]. After this heating, it was cooled for 30 minutes and the solution was centrifuged, washed with 10 mL of water / acetone 1:1 (v/v), for three times, and was dried in an oven during 12 h at 120 °C. This oxidizing sample of MWCNT was identified as O-MWCNT.

### 1.1.2 Functionalization

A sample with 0.50 g of O-MWCNT, were dispersed in 50 mL of anhydrous ethanol via sonication for 30 minutes. The suspension was then heated at 60 °C for another 30 minutes, and treated with 0.5 mL the 3-aminopropyltriethoxysilane under continuous stirring for 4 h at 55 °C to 65 °C. This product was centrifuged and washed four times with water, and then with acetone. It was dried in an oven at 80 °C for 20 h. This sample was identified as Si-MWCNT.

U-MWCNT, O-MWCNT and Si-MWCNT were analyzed under FTIR, with KBr support, using a Perkim Elmer Spectrum One equipment.

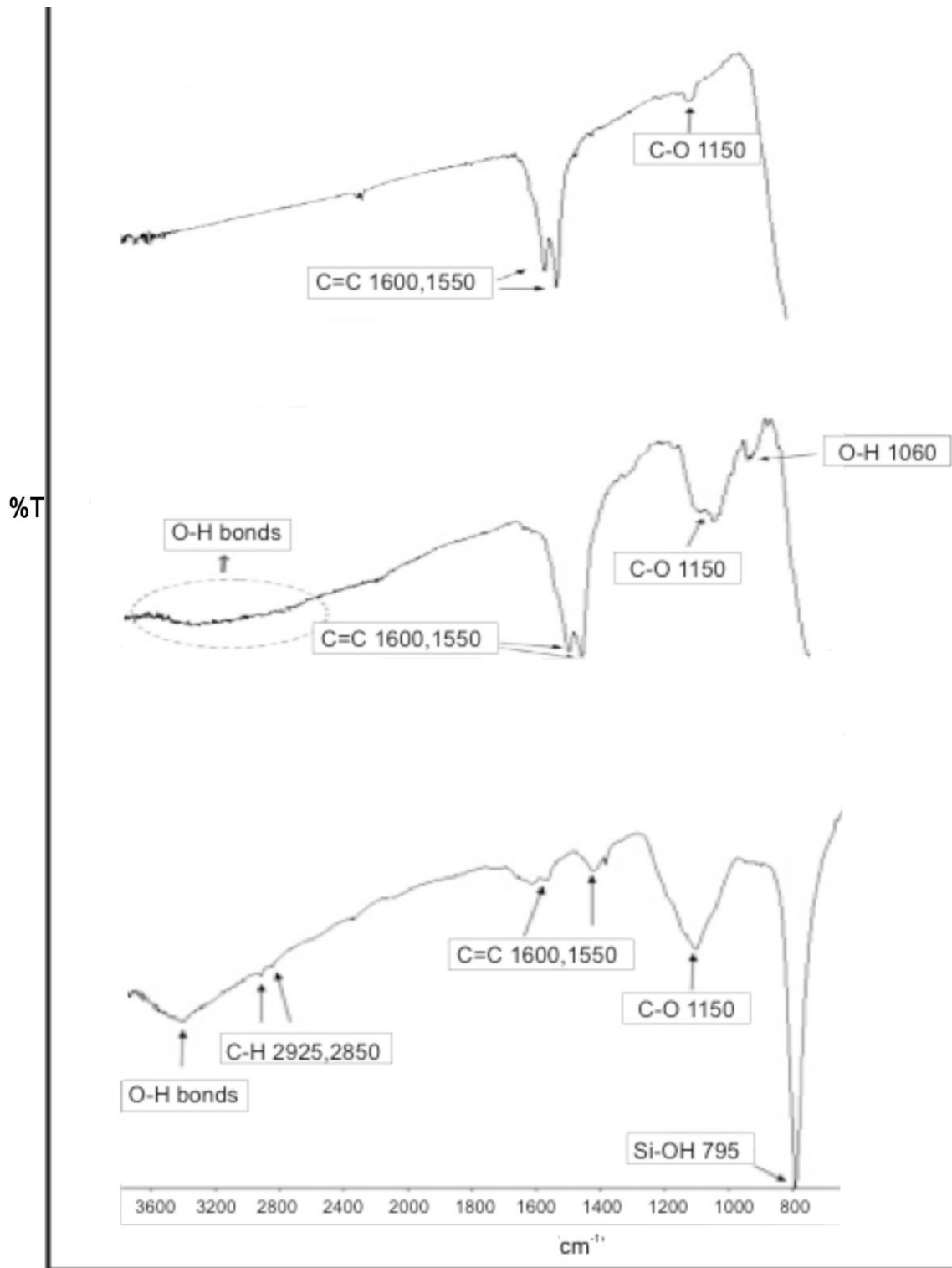
### 1.1.3 Nanocomposites

A phenol/epoxy, Aradite<sup>®</sup> LY 5052 mix with Aradur<sup>®</sup> 5052 hardener, used in aeronautic structures, were prepared with concentrations of 0.2 and 0.5% of Si-MWCNT, named respectively 02-MWCNT and 05-MWCNT samples. For the best dispersion of the Si-MWCNT, it was prepared as a mix of 100 mL of ethanol and sonication for 30 minutes. Then, at the mixture it was added the epoxy resin and the mixture was stirred for 2 h at 70 °C to 80 °C until total ethanol evaporation. A nanocomposite was prepared with the addition of hardener into epoxy filled with nanotubes, sonicated for 30 minutes, degassed for 15 minutes and dropped in to a PTFE mold. The resin was cured 24 h at 25 °C and post-cured for 10 h at 80 °C. Flexural, impact and tensile strength tests were performed according to ASTM D790-97, ASTM D6110-08 and D3039M-08 respectively.

