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# Functionalization of Multi-Walled Carbon Nanotube and Mechanical Property of Epoxy-Based Nanocomposite

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**ABSTRACT:** The focus of this study is to evaluate the effect of carboxyl and amino functionalization of multi-walled carbon nanotubes on the mechanical property of the epoxy resin filled with modified carbon nanotubes. The carbon nanotubes were treated with sulfuric and nitric acids and also with hexamethylenediamine. The presence of acid and amine chemical groups on the carbon nanotube surface was confirmed by X-ray photoelectron spectroscopy. The composites were produced with epoxy resin and modified carbon nanotubes. Vickers hardness tests were carried out on the composites and neat resin. The results showed an increase of hardness in the composite prepared with functionalized carbon nanotubes. This phenomenon is due to the fact that the chemical interaction between modified carbon nanotube and epoxy resin is much stronger than between pristine carbon nanotube and epoxy resin. This stronger interaction is related to the presence of functionalized carbon nanotubes.

**KEYWORDS:** Epoxy matrix composite, Carbon nanotubes, Vickers hardness.

## INTRODUCTION

Carbon nanotubes (CNTs) were discovered in 1991 by Sumio Iijima (Iijima, 1991) and they have attracted a worldwide attention due to their outstanding thermal, electronic and mechanical properties (Shin *et al.* 2013; Wang and Liew 2015). Therefore, one of the most promising applications is as reinforcing fillers (Shen *et al.* 2007; Bhuiyan *et al.* 2013).

The introduction of CNTs in the polymer matrix started in 1994. Since then, investigations have been addressed to improving the polymer properties when compared to the base polymer (Saeb *et al.* 2015). The effects of CNTs on rheological, thermal, electrical and mechanical properties of thermoset polymers are well known, but in the recent years epoxy resin have brought more attention due to its extremely good chemical and corrosion resistance, acceptable adhesion behavior and remarkable mechanical characteristics (Li and Shimizu 2009; Chen *et al.* 2014).

The composite filled with CNTs have attracted the attention of aeronautics industries, since it offers a great weight reduction if a metallic material is replaced by nanocomposites. The superior strength-to-weight ratio provided by this material results in the reduction of fuel consumption, which is one of the major challenges for the aerospace industry, such as military and commercial aircrafts, space vehicles, satellites, and others (Gohardani *et al.* 2014).

However, the CNT application as polymer filler has been hindered by some difficulties in the dispersion and low

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adhesion to matrix (Disfani and Jafani 2013). These facts limit significantly the CNT applications, since CNT tend to agglomerate due to Van der Waals force (Ratna *et al.* 2013). Researchers have added functional groups on the CNT surface to improve its dispersion. Many different kinds of CNT functionalization have been reported, such as carboxyl and amino groups, and these functionalizations improved the CNT dispersion in polymers (Wang *et al.* 2007; Qiu and Wang 2010).

The focus of this paper is to evaluate the effect of carboxyl and amino functionalization of CNTs on the mechanical property of the epoxy resin filled with modified CNTs. The functionalized CNTs were characterized by X-ray photoelectron spectroscopy (XPS). Moreover, functionalized CNTs were added to the polymer matrix and the Vickers hardness tests were carried out on the neat resin, composite with pristine CNT and composites with modified CNTs.

