

DODECYLAMINE FUNCTIONALIZATION OF CNT: THERMAL STABILITY AND DISPERSION

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ABSTRACT - In this work, a dispersion study of carbon nanotubes (CNTs) functionalized with carboxylic and alkanes groups in various solvents are performed. CNT was treated using H₂SO₄/HNO₃, and functionalized subsequently by dodecylamine (DDA). The surface modification was confirmed by Fourier transform infrared and X-ray photoelectron spectroscopy. The thermal stabilities were studied by Thermogravimetric analysis. The dispersion state of CNTs in the solvents was based on visual observations. Evaluation of the solvent influence by itself was also made. Results confirmed the presence of oxygen-containing and alkanes groups on CNTs surfaces. Dispersion stability was strongly dependent on solvent and carbon nanotubes surface interactions, which can vary with the chemical nature of the solvent. The study of dispersion stability of the nanotubes with different solvents is relevant to the full understanding of its applications.

1. INTRODUCTION

Since their discovery by Iijima in 1991, carbon nanotubes (CNTs) have attracted extensive attention from researchers due to the extraordinary mechanical, electrical, and thermal properties that make them very promising for use in material science applications (Ma *et al.*, 2010; Cavness *et al.*, 2012). These properties are: the Young modulus is around 1 TPa and the maximum tensile strength can reach 300 GPa, excellent electronic properties, exceptional thermal conductivity, etc. (Ham *et al.*, 2005; Cividanes *et al.*, 2013).

Even though carbon nanotubes have promising applications, the poor dispersion into solvents or polymers has been a fundamental problem that still remains. The dispersion states of the nanotubes involve complicated phenomena that are affected by at least two competitive interactions: the strong intrinsic van der Waals forces among the nanotubes, and the interaction between carbon nanotube filaments and the dispersion medium (Ham *et al.*, 2005). A simple method to overcome these problems is by the surface modification, adding functional groups to its surface. The functional groups can be carboxyl and amino groups, which have been an effective way to prevent the agglomeration and to improve CNTs solubility in several solvents (Zhao *et al.*, 2013; Cividanes *et al.*, 2012).

Several important issues relating to surface modifications and degree of dispersion should be clarified to enhance our understanding from scientific and technological perspectives (Kim *et al.*, 2012). Therefore, functionalization studies and the preparation of stable dispersions of CNT in organic solvents are challenging and great labor-intensive tasks (Mahajan *et al.*, 2013; Soares *et al.*, 2014).

The main focus of this work is to evaluate the multifunctionalization for introducing carboxyl and alkane groups onto the surfaces of carbon nanotubes. The resulting functionalized CNTs were characterized by Fourier transform infrared (FT-IR), X-ray photoelectron spectroscopy (XPS), Thermogravimetric analysis (TGA). Moreover, various solvents were used to evaluate the dispersion stability of the nanotubes.

2. EXPERIMENTAL

1.1. Materials

The carbon nanotubes samples used in this work were prepared by a chemical vapor deposition method at 850 °C in atmospheric pressure, as previously described elsewhere (Antunes *et al.*, 2011). This sample was labeled CNT-H.

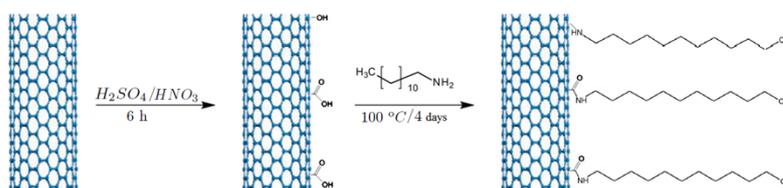
1.2. Surface modification of CNT with acid

A quantity of CNT-H (0.8 g) was treated with hydrochloric acid and added to a 120 ml (v/v 3:1) of sulfuric acid (H₂SO₄, Merck, 98%) and nitric acid (HNO₃, Vetec, 70%), in a 225 W ultrasonicator bath for 6 h at room temperature (Soares *et al.*, 2014). This sample was labeled CNT-Ac.

1.3. Functionalization with alkanes groups (DDA)

A amount (0.2 g) of acid modified CNTs (CNT-Ac) were dispersed in dodecylamine (DDA, C₁₂H₂₇N, Sigma, 98%, 150 ml). The mixture was maintained under magnetic stirring and heated to 100 °C for 4 days. Then, the material was subsequently separated by a vacuum filtration process using a polytetrafluorethylene (0.45 μm poro size) (Cividanes *et al.*, 2012; Soares *et al.*, 2014). This sample was labeled CNT-Am. Figure 1 presents of the surface reactions.

Figure 1 - Scheme of carbon nanotube surface modification



1.4. Characterization

FT-IR analysis was conducted in a FT-IR Spectrum One PerkinElmer spectrometer. XPS analysis of the carbon nanotube samples was performed on a commercial spectrometer (UNI-SPECS UHV), with Mg K α line ($h\nu = 1253.6$ eV) and a pass energy set at 10 eV. The thermal behavior of carbon nanotube was evaluated by using TGA 7 HT Perkin Elmer. Dispersibility tests were carried out using a total of 4 solvents whose total solubility parameter values (δ_{Total}) were quite different (Benazzouz *et al.*, 2014). The dispersibility classification was evaluated based on visual observations.

3. RESULTS AND DISCUSSION

FT-IR technique was used to evaluate the presence of chemical groups on CNT surfaces (spectra are not presented here). Bands at approximately 3445 cm^{-1} were observed in the spectra of all samples. That may be assigned to O-H stretching vibrations (Vukovic *et al.*, 2009; Behnama *et al.*, 2013). The spectrum also showed bands at 1630 cm^{-1} , which was assigned to the C=C stretching. It is an indication of the CNT graphitic structure presence (Zhao *et al.*, 2013; Behnama *et al.*, 2013).

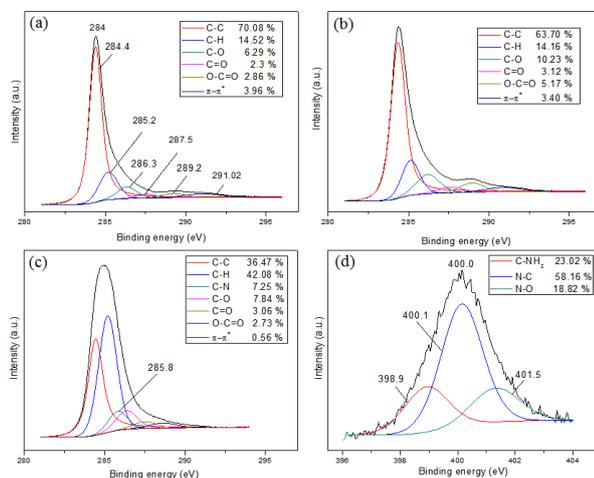
Spectrum of the sample CNT-Ac shows bands at 1726 cm^{-1} , which is due to the carbonyl stretch of the carboxylic acid group (Cividanes *et al.*, 2012; Rahimpour *et al.*, 2012; Vukovic *et al.*, 2009), and bands at 2920 and 2850 cm^{-1} . They may be assigned to asymmetric ($\nu_a\text{ CH}_2$) and symmetric ($\nu_s\text{ CH}_2$) stretching vibrations of methylene group, respectively (Vukovic *et al.*, 2009; Zhao *et al.*, 2013). These oxygenated groups indicate that the surface was successfully modified by acid.

Spectra of the sample CNT-Am shows that the band at 1726 cm^{-1} almost disappear and a new band at 1650 cm^{-1} appeared, that may be assigned to the amide carbonyl (C=O) stretching (Vukovic *et al.*, 2009; Cividanes *et al.*, 2012). Bands at approximately 1580 and 1180 cm^{-1} were observed in the spectrum. These bands are typically associated with N-H in-plane bending, and C-N stretching, respectively (Rahimpour *et al.*, 2012; Vukovic *et al.*, 2009; Cividanes *et al.*, 2012). Further confirmation of the functionalization process is the presence of bands in the range of $3600\text{-}3300\text{ cm}^{-1}$, which are due to the NH_2 stretch of the amine group overlapped with O-H stretching. The presence of nitrogenated groups must be confirmed by XPS, because there is a band overlap in the FT-IR analysis.

Figure 2 shows the XPS C1s and N1s spectra for the CNT-H, CNT-Ac and CNT-Am. The deconvoluted XPS C1s spectrum (Figure 2a-c) shows a main peak at 284.4 eV for all samples, which can be assigned to sp^2 hybridized carbon atoms of nanotube structure (Soares *et al.*, 2014). The peak centered at 285.2 eV , can be assigned to $\text{sp}^3\text{ C-CH}$ bonds, and it is related to defect sites in the CNT walls (Suna *et al.*, 2013; Soares *et al.*, 2014). Also presents peaks in the range of $286\text{-}289\text{ eV}$, that may be assigned to the peaks at C-O, C-N (286 eV), C=O (287 eV) e O-C=O (289 eV), and plasmon $\pi\text{-}\pi^*$ (291.2 eV) (Antunes *et al.*, 2011; Suna *et al.*, 2013). Figure 3d shows the N1s curve fitting and it is usually deconvoluted in three components at 400.1 eV (N-C), 398.9 eV ($\text{NH}_2\text{-C}$) and 401.5 eV (N-O) (Soares *et al.*, 2014).

The deconvoluted XPS C1s spectrum (Figure 2a-b) showed that the peaks in the range of $286\text{-}289\text{ eV}$ (oxygenated functional groups) increased in intensity. In addition, the intensity of the peak at 286.5 eV ($\text{sp}^3\text{ C-CH}$) was slightly decreased. The deconvoluted XPS C1s spectrum (Figura 2b-c) showed that most of the oxygen functional groups was removed during the functionalization with dodecylamine. Moreover, the XPS spectrum of the CNT-Am (Figure 2c) showed a new peak at 285.8 eV (C-N), which is due to nitrogenated functional group incorporated on the CNT-Am surface. Moreover, this spectrum showed that the $\pi\text{-}\pi^*$ component almost vanished. These results are in agreement with the FT-IR analysis, and they suggest that functional groups were successfully introduced on CNT surfaces by alkane groups treatment.

Figure 2 - Deconvoluted XPS peaks of (a) CNT-H C1s, (b) CNT-Ac C1s, (c) CNT-Am C1s, (d) CNT-Am N1s



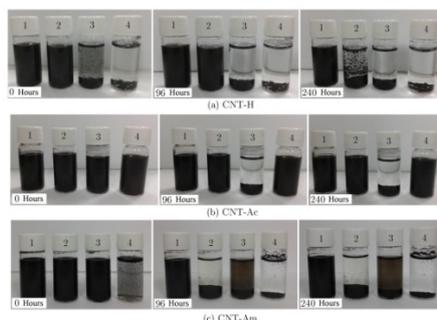
Thermogravimetric methods were performed for determining the thermal behavior of Samples CNT-H, CNT-Ac and CNT-Am in oxidizing atmosphere and the CNT purity in terms of metal and metal oxide contents. The results showed a significant weight variation started at 550 °C and the residual weight is above 10% for all samples. Taking into account that iron residue is an oxide, because of the presence of air during the TGA performance, the iron content is actually lower than showed (Huang *et al.*, 2003). In addition, the thermal gravimetric analysis showed that samples CNT-Ac and CNT-Am lost mass at temperatures less than 450 °C. However, sample CNT-H showed no mass loss at this temperature. This behavior is related to the decomposition of covalent organic groups introduced into the nanotube surface by the functionalization processes.

Figure 3 shows images of the dispersion states of the nanotubes in different solvents. The dispersion states were classified into three groups: dispersed, swollen and sedimented. Dispersion is considered dispersed if nanotube/solvent mixture forms a dark solution with no aggregation and precipitation after 240 h; swollen means that nanotubes are aggregated and a two-phases system is obtained; while in a sedimented dispersion all nanotubes are precipitated after 240 h.

It is interesting to note that all CNTs were highly dispersible in acetone, and the dispersion was evaluated as dispersed. Figure 3a shows the dispersion states of CNT-H. It was observed that the raw nanotube tended to aggregate in xylene and water and poor dispersion was obtained, being named sedimented. However, CNTs were agglomerated in ethanol, forming two phases and the dispersion was classified as swollen in ethanol. On the other hand, the dispersion state of CNT-Ac (Figure 3b) can be classified as dispersed in ethanol and water. These results suggest that the oxidation introduces polar groups (oxygen-containing groups) on CNTs surface, creating the electrostatic stability required for a long time stable dispersion in polar solvents (Vukovic *et al.*, 2009; Zhao *et al.*, 2013; Kim *et al.*, 2013; Kim *et al.*, 2012). Presumably, electrostatic repulsion between positive charges of functionalized CNTs with acid contributes to the stability (Behnama *et al.*, 2013). The dispersibility of

CNT-Am in ethanol and water was classified as sedimented, as shown in Figure 3c, probably due to the decrease of oxygen-containing groups on CNT surfaces (Zhao *et al.*, 2013).

Figure 3 - Images of (a) CNT-H, (b) CNT-Ac, (c) CNT-Am, in the solvents: (1) acetone, (2) ethanol, (3) xylene, (4) water, after sonication for 1 h.



4. CONCLUSIONS

All techniques confirmed that CNTs were successfully functionalized by acid and alkanes groups. TGA analyses showed that the functionalized CNTs lost organic groups introduced by surface modification with acid and dodecylamine at temperatures lesser than 450 °C. These groups were carboxyl and carbonyl groups, as they were observed in FTIR and XPS results. The dispersibility phenomenon is strongly dependent on specific interactions between the solvent and CNTs surface, which can vary with the chemical nature of the solvent. The surface modification with acid enabled the dispersion of the CNT in ethanol and water. Surface modification with DDA enabled the dispersion of CNT in xylene.

5. ACKNOWLEDGEMENTS

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