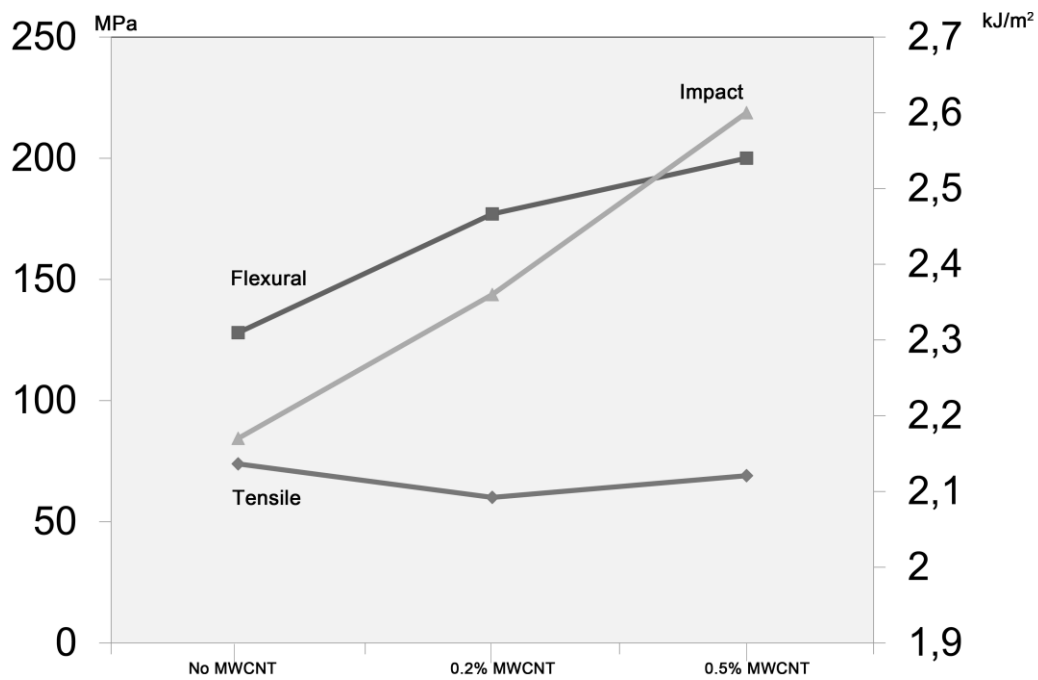
## 1.2 Results and discussion

The O-MWCNT were characterized by its solubility in polar solvents, while U-MWCNT were not solubilized. This result is consistent, once during oxidation process, a large number of carboxyl groups are formed on the surface, fact that gives them polar characteristic. A Fourier transform infrared (FT-IR) spectra of O-MWCNTs is shown in Fig. 1, confirming the oxidation effect by the presence of a peak at 1382 cm<sup>-1</sup> related to the presence of OH due to bending deformation in -COOH. Other two bands are observed, 1735 cm<sup>-1</sup> and 1154 cm<sup>-1</sup> corresponding to C=O and C-O, respectively. Finally the FT-IR spectrum, shown in Fig. 1, of Si-MWCNT demonstrates the silicon presence by the characteristic peak at 795 cm<sup>-1</sup>.

Phenol / epoxy nanocomposite showed an improvement, for 02-MWCNT and 05-MWCNT respectively, by 38% (177±12 MPa) and 56% (200±9.0 MPa), for flexural strength test and 9% (2.36±0.05) and 20% (2.61±0.06) for impact tests, in confrontation with net epoxy resin, Fig. 2., A analyses of variance (ANOVA) was performed and indicated significant differences in flexural and impact tests for different concentration of MWCNT, but no significant differences was encountered for tensile strength tests, it was due to the low fraction of filler and small length of NTC, witch is bellow a critical size to act as a load transfer reinforcement and a MWCNT agglomeration which act as matrix defect.



**Figure 1** - A Fourier transform infrared (FT-IR) spectra, showing the peaks of each bond, created in different steps of oxidation and functionalization. The first curve (top) show the net MWCNT, the second curve (middle) show the oxidizing and the last (bottom) the functionalized one.



**Figure 2** – Graphic showing the increase of mechanical properties, as flexural strength ■ and impact resistance ▲, for different fractions of MWCNT reinforcement. On the other hand, it wasn't observed improvement in tensile strength ◆ with the addition of MWCNT.

### 1.3. Conclusions

Phenol/epoxy nanocomposites with Si-MWCNT, synthesized by microwave sulfonitric oxidation followed by a functionalization with 3-APTES, and confirmed by FT-IR, showed improved up to 56% in flexural strength and 20% in impact resistance, using low fraction of filler as 0,5%. This improvement can be attributed to a better interaction between polymer and NTC by 3-APTES, witch reduces the molecular mobility with the increase of cross link bonds. The nanocomposites became more rigid than net resin.

In addition, especial attention was paid on dispersion of MWCNT into the resin, by the use of ultrasound stirring in all process steps.

The use of microwave in some steps reduced substantially the time of the process and the amount of MWCNT fragments.

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