

**The solvent effect on the sidewall functionalization of multi-walled carbon nanotubes with maleic anhydride**

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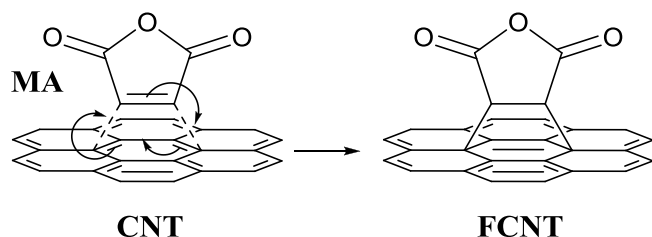
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**Abstract:** The Diels-Alder cycloaddition of maleic anhydride to multi-walled carbon nanotubes (MWCNT) was performed in dimethyl sulfoxide (DMSO) (190°C, 24 h) and in 2-chlorotoluene (150°C, 48 h). The functionalized MWCNT were characterized by thermogravimetry, elemental analysis, X-ray photoelectron spectroscopy, and potentiometric titration allowing a clear perception of the solvent involvement on the functionalization reaction. The MWCNT functionalized in DMSO presented acidity arising mostly from reaction with the solvent. The MWCNT modified in 2-chlorotoluene did not evidence chemical transformations that could be assigned to the solvent alone. The cycloaddition of maleic anhydride to anthracene, used as model compound for the MWCNT surface, confirmed that the reaction was fast in DMSO. Hydrolysis of the anhydride was catalysed by the MWCNT presence, but the cyclic anhydride structure was restored upon heating in this solvent at 185 °C. The work also confirmed the cycloaddition of maleic anhydride to CNT and DMSO was identified as the best solvent for the reaction, at 190 °C.

## 1. Introduction

Carbon nanotubes (CNT) exhibit unique electrical, thermal and mechanical properties [1]. However, the large  $\pi$ - $\pi$  interactions between tubes stabilize the CNT bundles and hinder their dispersion in other materials. Therefore, the CNT organic functionalization has been used as a valuable tool to improve their performance in various applications [2]. The CNT covalent functionalization by cycloaddition reactions has been intensively investigated over the past years. A major advantage of this type of reaction compared to oxidative methods is the possibility to bond a wide variety of functional groups to the CNT surface under relatively mild reaction conditions, avoiding the use of strong oxidizing acids that lead to CNT breakage [3]. The highly conjugated tubular network of a CNT can be involved in cycloaddition reactions either as dipolarophiles, dienophiles or as dienes. A variety of organic compounds were added

to the CNT surface. These reactions include ozonolysis [4,5], cycloaddition of dichlorocarbenes [6], cycloaddition of nitrenes [7], the Bingel reaction, [8] 1,3-dipolar cycloaddition of azomethine ylides [9], osmilation [10], epoxidation [11] and Diels-Alder cycloaddition of dienes and dienophiles [12-18]. In 2004 Delgado et al. [12] confirmed experimentally, for the first time, the viability of the Diels-Alder reaction of CNT with *o*-quinodimethanes generated in situ from the corresponding sulfone. In 2007 Skallariou et al. [13] also reported the reaction of *o*-quinodimethanes with CNT using benzocyclobutenes as diene precursors. In 2005 Zhang et al. [14] reported the Diels-Alder reaction of a variety of dienes with fluorinated CNT. According to the authors the alkene groups in the vicinity of fluorine atoms covalently attached to the CNT surface are more susceptible to react with the diene. To avoid the covalent modification of the CNT outer layer prior to the Diels-Alder addition reaction, Ménard et al. [15] (2006) used transition metals [19] and high pressure [20] to induce the reaction with 2,3-dimethoxy-1,3-butadiene. Recently Zydziaik et al. (2011) reported the CNT functionalization under mild experimental conditions through the Diels-Alder addition of cyclopentadiene linked to polymeric molecules [18]. Only a few reports are known on the reaction of maleic anhydride (MA) with CNT (Fig.1).



**Fig. 1 - CNT functionalization with MA.**

In 2007, Gergely et al. [21] combined MA (12.5 mass equivalents) with MWCNT in the presence of aluminium chloride (7.5 mass equivalents) and the mixture was refluxed for 48 h in 1,4-dioxane and THF. The TGA of the product showed a weight loss around 20 % between 250 and 700 °C. A similar reaction was described in 2010 by Munirasu et al. [17] using MWCNT and 20 mass equivalents of MA, benzyl ether as solvent and heating at 75 °C for 48 h. This reaction was performed in a closed vessel, under argon atmosphere. No evidence for functionalization was presented in the manuscript apart from

TGA weight loss (6.1 %) between 100 and 600 °C (the actual TGA curve was not included in the manuscript or the supporting information). In 2009, McPhail et al. [16] reported the reaction of single-walled carbon nanotubes (SWCNT) with an excess of MA in chloroform, with heating at 50 °C for 12 h, under nitrogen atmosphere. The TGA curve of the functionalized material evidenced a weight loss of 50 % in a range that includes the boiling point of MA (202 °C).

These literature results cast doubt on the possibility to perform the covalent functionalization of CNT with MA under mild temperature conditions (75 or 50 °C) [16,17]. This drawback was circumvented by the use of aluminum chloride [21], which can act as a catalyst in the process, but the approach may lead to difficulties in the complete removal of the metal from the functionalized product.

Performing the reaction under high temperature conditions is an alternative approach to promote the cycloaddition. The present work reports the reaction of CNT with MA at 150 °C and 190 °C using 2-chlorotoluene or dimethyl sulfoxide (DMSO) as solvent. The results suggest that DMSO may react with the CNT, but also show that MA may be covalently bonded to the CNT surface, maintaining the cyclic anhydride structure.

## **2. Experimental**

### *2.1. Materials*

CNT were manufactured by Nanocyl (Nanocyl<sup>®</sup> 7000 series) and presented an average diameter of 9.5 nm and a length of 1.5 μm. Maleic anhydride, dimethyl sulfoxide (DMSO, PA) and NaCl were obtained from Sigma, 2-chlorotoluene and DCl (38 wt % in D<sub>2</sub>O) were obtained from Fluka, ethanol and diethyl ether were obtained from Panreac and deuterated dimethyl sulfoxide (DMSO-d<sub>6</sub>, 99.80 % D) was obtained from Euriso-top. In the potentiometric titration study, the HCl (0.01 mol L<sup>-1</sup>) and NaOH (0.1 mol L<sup>-1</sup>) solutions were obtained from the corresponding 1 molar standard solutions (Fixanal<sup>®</sup>, Riedel de Haën<sup>®</sup>) using high purity water (R>18MΩ).

## 2.2. Analysis

*Nuclear Magnetic Resonance (NMR).* Model reactions of maleic anhydride and anthracene were analyzed by  $^1\text{H}$  NMR on a Varian Unity Plus ( $^1\text{H}$ : 300 MHz). *Thermogravimetric analysis (TGA).* TGA was performed on a Modulated TGA Q500 from TA Instruments. The samples were heated at  $10\text{ }^\circ\text{C min}^{-1}$  both under air and  $\text{N}_2$  atmosphere at a constant flow of  $50\text{ mL min}^{-1}$ . *Elemental Analysis.* The elemental analyses of C, H, O, N and S were carried out in a LECO Truspec Micro CHNS microanalysis apparatus with a LECO Truspec Micro O accessory for O analysis. The C, H, S and N were determined from the amounts of  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{NO}_2$  produced in the combustion of a portion of the sample (1 mg of sample was used for each assay, with two repetitions). Oxygen was determined from the amounts of CO and  $\text{CO}_2$  released in a pyrolysis at very high temperature, in a different portion of sample. The analyses were replicated therefore four different portions of sample were used. *Potentiometric titration.* Potentiometric titration followed a procedure previously described in the literature [22] and was performed on a TIM850 titration Manager Titralab from Radiometer Analytical SAS. Titrations were carried out under argon atmosphere, using a suspension of 100 mg of CNT in an aqueous solution of HCl ( $0.01\text{ mol L}^{-1}$ , 35 mL) with NaCl ( $0.01\text{ mol L}^{-1}$ ). The pH electrode (Radiometer, Red Rod, pH 0-14, E16M317) was protected with dialysis tubing (Sigma, permeability  $\text{MW}<12000$ ) to prevent damage of the electrode surface and to ensure the reproducibility of the experimental results. Before each titration, the dialysis tubing was washed with excess of distilled water and tested with the non-functionalized CNT (reference experiment). Titrations were performed with NaOH ( $0.1\text{ mol L}^{-1}$ ). Each sample was stirred for 30 min before the addition of NaOH (2 mL, followed by  $0.01\text{ mL min}^{-1}$  until  $\text{pH}=11$  was reached). Samples were kept under a constant stirring speed during all the procedure. *X-ray photoelectron spectroscopy (XPS).* Samples for XPS analysis were pressed into pellets. XPS measurements were made in a SPECS spectrometer with a Phoibos 100 hemispherical analyser. The base pressure in the UHV chamber was below  $1.0\times 10^{-7}\text{ Pa}$ . The X-ray radiation source was monochromatic Al  $\text{K}\alpha$  (1486.74 eV) at 200 W X-ray power and anode voltage of 14.00 kV. The photo-excited electrons were analysed in constant pass ener-

gy mode, using pass energy of 50 eV for the survey spectra and 10 eV for the high resolution core level spectra, and energy step of 0.5 eV and 0.1 eV, respectively. CasaXPS software was used for data processing. The compositions in atomic percent (at. %) were determined from the survey spectra by considering the integrated peak areas (after corrections for the mean free-path of the outgoing electrons and the transmission function of the analyser) of the main XPS peaks of the different elements and their respective sensitivity factors. Core level curve fitting in different components was performed using a Shirley background and a standard least squares algorithm. Each component was considered as a convolution of a Gaussian and a Lorentzian function (80:20). In the case of the S2p core level band, each component is a spin-orbit doublet with a 1:2 peak area ratio between S2p<sub>1/2</sub> and S2p<sub>3/2</sub> components. The separation between S2p<sub>1/2</sub> and S2p<sub>3/2</sub> components has been set to 1.2 eV, as expected for an ideal sulfur signal [23].

### *2.3. MA and anthracene in DMSO-d<sub>6</sub>*

Anthracene (7 mg, 0.04 mmol) and MA (4 mg, 0.04 mmol) were combined in 650  $\mu$ L of DMSO-d<sub>6</sub>. The mixture was heated at 185 °C for 10 min. The <sup>1</sup>H NMR spectrum of the solution was immediately run.

### *2.4. MA and CNT under solvent-free conditions*

A homogeneous mixture of MA and CNT (in a 1:1 weight ratio) was prepared in a mortar, with the assistance of a pestle (ca. 5 minutes). The mixture was kept in a closed vessel, at room temperature, for 24 h. A small aliquot was then combined with DMSO-d<sub>6</sub> and the solution was filtered. The <sup>1</sup>H NMR spectrum of the solution was immediately run.

### *2.5. Maleic acid and anthracene in DMSO-d<sub>6</sub>*

Anthracene (approximately 1 molar equivalent) was added to the NMR tube containing the previous sample, analysed by <sup>1</sup>H NMR in the experiment described in 2.4. The NMR tube was heated at 185 °C for 45 min. and the <sup>1</sup>H NMR spectrum of the solution was run.

## 2.6. Functionalization of CNT with MA in DMSO or 2-chlorotoluene

A suspension of CNT in a solution of MA in DMSO was heated at 190 °C for 24 h and a suspension of CNT in a solution of MA in 2-chlorotoluene was also heated at 150 °C for 48 h. For each solvent, the reaction was equally performed with the CNT, in absence of MA and with MA in the absence of CNT. The reaction conditions used in these experiments were summarized in Tables 1 and 3. After each experiment, the CNT were filtered using a PTFE membrane with a porosity of 0.2 µm and washed with 2 mL of the solvent used in the reaction. The solid material was then dispersed in ethanol (5 mL), sonicated for 15 min, filtered and washed with a copious amount of solvent (this procedure was performed twice). The same washing procedure was used once with diethyl ether. The modified nanotubes were dried in a vacuum pistol at 150 °C for 12 hours.

## 2.7. Hydrolysis of compound 2

DCl (38 wt % in D<sub>2</sub>O, 14 µL) was added to a solution of compound **2** (7 mg, 0.03 mmol) in DMSO-d<sub>6</sub> (650 µL). The hydrolysis reaction was carried out with stirring at room temperature and was followed by <sup>1</sup>H NMR.

## 3. Results and discussion

### 3.1. The reaction of CNT with MA in DMSO

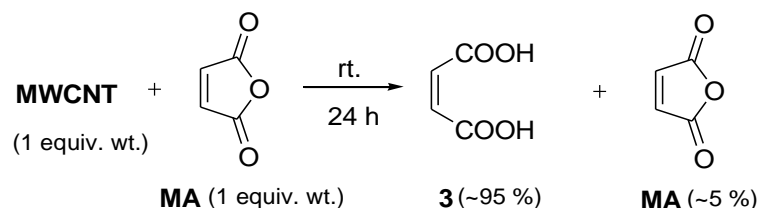
The experimental conditions used in this work for the CNT functionalization with MA were selected from a study where anthracene was used as a model compound for the CNT surface. The reaction was performed in DMSO, a solvent with a high boiling point (b.p. 190 °C), at 185 °C. This temperature would provide enough energy to induce the cycloaddition reaction, maintaining the anhydride in solution (m.p. 52-54 °C and b.p. 202 °C).

The experiment was performed in an NMR tube, containing a 1:1 molar ratio of anthracene and MA in deuterated DMSO. After 10 min at 185 °C, the adduct **2** was the only product identified in solution (Fig. 2).



**Fig. 2 - Formation of adduct 2 by reaction of MA and anthracene.**

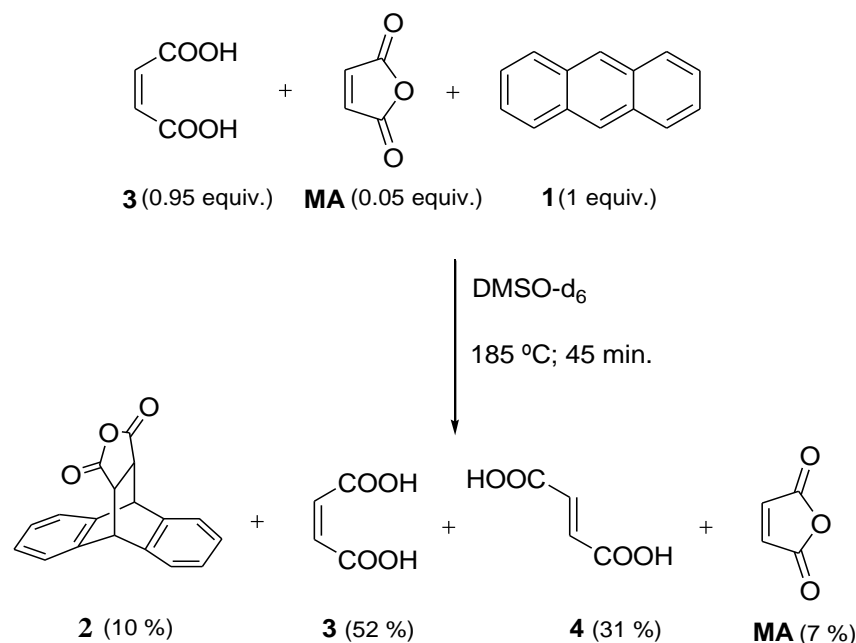
The chemical stability of MA in the presence of CNT was also evaluated by combining them in a mortar, in the absence of solvent. The solid mixture was kept in a closed vessel at room temperature for 24 h. Addition of DMSO-d<sub>6</sub> allowed the analysis of the soluble product mixture by <sup>1</sup>H NMR, indicating that maleic acid (**3**) and maleic anhydride were present in a 20:1 molar ratio (Fig. 3).



**Fig. 3 - Compounds soluble in DMSO-d<sub>6</sub> and extracted from the solid mixture of CNT and MA, after 24 h at room temperature.**

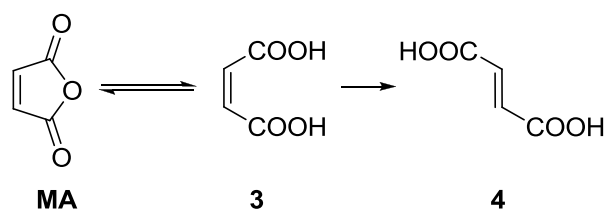
One molar equivalent of anthracene was added to the NMR tube and the mixture was heated at 185 °C for 45 min. The <sup>1</sup>H NMR spectrum registered before and after the heating process showed that maleic acid evolved to the thermodynamically more stable trans isomer (**4**, fumaric acid) [24]. Adduct **2** and MA were also formed in a small extent.





**Fig. 4 - Compounds soluble in DMSO-d<sub>6</sub> extracted from the mixture of CNT and MA after addition of anthracene and heating at 185 °C for 45 min..**

This study confirmed that the rate of hydrolysis of MA was enhanced by the CNT presence, in the absence of solvent. Heating a DMSO solution of anthracene in a mixture of maleic acid (95 %) and MA (5 %) resulted mainly in the isomerization of the acid (31 %). Cyclization to the anhydride also occurred in a small extent (12 %) leading to the formation of adduct **2** (10 %) together with unreacted MA (7 %). The formation of fumaric acid is an irreversible process (Fig.5). The cycloaddition only occurs with MA as the dienophile.



**Fig. 5 - Formation of maleic acid 3 and fumaric acid 4 from hydrolysis of MA.**

The information collected with this model reaction was used to rationalize the experimental conditions for the cycloaddition of MA to the CNT. The reaction was performed in DMSO at 190 °C (Table 1, Exp. 1) and the mixture was heated for 24 h to ensure that part of the maleic acid, formed by hydrolysis,

could partially regenerate MA in order to optimize the consumption of this chemical. The CNT were also heated in DMSO at 190 °C for 24 h, as a blank reaction (Table 1, Exp. 2).

**Table 1 - Experimental conditions for the functionalization of CNT with MA in DMSO (190 °C, 24 h).**

1	500	500	11.9	23.0	92.8
2	500	-	3.3	3.6	93.2
3	-	500	-	-	-

### 3.1.1. Thermogravimetric analysis

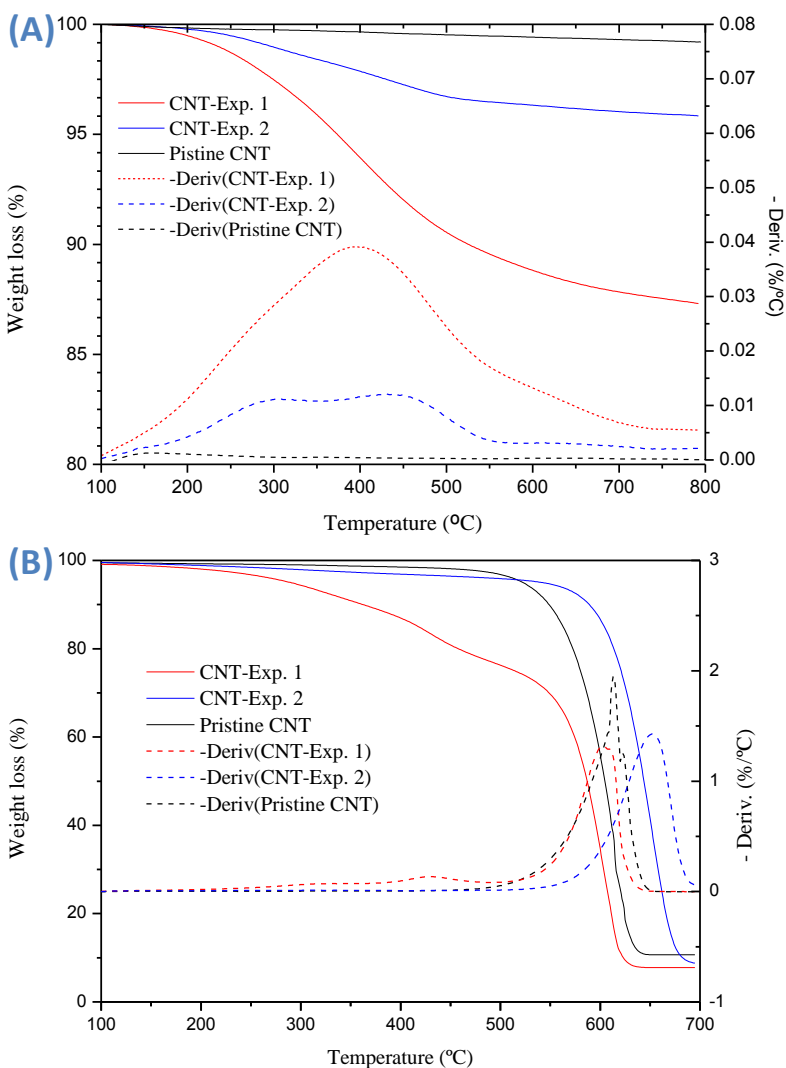
Thermogravimetric analysis of the pristine and functionalized CNT was performed in air and in N<sub>2</sub> atmosphere to study their thermo-oxidative and pure thermal stability, respectively (Fig. 6A and B). The oxidation of the pristine CNT (Fig. 6B) was initiated at 451 °C leading to 10.5 wt. % of residue above 689 °C. This residual mass can be associated to metal oxides incorporated in the CNT during the synthesis of this material. The functionalized CNT (Exp. 1) showed mostly two degradation steps between 200 and 500 °C, with a total weight loss of ca. 23 %, that may be assigned to oxidative degradation of the functional groups on the CNT surface under air flow (Fig. 6B). The maximum degradation rate of the CNT was observed at 606 °C, and at 653.5 °C all the carbonaceous material was consumed leaving a residue of 7.8 wt. %. The thermal stability of CNT-Exp. 1 was higher under inert atmosphere, the degradation processes starting above 250 °C and continuing until 600 °C, with a weight loss of approximately 11 % (Fig. 6A). When the same reaction was performed in the absence of MA (Exp. 2), the CNT presented a weight loss of 3.3 % in nitrogen, and 3.6 % in air flow at 500 °C (Fig. 6A and B), stabilizing the weight (in nitrogen), or accelerating until total CNT degradation (in air). Approximately 8 wt. % of residue remained after complete oxidation of the carbonaceous material. A remarkable increase in thermo-

oxidative stability was observed for the CNT-Exp. 2, presenting a maximum degradation rate in air at 650 °C, while for pristine CNT the same process was observed at 610 °C. Similar increase in thermal stability was reported for CNT with decreasing structural defects [25].

The slightly larger weight loss measured for the CNT-Exp. 2 at ca. 500 °C, relative to pristine CNT (Fig. 6A), indicates that DMSO or some degradation product formed at 190 °C (dimethyl sulfide, dimethyl disulfide or bis-(methylthio)methane) may react with the CNT surface. The first derivative of the TGA curve presented two peak temperatures at 300 °C and 430 °C.

Considering that the reaction of the CNT surface with DMSO cannot be prevented during the cycloaddition of MA in this solvent, the total weight loss, by TGA under N<sub>2</sub> atmosphere, of the functionalized CNT (CNT-Exp. 1) should include ca. 3.3 % of material generated by reaction with DMSO. The thermal degradation of the actual MA-CNT reaction products would be responsible for a weight loss of ca. 8.6 %. Performing the TGA in air resulted in a weight loss of 19.4 % in the range of 200 to 500 °C. The larger weight loss observed in air may be assigned to the loss of oxidized carbonaceous fragments due to extensive oxidation of the highly functionalized CNT surface under the conditions of the TGA.

Heating MA in DMSO at 190 °C for 24 h (Table 1, Exp. 3) resulted in a brown solution but no solid products were formed. This indicates that the functionalized CNT (isolated in Exp. 1) are not contaminated with by-products from the prolonged heating process of MA in DMSO. These contaminants remained in solution and were easily removed during the washing process.



**Fig. 6 - TGA curves (solid lines) and first derivative (dashed lines) of CNT-Exp. 1 (red lines), CNT-Exp. 2 (blue lines) and pristine CNT (black lines). The TGA experiments were performed in nitrogen (A) and in air (B) atmosphere.**

The functionalization of SWCNT with an excess of MA, previously reported in the literature by McPhail et al.[16] was performed in chloroform, at 50 °C for 12 h, under nitrogen atmosphere. The TGA of the product, performed under N<sub>2</sub> atmosphere, reported a weight loss of 50 % at 700 °C, but this weight loss occurred almost exclusively below 200 °C. Such temperature range may be associated with

the boiling point of MA (202 °C), suggesting that this compound could be adsorbed at the CNT surface. In the functionalization experiment conducted by Gergely et al. [21], MWCNT were combined with 12.5 mass equivalents of MA and 7.5 mass equivalents of aluminium chloride in a 1:1 mixture of 1,4-dioxane and THF. The mixture was refluxed for 48h and the TGA of the solid product showed a weight loss of approximately 20 % above 200 °C, with inflection points at temperatures around 300, 400 and 500 °C. These results partially agree with the TGA data collected in the present work for CNT-Exp 1, where a continuous increase in weight loss is observed above 200 °C reaching a maximum rate around 400 °C supports that a major product was present on the CNT surface. This weight loss was assigned to the cleavage of covalently bonded MA molecules.

### 3.1.2. Elemental analysis

Elemental analysis of CNT-Exp. 1 and CNT-Exp. 2 reveals the presence of sulfur and nitrogen, besides carbon, oxygen and hydrogen (table 2). Sulfur identified on the CNT surface may be associated with DMSO used as solvent that reacts or is adsorbed on the surface. The sulfur content was substantially higher for CNT modified with maleic anhydride (CNT-Exp.1) than for CNT refluxed in DMSO (CNT-Exp.2), reflecting a larger extent of functionalization by the solvent in the presence of MA. Traces of nitrogen were detected in all samples, including the pristine CNT, in a comparable amount, and may be assigned to contamination by atmospheric nitrogen. The amount of residue detected after complete oxidation of the samples (7-10 %) is in agreement with the results obtained by TGA in air atmosphere.

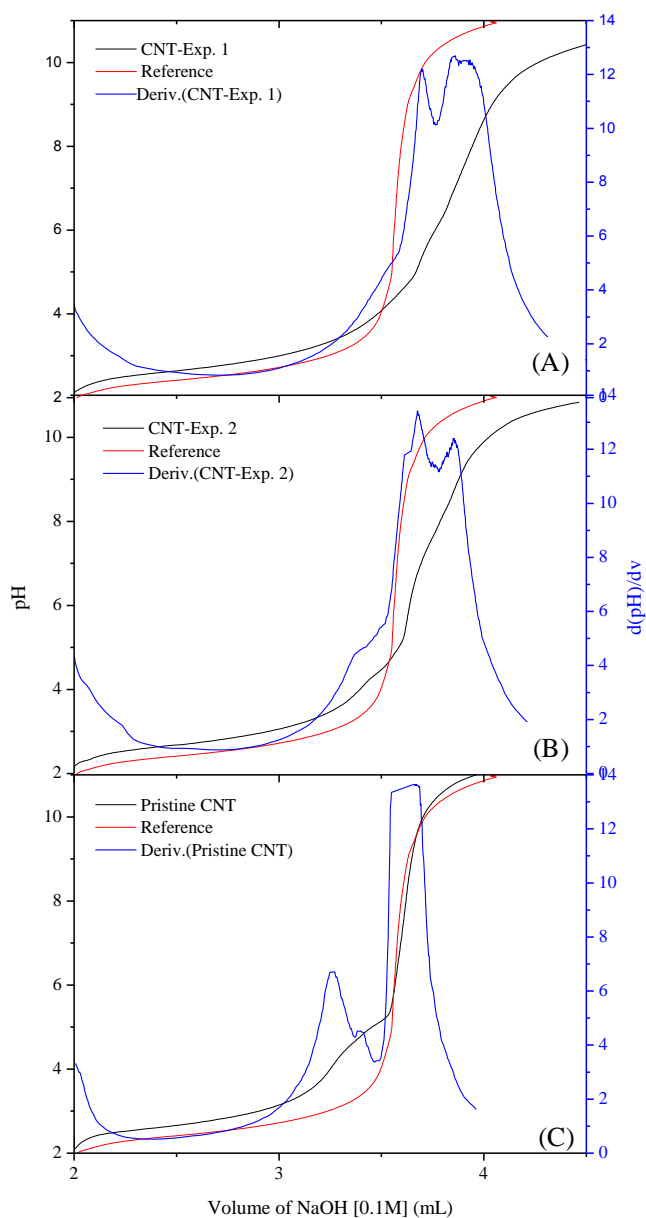
**Table 2 – Elemental analysis results of pristine CNT and functionalized CNT-Exp. 1 and CNT-Exp.2.**

	C	H	O	N	S	Cl	Al	MA	Residue
CNT-Exp. 1	81.84	1.35	8.14	1.32	0.14	7.21	0.099	0.016	
CNT-Exp. 2	90.09	0.62	1.88	0.43	0.19	6.79	0.021	0.005	

Pristine CNT	88.34	0.32	0.7	-	0.19	10.5	0.008	0.000
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### 3.1.2. Potentiometric titration

The acid-base properties of modified and pristine CNT were investigated by potentiometric titration in order to determine if the anhydride group attached to the aromatic surface was hydrolyzed during the functionalization process. For this study, a sample of 100 mg of CNT was suspended in 35 mL of a 0.01 M solution of HCl and 0.01 M of NaCl. The suspension was stirred under argon atmosphere for 30 min., followed by addition of a 0.1 M solution of NaOH. Reproducible results could only be obtained when the pH electrode was protected with dialysis tubing. The titration curve obtained for the pristine CNT suspension (Fig. 7, graphic C) showed that the amount of titrant required to reach pH 7 was approximately the same as the amount required for titration of the HCl solution (reference test). However pristine CNT suspension exhibited an additional inflection at pH around 3.3 assigned to the transformation of aluminium carbide (generated during the synthesis of the CNT [26]) to aluminum chloride upon addition of HCl [27]. Part of this contaminant may have been eliminated during the process of functionalization, possibly solubilized.



**Fig. 7 - Titration curves for the suspensions of CNT-Exp.1, CNT-Exp. 2 and Pristine CNT.**

The titration curve of the suspension of CNT modified only by the presence of DMSO (CNT-Exp. 2) showed that they are slightly acidic in relation to pristine CNT (Fig. 7, graphic B), supporting the previous assumption that the DMSO, used as solvent, was in part responsible for functionalization. The acidity measured for the suspension of functionalized CNT-Exp. 1 may also result from oxidation promoted by DMSO at 190 °C, and from carboxylic acids generated by hydrolysis of the anhydride groups during the cycloaddition reaction with MA and/or during the titration test, performed in aqueous 0.01 M HCl

solution. The total acidity obtained for the functionalized CNT-Exp. 1 (Fig. 7, graphic A) was the result of reaction with MA and with the solvent and the contribution of acid groups formed in the presence of solvent (CNT-Exp.2) should be subtracted from the global pH value.

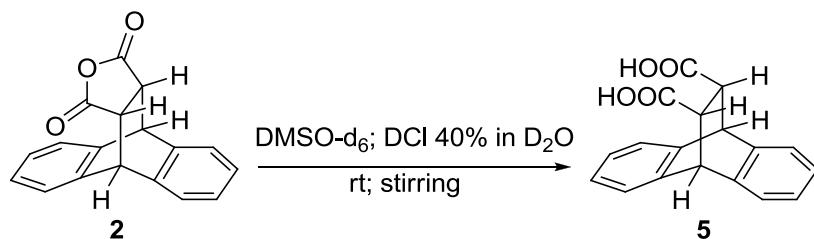
Table 3 summarizes the number of equivalents of H<sup>+</sup> for each titration, calculated from the volume of NaOH of the last inflection point in the derivative curve (Fig. 7). The acidity for the CNT-Exp. 1 was only slightly higher than that of CNT-Exp 2. This indicates that, during the functionalization of CNT with MA (Exp. 1) the hydrolysis of the anhydride groups bonded to the CNT surface occurs only in a small extent. On the other hand, under the titration conditions (aqueous solution at pH 2), it was also expected that some hydrolysis would be induced during the experiment.

**Table 3 - H<sup>+</sup> equivalents quantified for 100 mg of sample using the last inflection point of the titration curve in fig. 7.**

CNT-Exp. 1	0.40	4.0 ± 0.03
CNT-Exp. 2	0.39	3.9 ± 0.02
Reference	0.36	3.6 ± 0.02

Compound **2** was used again as a model of the functionalized CNT surface to understand the rate of hydrolysis of the anhydride groups in the presence of HCl. The experiment was performed in an NMR tube, combining a DMSO-d<sub>6</sub> solution of compound **2** with 6.6 molar equivalents of DCl (38 % in D<sub>2</sub>O) at room temperature (Fig. 8). The mixture was kept under stirring conditions and the <sup>1</sup>H NMR spectrum was registered at regular intervals. The relative ratio of compounds **2** and **5** was calculated for each spectrum and the percentage of the dicarboxylic acid **5** in the mixture was plotted with time (Fig. 9).

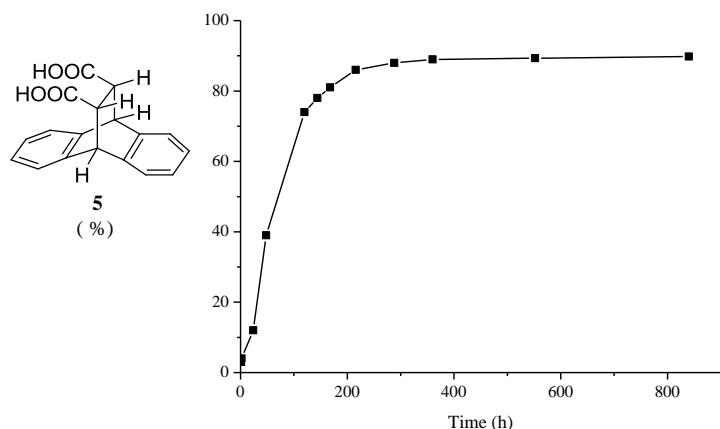




**Fig. 8 - Formation of product 5 from compound 2.**

The data indicates that the hydrolysis of compound **2** at room temperature occurs very slowly with a conversion of 12 % after 24 h. The ratio of hydrolyzed compound **5** tends to stabilize at 89 % after approximately 8 days. The titration of the modified CNT was an experiment performed within approximately 4 h and from the study presented in Fig. 9, the extent of hydrolysis induced by HCl should not exceed 4 %. The anhydride groups on the external carbon layer should remain essentially in a non-hydrolyzed form and this explains the low acidity measured for the functionalized material (Table 2, CNT-Exp.1), similar to the acidity value determined for the CNT modified by heating in DMSO at 190 °C (Table 2, CNT-Exp.2).

Heating a solution of compound **5** in DMSO- $d_6$ , at 185 °C, resulted in the total conversion into the anhydride **2** after 10 min.. This observation is in agreement with what was reported for succinic acid that also converts into the anhydride at 200-250 °C [27].



**Fig. 9 - Molar percentage of compound 5 generated by hydrolysis of compound 2 in the presence of DCI for 850 h, measured by  $^1\text{H}$  NMR.**

### 3.1.3. XPS analysis

Table 4 shows the surface atomic (at. %) composition of pristine CNT, CNT obtained in Exp. 1 and Exp. 2 determined by XPS.

**Table 4 - Surface composition (at. %) calculated from XPS survey spectra.**

CNT-Exp. 1	91.62	87.76	7.18	9.16	1.20	3.08	0.104	
CNT-Exp. 2	97.68	96.62	2.07	2.73	0.25	0.65	0.028	
Pristine CNT	99.29	99.06	0.71	0.94	-	-	0.010	-

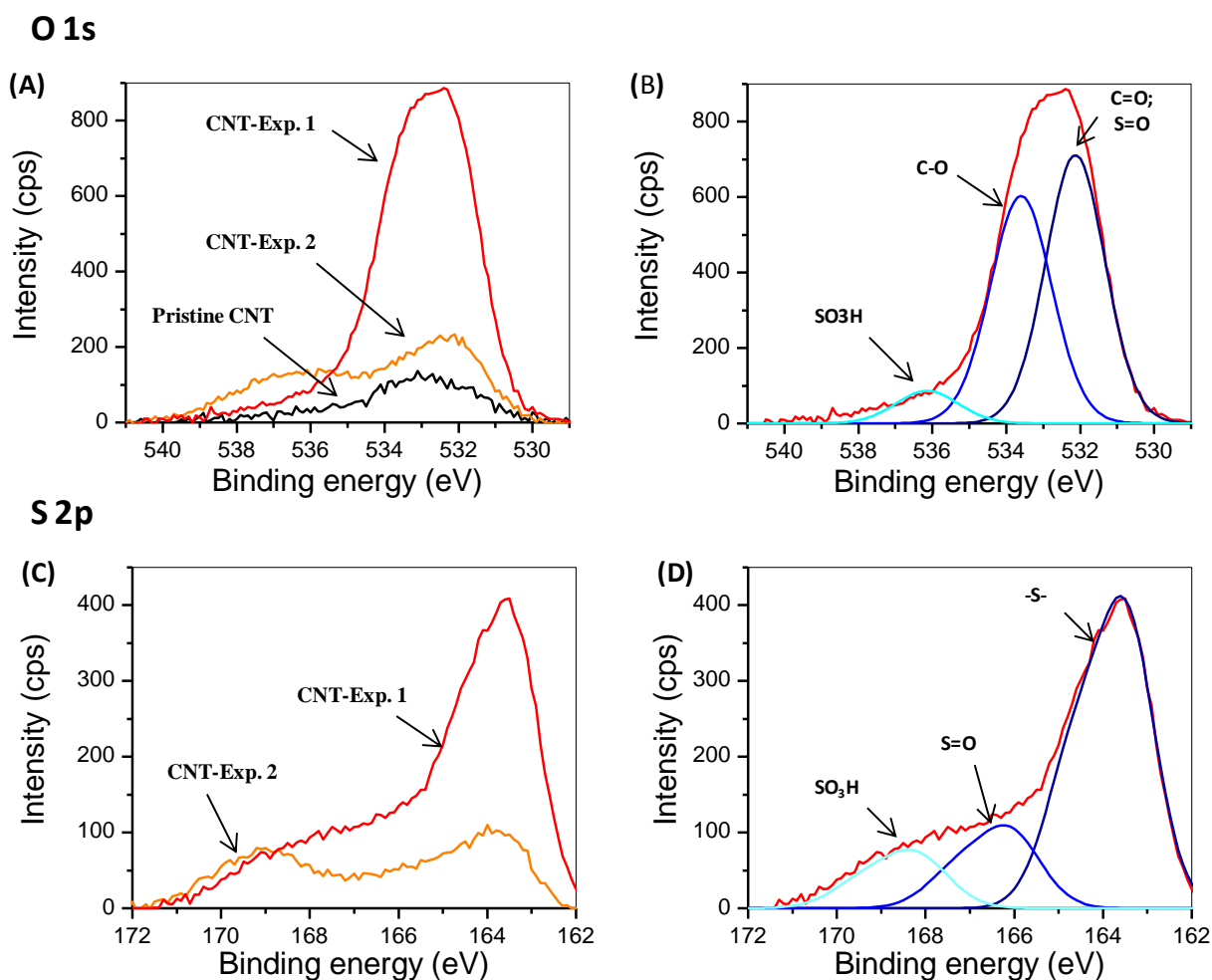
Pristine CNT show an oxygen content of 0.71 at. %, previously assigned to alcohol groups by Paiva et al. [24].

Heating the CNT in DMSO in the absence of MA (CNT-Exp. 2) led to the introduction of sulfur and enhancement of the oxygen content. The presence of sulfur (0.25 at. %) confirmed that DMSO was not inert during the heating process. Part of this sulfur may be associated with oxygen as sulfonic acid groups and this is supported by the background-corrected O1s core level spectrum of CNT-Exp.2 (graph A; Fig. 10), where the component at ~536 eV has already been related to oxygen bonded to sulfur in sulfonic acids [28, 29, 34]. This also matches the peak maximum for the S2p<sub>3/2</sub> component at BE ~169 eV (graph C; Fig. 10), ascribed to this chemical group. The peak maximum for the S2p<sub>3/2</sub> component at BE ~163.5 eV can be assigned to the presence of methyl sulfides. According to the literature, protonated DMSO can react with phenols, where the aromatic ring is activated to electrophilic attack, to form a sulfonium salt that can be decomposed by heating to give hydroxyaryl methylthioethers [30]. The hydroxyl groups present in the pristine CNT could induce a similar type of reaction, with formation of methyl sulfides in the neighbouring carbon atom. The spectrum of O1s for CNT-Exp.2, with a low sig-

nal-to-noise ratio, was not deconvoluted, however, it is apparent that sulfides and sulfonic acids are present in similar, low atomic ratio. The existence of traces of sulfoxides at BE 166.1 eV cannot be excluded. The remaining oxygen that is not associated to sulfur and does not come from pristine CNT may be related to the formation of alcohols and carboxylic acids produced under reflux conditions in the presence of atmospheric oxygen. In summary, the XPS analysis confirms that DMSO reacts with the CNT surface, and that carbon atoms adjacent to hydroxyl groups are particularly susceptible to electrophilic attack. Sulfonation and thiomethylation are the major processes under the experimental conditions used. Extra phenolic and carboxylic acid groups are also incorporated as a result of surface oxidation.

The background-corrected O1s core level spectrum for CNT-Exp. 1 and its deconvolution are displayed in Fig. 10, graphs A and B respectively. In this case, reaction of the CNT surface with DMSO cannot be excluded, masking the expected O1s band for maleic anhydride where the two components at ~532 eV (doubly-bonded oxygen in O-C=O) and ~534 eV (singly-bonded oxygen in O-C=O) should appear in a 2:1 atomic ratio [31, 32]. As can be seen in graph B of Fig. 10, this is not the case, as we should consider the contribution of the oxygen-containing groups previously present in the sample (alcohol groups) that reinforce the signal at ~534 eV, and of the oxygen bonded to sulfur in sulfoxides (BE of ~532 eV) [33], overlapping with the signal for the doubly-bonded oxygen in maleic anhydride. As referred before, the background-corrected O1s core level spectrum for exp. 1 has been deconvoluted into 3 components, with peaks maxima at BE 532.1, 533.6, and 536.1 eV with the corresponding atomic percentages of 49.9, 43.9 and 6.4 (graph B; Fig. 10). As observed for CNT-Exp. 2, the component with peak maximum at BE of 536.1 can be attributed to sulfonic acids and this matches the peak maximum for the S2p<sub>3/2</sub> component at BE ~168.2 eV (graph D; Fig. 10). The background-corrected high resolution S2p core level spectrum for CNT-Exp. 1 (graph C, Fig. 10), was deconvoluted into two additional peaks with maxima for the S2p<sub>3/2</sub> component at BE 163.5 eV and 166.1 eV that can be attributed to sulfides and sulfoxides [29, 35, 36], respectively. The atomic percentage of sulfur (at. %) in sulfides, sulfoxides and sulfonic acids was 67.9 %, 18.8 % and 13.2 %, respectively, indicating a higher extent of methylsulfonyl-

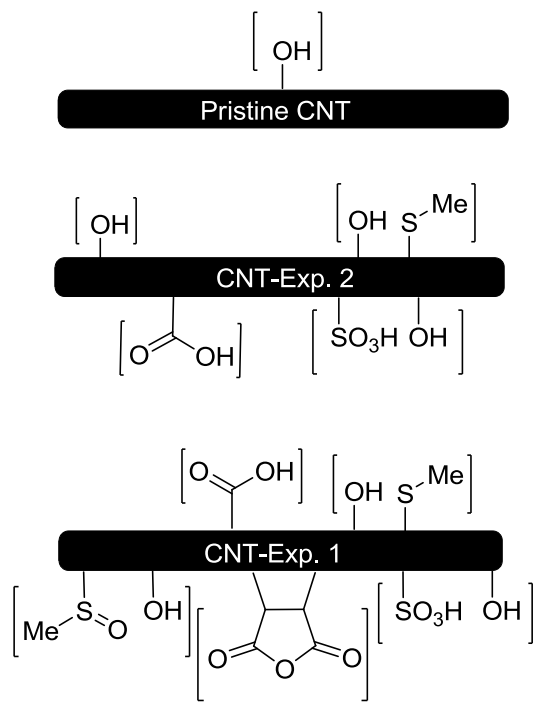
tion. In conclusion, the XPS analysis evidences sulfonation and thiomethylation of the CNT surface, possibly in adjacent positions to aromatic hydroxyl groups. Extra sulfoxides may also be formed and it was assumed that they could result from oxidation of part of the thiomethyl groups. Oxidation of the CNT surface leads to some carboxylic acids and phenols. When all the oxygen atoms of these species are accounted for, the result is a comfortable 2:1 ratio of doubly-bonded oxygen ( $\text{O}-\text{C}=\text{O}$ ) and singly-bonded oxygen in ( $\text{O}-\text{C}-\text{O}$ ), assigned to the cycloaddition of maleic anhydride. Considering a direct correlation between atomic % and molecular % for the functional groups bonded to the CNT surface (summarized in Fig 11), we calculated the molar % of MA in relation to the total number of moles of functional groups (excluding the hydroxyl group) incorporated through the functionalization process. This indicates that the reaction with maleic anhydride occurred to an extent that slightly exceeds 50 % (see supporting information for details).



**Fig. 10 - A) Background-corrected high resolution O1s core level XPS spectra for pristine CNT, CNT-Exp. 1 and CNT-Exp. 2. B) Deconvolution of the spectrum for CNT-Exp. 1 into 3 components at BE 532.1 eV, 534.6 eV, and 536.1 eV. C) Background-corrected high resolution S2p core level XPS spectra for CNT-Exp. 1 and CNT-Exp. 2. D) Deconvolution of the spectrum for CNT-Exp. 1 into 3 components at BE 163.5 eV, 166.1 eV, and 168.2 eV.**

#### *3.1.4. Potentiometric titration and XPS analysis*

XPS analysis of the pristine CNT confirmed the presence of oxygen, previously assigned to phenolic groups [24]. The titration revealed a neutral behaviour for this material, indicating that the acidity of the phenolic substituent could not be detected by this method. This means that the acidity determined for the functionalized CNT (CNT-Exp. 1 and CNT-Exp. 2) must be related to the presence of sulfonic and carboxylic acids on their surface. Sulfonic acids were clearly quantified by XPS and the titration data reveals the global acidity. These results were combined and allowed the quantification of the carboxylic acid groups formed in each experiment: 0.125 at % of sulfur in sulfonic acids and 0.486 at % of oxygen in carboxylic acids for CNT Exp 2 and 0.158 at % of sulfur in sulfonic acids and 0.676 at % of oxygen in carboxylic acids for CNT Exp 1. These calculations are detailed in the supplementary data. The functional groups bonded to the pristine and treated CNT, detected by XPS, are represented in Fig. 11.



**Fig. 11 – Functional groups at the surface of pristine CNT, CNT-Exp. 2 and CNT-Exp. 1.**

### 3.2. The reaction of CNT with MA in 2-chlorotoluene

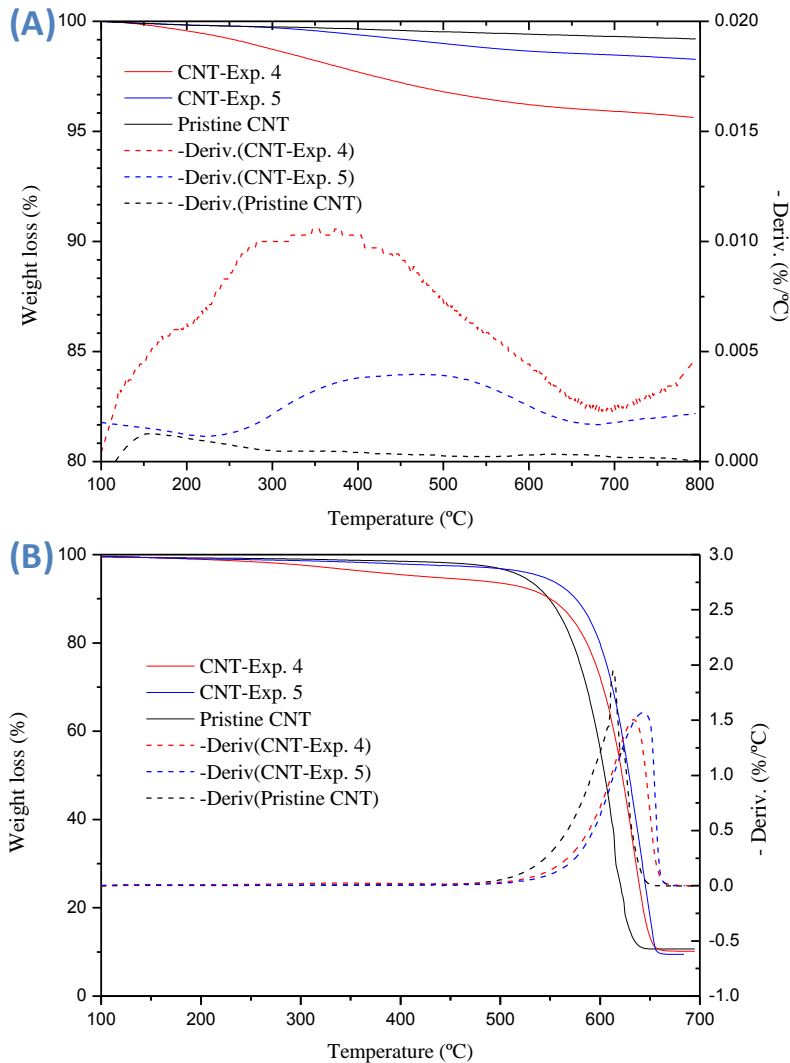
Considering that DMSO was not an inert solvent and contributed to the modification of the CNT surface, a separate functionalization experiment was performed using 2-chlorotoluene as solvent. The reactions were carried out at 150 °C for 48 h (Table 5).

**Table 5 - Experimental conditions for the functionalization of CNT with MA in 2-chlorotoluene (150 °C, 48 h).**

4	500	500	3.7	5.3	90.9
5	500	-	0.9	1.9	90.2
6	-	500	-	-	-

#### 3.2.1. Thermogravimetric analysis

The TGA curves obtained for the CNT heated in 2-chlorotoluene in the presence of MA (CNT-Exp.4) and in the absence of MA (CNT-Exp.5) indicated a lower level of functionalization (Fig. 12).



**Fig. 12 - TGA curves (solid lines) and first derivate (dash lines) of CNT-Exp. 4 (red lines), CNT-Exp. 5 (blue lines) and pristine CNT (black lines). The TGA experiments were performed in nitrogen (A) and in air (B) atmosphere.**

The TGA curves obtained in nitrogen and in air atmosphere for the CNT heated in 2-chlorotoluene in the presence of MA (CNT-Exp.4) and in the absence of MA (CNT-Exp.5) are presented in Fig. 12 A and B. The weight of CNT-Exp. 4 presented a slow decrease from 250 °C to approximately 500 °C and stabilized at higher temperature in nitrogen (Fig. 12 A), or decreased abruptly in air (with an inflection tem-

perature at 613 °C) leaving a residue of 10.5 wt. % (Fig. 12 B). The results obtained in nitrogen (Fig. 12 A) show a lower level of functionalization of the CNT-Exp. 4 compared to CNT-Exp.1. The effect of refluxing in solvent resulted in a 0.9 % weight loss in nitrogen at 800 °C, indicating that the incorporation of MA on the CNT surface accounts for 2.8 % of weight loss. In air atmosphere, a comparable weight loss of 3.4 % from 200 to 500 °C reflects the reduced extent of oxidation of CNT-Exp. 4 relative to CNT-Exp. 1, and a poorly functionalized CNT surface.

### 3.2.2. Elemental analysis

Elemental analysis of CNT-Exp. 4 and CNT-Exp. 5 reveals the absence of sulfur and the presence of nitrogen, carbon, oxygen and hydrogen (table 6). This confirms that sulfur is associated with the use of DMSO as solvent, replaced in the current experiments by 2-chlorotoluene. Traces of nitrogen detected in all samples, may again be due to the nitrogen content of air in the atmosphere. Elemental analysis of CNT-Exp. 4 exhibits a higher content of oxygen compared with that of CNT-Exp.5 and pristine CNT, mainly due to the incorporation of maleic anhydride on the CNT surface (table 5). As observed before for samples prepared in DMSO, the amount of residue detected after complete oxidation is in agreement with the results obtained by TGA in air atmosphere. The reflux of CNT in 2-chlorotoluene does not reduce significantly the content of metal oxides in pristine CNT.

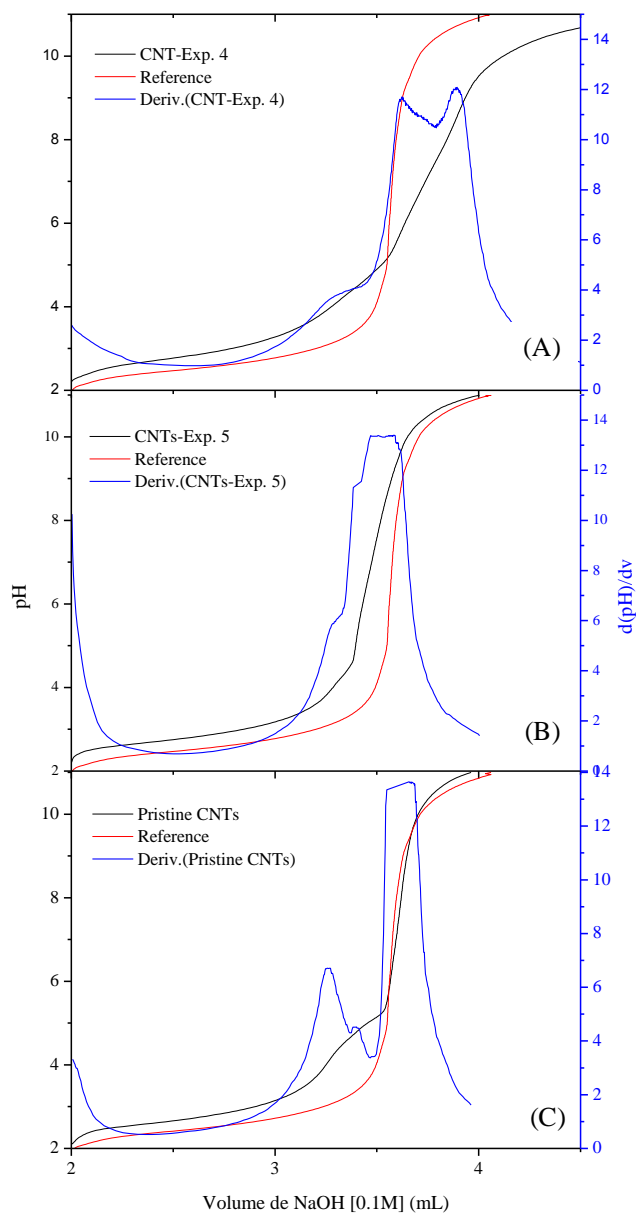
**Table 5 – Elemental analysis results of pristine CNT and functionalized CNT-Exp. 4 and CNT-Exp.5.**

CNT-Exp. 4	87.4	0.66	2.73	0.10	9.11	0.031
CNT-Exp. 5	88.86	0.43	0.84	0.11	9.76	0.009
Pristine CNT	88.34	0.32	0.7	0.19	10.5	0.008

### 3.2.2. Potentiometric titration



The acid-base properties of the CNT modified in CNT-Exp.4 and Exp.5 were studied following an experimental procedure analogous to the previously described for the titration of the CNT obtained in Exp.1 and Exp.2 (Fig. 13).



**Fig. 13 - Titration curves for the suspensions of CNT-Exp. 3, CNT-Exp. 4 and Pristine CNT.**

Table 6 summarizes the total number of  $H^+$  equivalents calculated from the titration curves presented in Fig. 13.

Titration of the suspension of pristine CNT indicated their neutral behaviour, since the total number of acid equivalents determined was coincident with that measured for the reference test. For CNT obtained in Exp.5, the titration curve was close to that recorded for non-functionalized CNT, suggesting that the solvent did not significantly affect its acidity. Regarding the CNT obtained in Exp.4 only a slight increase in the acidity was observed relative to the pristine CNT.

**Table 6 - H<sup>+</sup> equivalents quantified for 100 mg of sample using the last inflection point of the titration curves in Fig. 13.**

CNT-Exp.4	0.39	3.9 ±0.03
CNT-Exp. 5	0.36	3.6 ± 0.02
Reference	0.36	3.6 ± 0.02

### 3.2.3. XPS analysis

Table 7 shows the surface composition of pristine CNT and CNT obtained in Exp. 4 and Exp. 5 determined by XPS.

**Table 7 - Surface composition calculated from XPS survey spectra.**

CNT-Exp. 4	98.45	97.94	1.55	2.06	0.021
CNT-Exp. 5	98.92	98.57	1.08	1.43	0.014
Pristine CNT	99.29	99.06	0.71	0.94	0.010

The background-corrected high resolution O1s core level spectrum for CNT-Exp. 4 (graph B, Fig. 14), was deconvoluted into three additional peaks with maxima for the O1s component at BE  $\sim$ 532 eV (doubly-bonded oxygen in O-C=O),  $\sim$ 534 eV (singly-bonded oxygen in O-C=O) and  $\sim$ 536 eV, that can be assigned to adsorbed oxygen. Hydrolysis of the anhydride groups with subsequent formation of carboxylic acids was confirmed by potentiometric titration and may be responsible for the slight enhancement of the peak at  $\sim$ 534 eV compared with that at  $\sim$ 532 eV, expected to be present in a 1:2 atomic ratio. CNT heated in 2-chlorotoluene (CNT-Exp.5) shows an extra content in oxygen relative to pristine CNT (graph A, Fig. 14) that may be assigned to adsorbed oxygen during the heating process, carried out in an open atmosphere during 48 h.

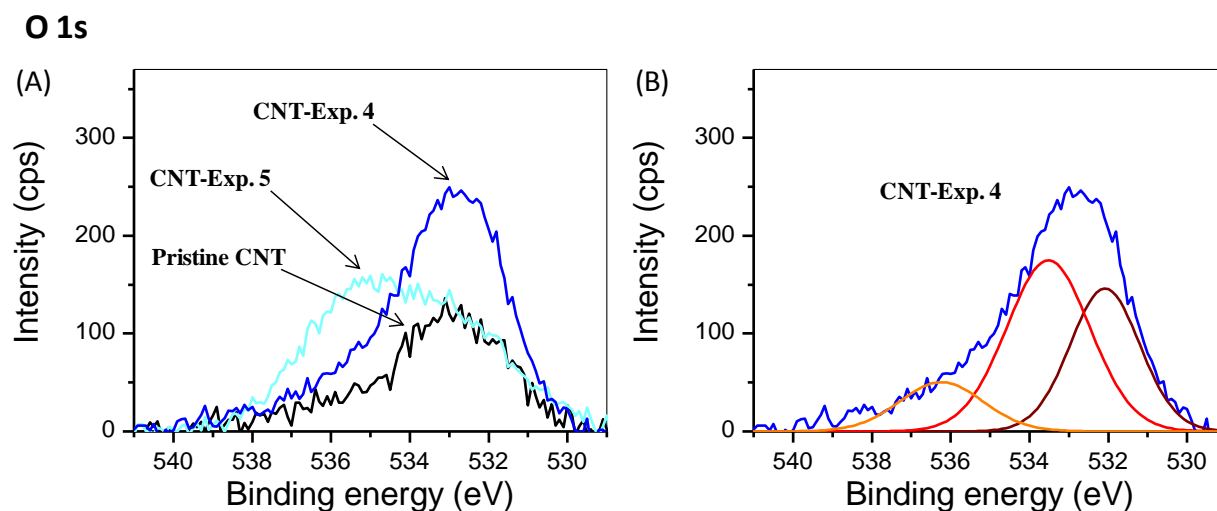


Fig. 14 - A) Background-corrected high resolution O1s core level XPS spectra for pristine CNT, CNT-Exp. 4 and CNT-Exp. 5. B) Deconvolution of the XPS spectrum for CNT-Exp. 4 into 3 components at BE  $\sim$ 532 eV,  $\sim$ 534 eV, and  $\sim$ 536 eV.

### 3.3. The solvent effect on the functionalization of CNT with MA

TGA (in air) and elemental analysis data, obtained for all the samples, was used to calculate the grafting density of MA (Table 8). As explained in detail in the supporting information, the grafting ratio of MA on the CNT was estimated from the increase of the oxygen content of the functionalized CNT (subtract-

ing the effect of the solvent) compared to the pristine CNT, according to an approach previously described in the literature [37].

**Table 8 – Grafting ratios of MA functionalized CNT-Exp.1 and CNT-Exp.4 based on TGA and elemental analysis (EA) for C and O atomic content.**

CNT-Exp. 1	TGA	18.2	1.86
	EA	16.0	1.22
	average	17.1	1.54
CNT-Exp. 4	TGA	4.1	0.41
	EA	4.4	0.45
	average	4.25	0.43

For the TGA data, the experiment performed in air atmosphere was considered comparable to the elemental analysis conditions, where combustion/pyrolysis is used. The weight loss assigned to MA functionalization of both samples and used in the calculations was recorded on the temperature interval 370 – 500 °C, between two inflection points of the TGA curve.

The XPS data, although extremely valuable to clarify the chemical transformations occurring on the CNT surface, was not used to calculate grafting densities, as the values obtained would not be comparable to the TGA and EA results. This technique identifies the atomic ratio of the elements on the CNT surface and the wt. % do not account for carbon atoms of the internal layers of the multiwall CNT used in this work.

The values collected in Table 8 reveal that comparable grafting ratios are obtained independently, from TGA and EA. A fourfold of MA is incorporated on the CNT when DMSO was used as solvent. The av-

erage values provided in Table 8 evidence a successful Diels-Alder cycloaddition, especially under these experimental conditions.

#### 4. Conclusions

The CNT surface, known to behave as a dienophile in Diels-Alder cycloadditions, can also act as a diene by reaction with an activated dienophile such as maleic anhydride. The reaction occurred in DMSO (190 °C, 24 h) and in 2-chlorotoluene (150 °C, 48 h). The extent of functionalization was higher in DMSO, according to evidence obtained by TGA, performed in air or N<sub>2</sub> atmosphere, elemental analysis and XPS analysis.

Heating the CNT in DMSO induced some chemical transformations on the external layer, namely the formation of sulfonic acids and methylthioethers, but this was not the case when the heating process was carried out in 2-chlorotoluene.

The stability of maleic anhydride in the presence of CNT was studied at room temperature in the absence of solvent. Maleic acid was the major product identified by <sup>1</sup>H NMR after 24 h in contact.

Anthracene was used as a model compound for the conjugated aromatic system and the Diels-Alder reaction with MA in DMSO was complete after 10 min. at 185 °C. The study of the experimental conditions leading to hydrolysis of the anhydride indicated that, after 24 h at room temperature and in the presence of 6.6 equivalents of HCl, only 12% of the diacid was formed. The dicarboxylic acid cyclized to the anhydride upon heating at 185 °C in DMSO and the conversion was complete after 10 min..

The potentiometric titration of the suspensions of modified CNT required the protection of the pH electrode with a dialysis tube. The results indicated that the acidity of the CNT functionalized in DMSO was due to the presence of acid groups formed during the heating process. XPS analysis identified sulfonic acids arising from sulfonation and carboxylic acids due to oxidation under the experimental conditions used (reflux in open atmosphere). The CNT functionalized in 2-chlorotoluene were not significantly modified by the solvent, but the extent of functionalization was substantially lower. These results were

supported by elemental analysis, that shows the presence of sulphur and an increase in the oxygen content for CNT modified in DMSO. When the heating process was performed in 2-chlorotoluene the oxygen content remained similar to that registered for pristine CNT. The reaction of the CNT with MA clearly reinforces the oxygen content of the surface.

The Diels-Alder cycloaddition of MA to the CNT is favored in DMSO by heating at 190 °C for 24 h, as confirmed by the grafting density calculations from TGA and elemental analysis data, that show an average of 17.1 wt. % of MA. Hydrolysis of the anhydride, that was likely to occur under the catalytic effect of the CNT, is hindered under the temperature conditions used in the experiment.

The functionalization of CNT incorporating the anhydride moiety is highly convenient, as this group behaves as a reactive and versatile reagent for coupling with different molecules through nucleophilic addition.

### **Acknowledgments**

The authors gratefully acknowledge the financial support by the Centro de Química and Instituto de Polímeros e Compósitos of the University of Minho and Fundação para a Ciência e Tecnologia through the Portuguese NMR network (RNRMN), the Project F-COMP-01-0124-FEDER-037302 (ref. FCT PEst-C/QUI/UI0686/2013) FEDER-COMPETE, Project PEst-C/CTM/LA0025/2013 (Strategic Project - LA 25-2013-2014) and also for a Post-doc grant awarded to RF Araújo (SFRH/BPD/88920/2012).

### **References**

- [1] Baughman R, Zakhidov A, Heer W. Carbon Nanotubes-the Route Toward Applications. *Science* 2002, 297: 787-797.
- [2] Schnorr J, Swager T. Emerging Applications of Carbon Nanotubes. *Chem Mater* 2011; 23: 646-657.
- [3] Georgakilas V, Tagmatarchis N, Pantarotto D, Bianco A, Briand J, Prato M. Amino acid functionalisation of water soluble carbon nanotubes. *Chem Commun* 2001: 3050-3051.

- [4] Banerjee S, Wong S. Rational Sidewall Functionalization and Purification of Single-Walled Carbon Nanotubes by Solution-Phase Ozonolysis. *Phy Chem B* 2002; 106: 12144-12151.
- [5] Lau C, Cervini E, Clarke E, Markovic E, Matisons J, Hawkins E, et al. The effect of functionalization on structure and electrical conductivity of multi-walled carbon nanotubes. *J. Nanopar. Res.* 2008; 10: 77-88.
- [6] Hu H, Zhao B, Hamon MA, Kamaras K. Sidewall Functionalization of Single-Walled Carbon Nanotubes by Addition of Dichlorocarbene. *J. Am. Chem. Soc.* 2003, 125: 14893-14900.
- [7] Holzinger M, Abraham J, Whelan P, Graupher R, Ley L, Hennrich F, et al. Functionalization of Single-Walled Carbon Nanotubes with (R-)Oxycarbonyl Nitrenes. *J. Am. Chem. Soc.* 2003, 125: 8566-8580.
- [8] Coleman KS, Bailey SR, Fogden S, Green MLH. Functionalization of Single-Walled Carbon Nanotubes via the Bingel Reaction. *J. Am. Chem. Soc.* 2003, 125: 8722-8723.
- [9] Alvaro M, Atienzar P, Cruz P, Delgado JL, Garcia H, Langa F. Sidewall Functionalization of Single-Walled Carbon Nanotubes with Nitrile Imines. Electron Transfer from the Substituent to the Carbon Nanotube. *J. Phy. Chem. B* 2004, 108: 12691- 12697.
- [10] Cui J, Burghard M, Kern K. Reversible Sidewall Osmylation of Individual Carbon Nanotubes. *Nano Lett.* 2003, 3: 613-615.
- [11] Ogrin D, Chattopadhyay J, Sadana AK, Billups WE, Barron AR. Epoxidation and Deoxygenation of Single-Walled Carbon Nanotubes: Quantification of Epoxide Defects. *J. Am. Chem. Soc.* 2006, 128: 11322-11323.
- [12] Delgado JL, Cruz P, Langa F, Urbina A, Casado J, Juan TLN. Microwave-assisted sidewall functionalization of single-wall carbon nanotubes by Diels–Alder cycloaddition. *Chem. Commun.* 2004: 1734-1735.
- [13] Sakellariou G, Ji H, Mays HW, Hadjichristidis N, Baskaran D. Controlled Covalent Functionalization of Multiwalled Carbon Nanotubes using [4 + 2] Cycloaddition of Benzocyclobutenes. *Chem. Mater.* 2007, 19: 6370-6372.
- [14] Zhang L, Jianzhong Y, Edwards CL, Alemany LB, Khabashesku VN, Barron AR. Diels–Alder addition to fluorinated single walled carbon nanotubes. *Chem. Commun.*, 2005: 3265-3267.

- [15] Ménard-Moyon C, Dumas F, Doris E, Mioskowski C. Functionalization of Single-Wall Carbon Nanotubes by Tandem High-Pressure/Cr(CO)<sub>6</sub> Activation of Diels-Alder Cycloaddition. *J. Am. Chem. Soc.* 2006, 128: 14764-14765.
- [16] McPhail MR, Sells JA, He Z, Chusuei CC. Charging Nanowalls: Adjusting the Carbon Nanotube Isoelectric Point via Surface Functionalization. *J. Phys. Chem. C* 2009, 113:14102-14109.
- [17] Munirasu S, Albuérne J, Boschetti-de-Fierro A, Abetz V. Functionalization of Carbon Materials using the Diels-Alder Reaction. *Macromol. Rapid Commun.* 2010, 31: 574-579.
- [18] Zydziak N, Hübner C, Bruns M, Barner-Kowollik C. One-Step Functionalization of Single-Walled Carbon Nanotubes (SWCNT) with Cyclopentadienyl-Capped Macromolecules via Diels\_Alder Chemistry. *Macromolecules* 2011, 44: 3374-3380.
- [19] Semmelhack MF. *Comprehensive Organometallic Chemistry II*. Oxford: Abel, Stone, wilkinson. 1995: 979-1038.
- [20] Matsumoto K, Hamana H, Iida H. Compendium of Cycloaddition Reactions under High Pressure *Helv. Chim. Acta* 2005, 88: 2033-2234.
- [21] Gergely A, Telegdi J, Mészáros E, Pászti Z, Tárkányi G, Kármán, FH, Kálmán E. Modification of multi-walled carbon nanotubes by Diels-Alder and Sandmeyer reactions. *J. Nanosci. Nanotechnol.* 2007, 7(8): 2795-2807.
- [22] Gorgulho HF, Mesquita JP, Gonçalves F, Pereira MFR, Figueiredo JL. Characterization of the surface chemistry of carbon materials by potentiometric titrations and temperature-programmed desorption. *Carbon* 2008, 46: 1544-1555.
- [23] Haenel MW. Recent progress in coal structure research. *Fuel* 1992, 71, 1211-1223.
- [24] Concise Encyclopedia Chemistry. Jakubke, Jeschkeit. 1993: 52.
- [25] Bom D, Andrews R, Jacques D, Anthony J, Chen B, Meier MS et al. Thermogravimetric Analysis of the Oxidation of Multiwalled Carbon Nanotubes: Evidence for the Role of Defect Sites in Carbon Nanotube Chemistry. *Nano Letters* 2002, 2 (6): 615-619
- [26] Paiva MC, Simon F, Novais RM, Ferreira T, Proença MF, Xu W, et al. Controlled Functionalization of Carbon Nanotubes by a Solvent-free Multicomponent Approach. *Acs Nano* 2010, 4: 7379-7386.



- [27] Mesch W, Wittwer A. