



# Effects of Amine Molecular Structure on Carbon Nanotubes Functionalization

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Three amines with different molecular structure, triethylenetetramine (TETA) and two polyetheramines (Jeffamine D-230 and Jeffamine T-403) were employed to functionalize multi-walled carbon nanotubes (MWCNT) previously oxidized by acid treatment. The functionalized MWCNT were characterized by Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy, UV-vis spectroscopy and the surface modification was investigated by field emission scanning electron microscopy (FE-SEM). Thermogravimetric analysis (TGA) was employed to quantify the amount of amine groups anchored to MWCNTs. The results have shown that the efficiency of amine functionalization is in the order TETA > D-230 > T-403, thus showing that amine chemical structure and molecular weight are important parameters on functionalization of carbon nanotubes.

**Keywords:** Multiwalled Carbon Nanotubes, Functionalization, Amine.

## 1. INTRODUCTION

Carbon nanotubes (CNTs) present excellent characteristics which have promising potential for a wide range of applications as new functional materials and devices.<sup>1-3</sup> These applications all benefit from the nanosized structure, large surface area and high electrical conductivity with low content of CNTs. However, the dispersion of CNTs in organic solvents or in polymer matrices has been a consistent issue because of their strong tendency to form agglomerates due the high van der Waals interactions.

Many efforts have focused on enhancing the dispersion of CNTs by surface treatments and others physical methods. Techniques aimed at improving functionalities of CNTs surface include chemical treatments using high concentration acids,<sup>4</sup> plasma,<sup>5</sup> UV/ozone<sup>6</sup> sheathing or wrapping the CNTs with polymer chains,<sup>7</sup> grafting of CNTs with a thin layer of polymer chains based on plasma,<sup>8</sup> amongst others. The acid treatment is aimed at creating defects and covalent sidewall derivations by an oxidative process with strong acids such as HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, or a

mixture of them,<sup>4,9-13</sup> or with oxidants such as KMnO<sub>4</sub> or OsO<sub>4</sub>.<sup>14</sup> Physical methods include the utilization of ultrasound,<sup>15</sup> ball mill,<sup>16</sup> vibration mill<sup>17</sup> or two-roller mill.<sup>18</sup>

Generally, it is believed that the chemical modification of nanotube starts from the defect sites, i.e., heptagon-pentagon pairs that are under heavy strain, while others non-sp<sup>2</sup> defect sites on the tubes, such as -CH and -CH<sub>2</sub> are attacked next. In the presence of strong oxidizing agents, the integrated graphene structure is also attacked to create additional defect sites that can subsequently react with the oxidizing agent.

These oxidative processes introduce several oxidized carbon species, -OH, -C=O, -COOH that can improve the dispersion and processability of CNTs in the polymeric matrix. The introduction of carboxylic groups to nanotubes by oxidative procedures gives access to a large number of functional groups by transformation of the carboxylic functions, and provides anchoring groups for further modification. From carboxylic acids, amides can be formed via carboxyl chlorides that allow for the reaction of oxidized nanotubes with aliphatic amines, aryl amines, amino acid derivatives, peptides, amino-group-substituted dendrimers and other nucleophiles.<sup>19</sup> This kind of functionalization

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can allow further dispersion of CNTs in epoxy or other polymer matrices.

The purpose of this study has been to functionalize oxidized multiwalled nanotubes (MWCNTs) with three amines of different chemical structure and molecular weight. The functionalized MWCNTs have been characterized by Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy and UV-vis spectroscopy. The surfaces of functionalized and non-functionalized MWCNTs have been analyzed by field emission scanning electron microscopy (FE-SEM). Finally, the quantification of amine anchored to MWCNTs has been carried out by thermogravimetric analysis (TGA).

## 2. EXPERIMENTAL DETAILS

### 2.1. Materials

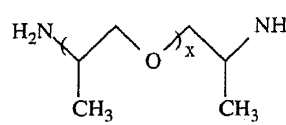
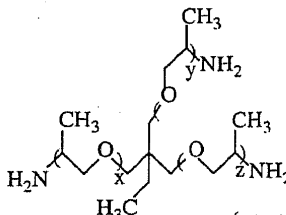
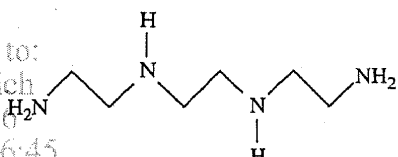
MWCNTs-3100 (95% purity, supplied by Nanocyl) synthesized by thermal chemical vapor deposition were used in this study. Though not shown, a slight weight loss was observed by TGA between 450 °C and 650 °C, in nitrogen atmosphere, without losses at lower temperatures, thus proving their high purity.<sup>20</sup> Polyetheramines, Jeffamine D-230 and T-403 were purchased from Huntsman and triethylenetetramine (TETA) from Aldrich. Sulfuric acid (96%) and nitric acid (65%) were purchased from Panreac. Tetrahydrofuran (THF) and thionyl chloride (SOCl<sub>2</sub>) were used as received from Aldrich and Acros Organics, respectively.

### 2.2. Purification and Functionalization

Previous to the carboxylation treatment, the nanotubes were sonicated for 30 min putting 15 mg MWCNT in 500 mL ethanol to separate the agglomerates and to be further able to attack each MWCNT.<sup>18</sup> Then, they were filtered through a 0.45 μm Millipore PTFE filter membrane and the resulting MWCNTs were dried overnight in a vacuum oven at 120 °C. The acid treatment was performed in an ultrasonic bath (Selecta Ultrasons-H model, which has a nominal frequency of 40 kHz with power of 950 W) using a mixture of H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> (3:1 in volume) at 30 °C for 2 h. The resulting MWCNTs were washed using deionized water until the pH of the filtrate was 7 and then dried overnight in a vacuum oven at 120 °C. In order to convert carboxyl group on MWCNTs into acyl chloride group, the oxidized multiwalled nanotubes (MWCNT-COOH) were stirred at 70 °C for 24 h employing excess amount of SOCl<sub>2</sub> and 1 mL anhydrous dimethylformamide (DMF). After cooled down to room temperature, the mixture was centrifuged and washed with anhydrous THF several times. The solid was dried at room temperature under vacuum.

A mixture of MWCNT-COCl and polyetheramines (in excess) was heated under N<sub>2</sub> at 90 °C for 72 h. On the other hand, a mixture of MWCNT-COCl and TETA (in

**Table I.** Structure of amine compounds used for CNT functionalization.

Product	Structure	Mean Molecular Weight (g/mol)
D-230		230
T-403		440
TETA		151

excess) was heated under N<sub>2</sub> atmosphere at 120 °C for 96 h. After cooled down to room temperature, the resulting nanotubes (f-MWCNT) were washed three times with ethanol and filtered through a PTFE filter with a 0.45 μm pore size. The solid was dried at room temperature under vacuum.

The structure of amine compounds for different functionalization are listed in Table I. Figure 1 illustrates the scheme for proposed chemical reactions.

### 2.3. Characterization

Fourier transform infrared spectroscopy spectra were recorded on a Nicolet Nexus spectrophotometer. The samples for FT-IR investigation were prepared using 0.15 mg nanotubes per gram KBr. Thermogravimetric analysis was performed using a TGA/SDTA851e instrument, Mettler Toledo. Samples were placed in aluminum crucibles. An empty aluminum crucible was used as reference. Samples were heated over a temperature range of 25–1000 °C at a scanning rate of 10 °C/min under N<sub>2</sub> atmosphere with a gas flow rate of 10 mL/min. All the samples were dried in vacuum during 48 h before the analysis.

A quartz cuvette with a liquid dispersion of MWCNTs was used for UV-vis spectra, using a Spectronic Genesis TM5 model. The liquid dispersion was prepared with 0.1 mg MWCNT added to 10 mL DMF, and then the dispersion was ultrasonicated for 10–15 min.

The effect of the functionalization on the structural integrity of the MWCNTs was investigated by Raman spectroscopy using an i-Raman™ spectrometer, B&W

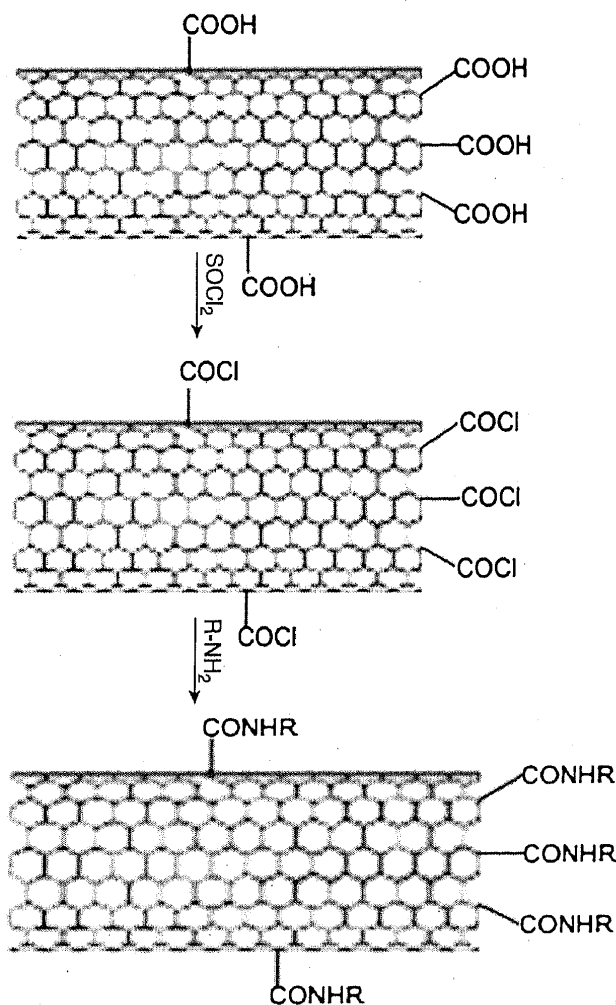


Fig. 1. Schematic representation of carboxyl-terminated MWCNTs followed by treatment with thionyl chloride and subsequent amidation.

TEK, at excitation wavelength of 785 nm from He-Ne laser.

The modified nanotubes were analyzed by TGA to quantitatively determine the amount of the attached molecules. FT-IR, UV-vis and Raman spectroscopy were utilized to detect the presence of these attached molecules and to characterize the changes on MWCNTs.

The morphology of pristine and f-MWCNT samples was studied by scanning electron microscopy at 5 kV using a Zeiss LEO 982 GEMINI field emission scanning microscope.

### 3. RESULTS AND DISCUSSION

Figure 2 shows FTIR spectra of MWCNT-COOH and f-MWCNT. The spectrum of MWCNT-COOH shows two characteristic vibrational modes, one at  $1712\text{ cm}^{-1}$  indicative of C=O group and the other at  $1540\text{ cm}^{-1}$  associated with the stretching of carbon nanotubes backbone C=C. The C=O stretching frequencies shifted from  $1712\text{ (MWCNT-COOH)}$  to  $1640\text{ cm}^{-1}$  (f-MWCNTs) thus

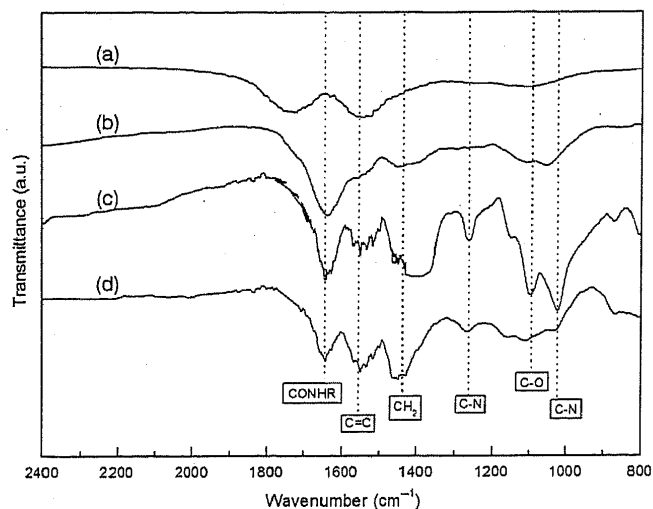


Fig. 2. FT-IR spectra of: (a) acid treated MWCNTs and amine functionalized MWCNTs, (b) T-403-MWCNT, (c) D-230-MWCNT and (d) TETA-MWCNT.

indicating the formation of amide linkages (CONHR). The MWCNT backbone vibration appears in all spectra. However it should be noticed that in the case of MWCNT modified with T-403, this peak is broader than in the case of TETA-MWCNT, probably due to the overlap between the C=C stretching and the N-H stretching of amine groups. The influence of the amine type in the f-MWCNT transmittance is also notorious in the peak around  $1420\text{ cm}^{-1}$ . In this wavenumber region two vibrations could appear: C=C ring stretching ( $1450\text{ cm}^{-1}$ ) and C-H bending vibrations of the alkyl chain ( $1420\text{ cm}^{-1}$ ).

However, comparing the spectra b-d with that of MWCNT-COOH, it is clear that another bands associated with the amine anchoring on the nanotubes can be seen in the f-MWCNT spectra. Indeed, the peak at  $1250\text{ cm}^{-1}$  due to C-N stretching of amide groups, and the peak at  $1030\text{ cm}^{-1}$ , associated with C-N stretching vibrations.

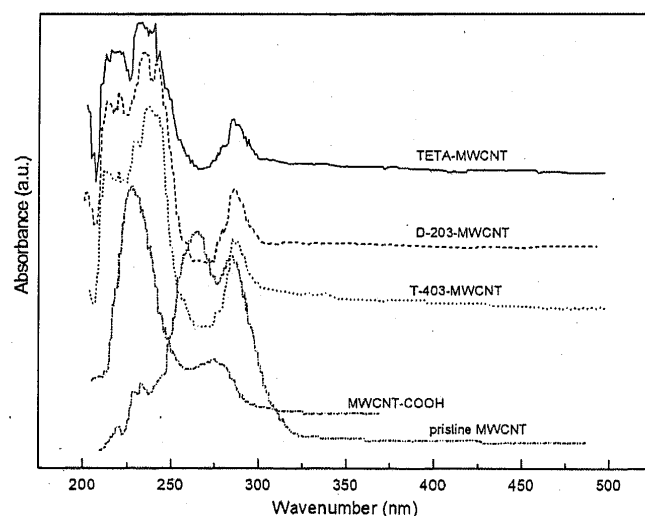


Fig. 3. UV-vis spectra of pristine, oxidized and amine-functionalized MWCNT.

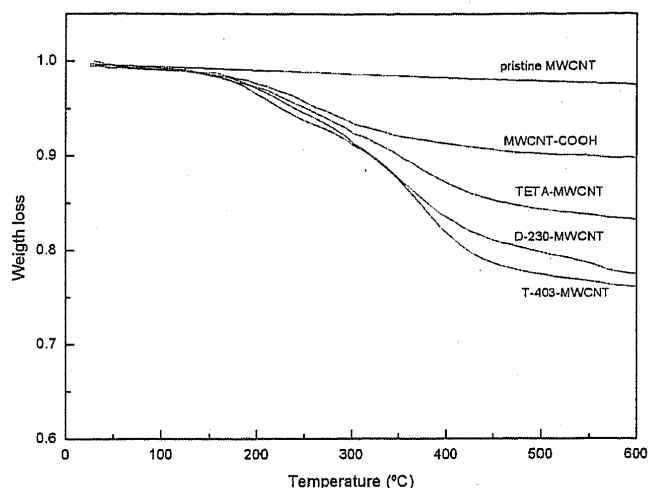


Fig. 4. Thermogravimetric analysis of pristine, oxidized and amine-functionalized MWCNTs.

The UV-vis spectrum of pristine MWCNTs, MWCNT-COOH and f-MWCNTs, dispersed in DMF are shown in Figure 3. The spectrum of pristine MWCNTs suspension shows two absorption peaks, around 283 and 264 nm. Wang et al.<sup>21</sup> observed the UV absorption of SWCNT at 256 nm. Yang et al.<sup>22</sup> reported for purified MWCNTs a broad peak between 200 and 320 nm centred at 260 nm which they attributed to  $\pi-\pi^*$  electron transition in MWCNTs. Theoretical calculations in fullerene<sup>23</sup> predict for isolated fullerene absorption peaks at 266 and 331 nm. In the suspension of oxidized-MWCNT, above mentioned peaks are overlapped in a small peak located between them 278 nm, which could be associated to carboxylic group. The amine-functionalized MWCNTs show two peaks at 238 and 213 nm, as the absorption wavelength of C=O peak shifted from 228 to 238 nm due to the anchoring of NH<sub>2</sub> group onto the carboxylic group. The absorption peak at 213 nm can be ascribed to C-N bonding of the amide group formed.

Thermal behavior of the nanotubes was measured by TGA (Fig. 4). TGA scan of pristine MWCNTs shows a small weight loss, which is around 3 wt% below 600 °C, whereas that for MWCNT-COOH is around 10 wt% and in the case of amine-functionalized MWCNTs is between 17 and 24 wt%. Besides, the onset temperatures of MWCNT-COOH and amine-functionalized MWCNTs become dramatically lower, which is due to the fact that the additional

organic functional groups are decomposed before the onset of weight loss decomposition of MWCNTs structure.<sup>24,25</sup>

Taking into account that TGA technique can be applied to analyse the effectiveness of grafting to MWCNT,<sup>22,26</sup> thermogravimetric curves have been used to quantify the weight fraction of organic chains bonded to MWCNTs. Table II shows TGA results for each amine employed. The values do not match the theoretical estimates for a complete COOH-amine reaction. As shown in Table II, taking into account that two steps are needed for achieving the functionalization with amine groups from the acid groups, a high yielding was obtained through chlorine and amine reactions.

From TGA results, it can be concluded that steric effects due to different chemical structures can be an important parameter for functionalization with amine groups from COOH groups as the yielding achieved with the amine of highest molecular weight T-403 (branched molecule with methyl groups attached to the end-chain carbon bonded to the primary amine, which results in steric hindrance effects) was slightly lower than the half of that obtained for the other two amines of lower molecular weights, which present straight-chain structures with lower steric effects.

Figure 5 shows FE-SEM micrographs of pristine and TETA-functionalized MWCNTs. As representative for the three amines functionalization, the micrograph for TETA-functionalized MWCNTs is very similar to those reported in the literature for other amine-functionalized MWCNT,<sup>27</sup> showing that after the organic compound was chemically grafted onto MWCNTs, the nanotubes were covered with TETA, and thus the diameter increase from around 25 nm for pristine MWCNTs until 60 nm for the functionalized ones.

Raman spectroscopy has been applied for characterization of carbon family including CNTs.<sup>24,28</sup> The correlation between Raman spectra and structural changes in graphite materials, in particular CNTs, has been studied and described in the literature.<sup>29-32</sup> As shown in Figure 6, Raman spectrum of MWCNT displays two obvious peaks: the well known D band around 1300 cm<sup>-1</sup>, which is a double-resonance Raman mode, is usually understood as a measurement of structural disorder coming from amorphous carbon and any defects,<sup>22,33</sup> and the G-band around 1590 cm<sup>-1</sup>, which is associated to the tangential-mode peaks.<sup>22,34</sup> G band is generated by sp<sup>2</sup> carbons while D band exists because of vibration of sp<sup>3</sup> carbons or some

Table II. Weight fraction of organic groups and I<sub>D</sub>/I<sub>G</sub> ratio on functionalized CNT.

Organic compound	TGA			RAMAN	
	MWCNT fraction (wt%)	Organic fraction (wt%)	Organic groups (mol/g MWCNT)	Compound	I <sub>D</sub> /I <sub>G</sub>
COOH		10.2	2.47 × 10 <sup>-3</sup>	Pristine MWCNT	2.14
TETA	83.5	16.5	1.35 × 10 <sup>-3</sup>	MWCNT-COOH	2.42
D-230	77.6	22.4	1.25 × 10 <sup>-3</sup>	TETA-MWCNT	2.44
T-403	76.1	23.9	7.2 × 10 <sup>-4</sup>		

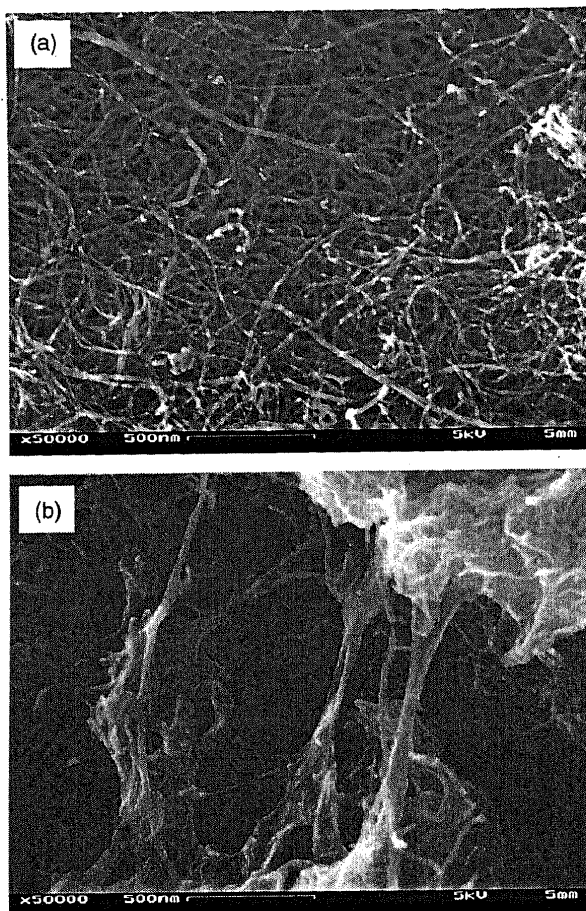


Fig. 5. FE-SEM images of: (a) pristine MWCNT and (b) TETA-MWCNT.

disordered carbon structure. Several authors<sup>22, 24, 35</sup> concluded that when polymer chains are grafted to the surface of SWCNT via covalent bond, the original  $sp^2$  carbons are converted to  $sp^3$  carbons, and therefore the relative of  $sp^3/sp^2$  peak intensity ratio should increase. The intensity

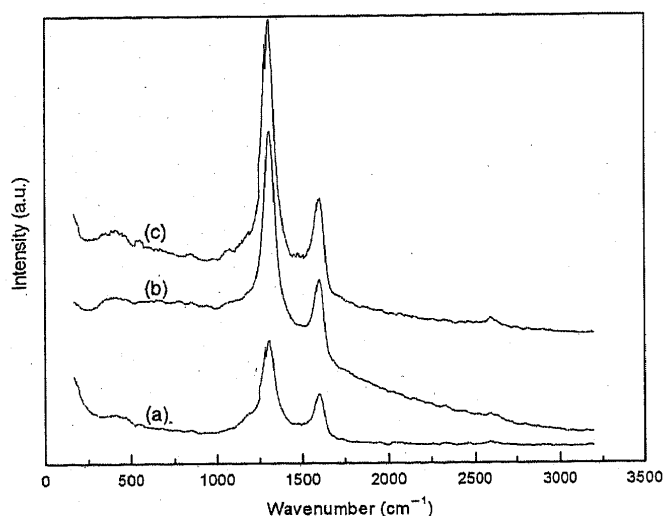


Fig. 6. Raman spectroscopy results for the (a) pristine MWCNT, (b) MWCNT-COOH and (c) TETA-MWCNT.

ratio between D band ( $I_D$ ) and G band ( $I_G$ ) is indicative of a basic structural change in the MWCNTs, with a greater value of this parameter implying more defects.

The Raman spectra of pristine MWCNT, oxidized MWCNT and amine-functionalized MWCNT are given in Figure 6. The value of  $I_D/I_G$  ratio, obtained from integrated areas<sup>36</sup> are summarized in Table II. Figure 6 shows that the anchoring of functional groups on MWCNTs caused an increase in the  $I_D/I_G$  ratio compared with that of the pristine MWCNTs, indicating an increase of  $sp^3$  carbons on the nanotubes upon functionalization. Moreover the overtone of the D-band, observed at  $2600\text{ cm}^{-1}$ , increased with the acid treatment and also with the amine functionalization. These results indicate that the MWCNTs were effectively functionalized with amine groups cleaved in the previously grafted acid groups. To analyze amine groups physical adsorption onto MWCNT, Raman spectra should be observed at low energy modes (mode known as radial breathing mode, typically between  $150$  and  $350\text{ cm}^{-1}$ ).<sup>34</sup> This mode is poorly determined in the reported spectra. However, the fact that any displacement, in frequency, is not seen in the band D suggests that the non covalent functionalization was small even if it existed.<sup>37</sup>

#### 4. CONCLUSIONS

Amino-functionalized carbon nanotubes were prepared after carboxylation, acylation and amidation steps. Three amines with different molecular structure were used. FT-IR and FE-SEM studies confirmed that MWCNTs were amine-functionalized. Raman spectra, when applied to TETA functionalized MWCNTs, suggest that the functionalization occurred by covalent bonding. As can be concluded from TGA results, the effectiveness of amine functionalization seemed to be dependent on amine chemical structure and molecular weight. Indeed due to steric restrictions, the amine with higher molecular weight, Jeffamine T-403 (branched molecule with methyl groups attached to the carbon bonded to primary amine groups) showed lower functionalization degree compared with the amines with lower molecular weights, D-230 and TETA, which present a straight-chain structure, with lower steric effects. Among D-230 and TETA, the last one showed higher functionalization effectiveness, possibly due to the absence of methyl groups attached to the carbon bonded to amine groups. These features open up new perspectives of functionalization by selecting different amines to functionalize MWCNTs.

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