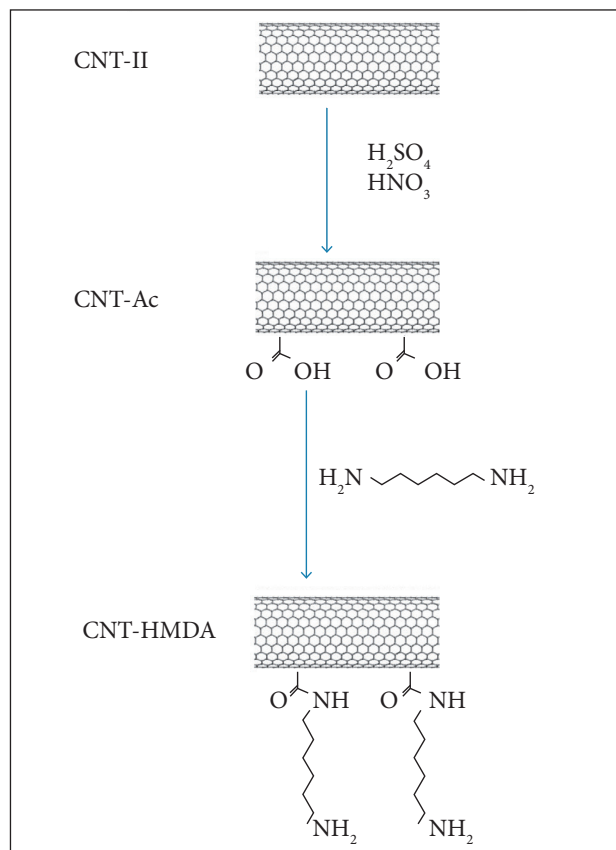
## EXPERIMENTAL MATERIALS

The CNTs used in this study were acquired from Laboratório Associado de Sensores e Materiais – Instituto Nacional de Pesquisas Espaciais (LAS/INPE) and prepared by a chemical vapor deposition method, as described in a previously study (Antunes *et al.* 2011). CNT was purified, performed an oxidative acid treatment and then the functionalization step was performed (Jin *et al.* 2011). The functionalized sample was labeled as CNT-H.

## SURFACE MODIFICATION AND FUNCTIONALIZATION OF CARBON NANOTUBES

A quantity of CNT-H (0.8 g) was added to 90 mL of sulfuric acid ( $\text{H}_2\text{SO}_4$ , Merck, 98%) and 30 mL (v/v 3:1) of nitric acid ( $\text{HNO}_3$ , Vetec, 70%), in an ultrasonicator bath with power of 225 J/s for 6 h at room temperature. This specimen was called CNT-Ac.

The specimen CNT-Ac (0.3 g) was dispersed in 150 mL of hexamethylenediamine (HMDA,  $\text{NH}_2(\text{CH}_2)_6\text{NH}_2$ , Aldrich, 70%). The mixture was maintained under stirring and heating at 100 °C for 4 days. Then, the modified CNTs were filtered through 0.45  $\mu\text{m}$  of polytetrafluorethylene (PTFE) and they were named as CNTHMDA. Figure 1 presents an illustration of surface modification.



**Figure 1.** Surface modification and functionalization.

## PREPARATION OF NANOCOMPOSITES AND NEAT RESIN

The nanocomposites (CNT-H/epoxy, CNT-Ac/epoxy and CNT-HMDA/epoxy) and the neat resin (epoxy) were synthesized with epoxy resin diglycidyl ether of bisphenol A (DGEBA), diaminodiphenylmethane (DDM) and 0.2% wt of CNT.

## CHARACTERIZATION AND MEASUREMENTS

XPS analysis of the CNT samples was carried out on a commercial spectrometer (UNI-SPECS UHV), with Mg K $\alpha$  line ( $h\nu = 1253.6$  eV) and a pass energy set at 10 eV. Vickers hardness measurements were carried out on samples in a diamond Vickers indenter Tester FM-700, where a 0.2 kgf load was applied for 10 s. The hardness value HV (in GPa) was calculated from the indentation load and the diagonal of the Vickers imprint. Thirty two indents were made on each surface keeping an appropriate distance from the sample edges and between indentation marks, avoiding boundary effects (confidence intervals: 95%). The entire computational environment was developed in R program, a statistical computational and graphical environment.

## RESULTS AND DISCUSSION

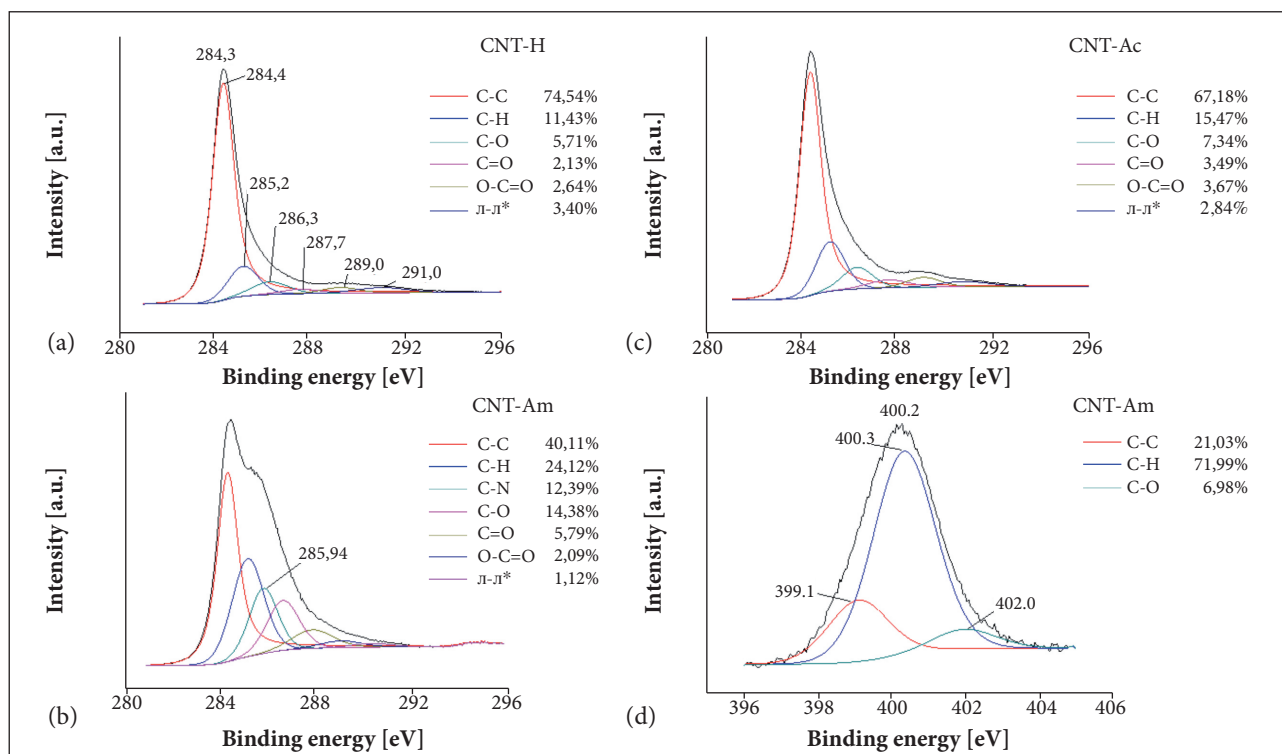
Figure 2 shows the XPS analysis on the samples CNT-H, CNT-Ac and CNT-HMDA. The deconvolution of XPS C 1s spectra shows a main component at 284.4 eV, which is related to aromatic carbon bonding (C-C  $sp^2$ ) from the hexagon walls of the CNTs. The peak centered at 285.2 eV refers to C-CH  $sp^3$  bond, which is related to defects in the aromatic structure and that ranging 285.2 – 285.9 eV may be related to hydrocarbon from surface contamination. In addition, other peaks may be assigned to chemical bindings of C-O at 286.3 eV, C=O at 287.7 eV and O-C=O at 289 eV. The plasmon  $\pi-\pi^*$  peak has placed at 291 eV. The deconvolution of XPS N 1s spectra (Fig. 2d) shows three peaks: C-NH<sub>2</sub> at 399.1 eV; N-C at 400.3 eV and N-O at 402 eV.

The evidence on the XPS spectra in Figs. 2a and 2b is that the sample CNT-Ac has a higher percentage of C-O, C=O and O-C=O groups than the sample CNT-H, which indicates the presence of carboxyl group on the CNT-Ac surface. In addition, Fig. 2c shows the presence of C-N chemical group, indicating the presence of nitrogenated functional group on the CNT surface. The deconvolution of XPS C1s spectra (Figs. 2a, 2b and 2c) shows that the amount of chemical groups related to peak at 285.2 eV (C-CH  $sp^3$ ) increases in the following order:

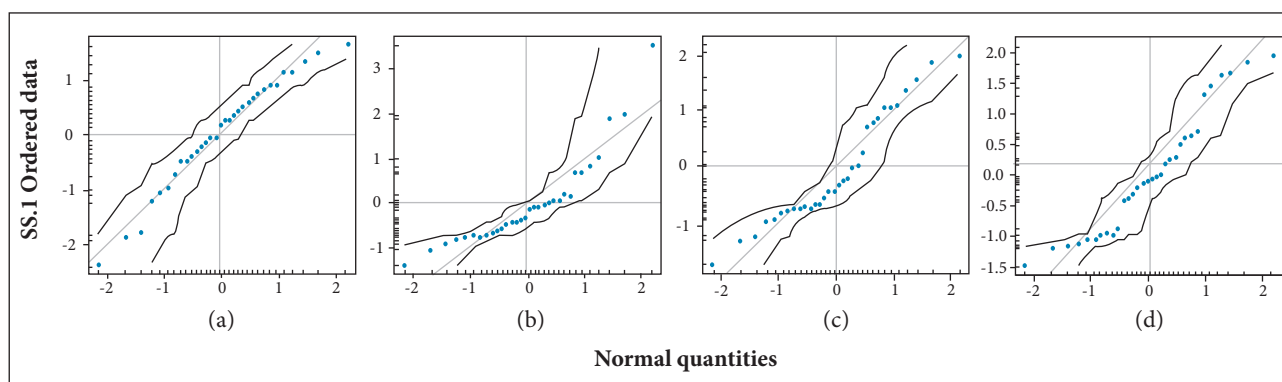
CNT-H < CNT-Ac < CNT-HMDA. This increase is related to an increase in the defects on the CNTs wall, which contributes for adding functional groups on the CNT-Ac and CNT-HMDA surfaces (Figs. 2b and 2c) (Komarova *et al.* 2015).

The distribution of hardness results can be seen in Fig. 3. It is noticed that the hardness measurements are randomly distributed in the confidence intervals, where the data normality (p-value < 0.001) was admitted.

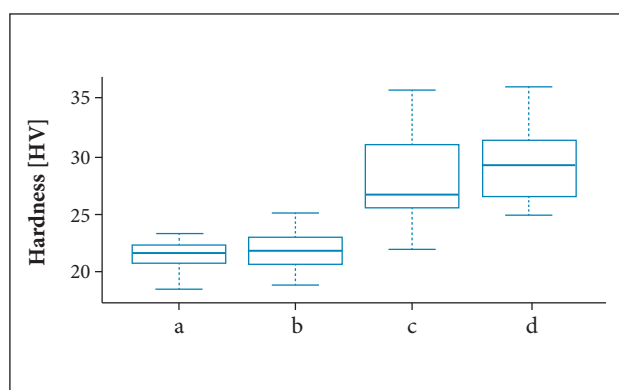
Figure 4 shows the box-plot of different composites (CNT = 0.2 wt.%). It is noticed from Figs. 4a and 4b that the adding of CNT in the resin without surface modification produces a slight increase in the average hardness from 21.33 to 21.69 HV (significantly same values; p-value = 0.487). It is known that functionalized CNTs have more disorganized microstructure compared to pristine CNT, which leads to greater dispersion of CNTs, hence functionalized CNTs have better interfacial bonding with the polymer matrix (Cividanes *et al.* 2012). In addition, Figs. 4c and 4d show an increase in the average hardness of about 30% in the composite prepared with CNT-Ac. Afterwards, in the CNT-HMDA sample, the hardness increased from 27.95 to 29.56 (statistically different values; p-value = 0.06). It may be attributed to the presence of amine functional groups onto CNT surfaces (Liu and Wagner 2005; Martinez-Hernandez *et al.* 2010; Gkikas and Paipetis 2015).



**Figure 2.** XPS spectra regarding (a) CNT- H C 1s; (b) CNT- Ac C 1s; (c) CNT- HMDA C 1s; (d) CNT- HMDA N1s.



**Figure 3.** Normal Q-Q Plot. (a) Epoxy; (b) CNT- H/epoxy; (c) CNT- Ac/epoxy; (d) CNT- HMDA/epoxy.



**Figure 4.** Vickers hardness of the samples: (a) Epoxy; (b) CNT- H/epoxy; (c) CNT- Ac/epoxy; (d) CNT- HMDA/epoxy.

On the other hand, it appears that CNT additions significantly increase the composite sample variability in the hardness ( $p$ -value < 0.001). The high variability of the hardness results may be attributed to CNTs dispersion in the polymer matrix, which can affect the final nanocomposite properties (Song and Young 2005; Bal and Samal 2006; Cividanes *et al.* 2012).

The average hardness of the CNT-HMDA/epoxy composite is higher than the average hardness of the CNT-Ac/epoxy composite. However, if we analyze the maximum deviation values, both hardness seem to be closer.

## CONCLUSIONS

The CNTs functionalized with acid and HMDA were submitted to XPS analysis and it was observed the presence of the carboxyl and amine groups, which confirms the functionalization success. The results showed that the neat resin and CNT-H composite have almost the same hardness. The functionalization has increased the hardness of CNT-Ac and CNT-HMDA composites, regardless of the maximum deviation values of CNT-Ac and CNT-HMDA composites are almost the same, although the amine-functionalized composite has presented the highest average hardness value among all composites.

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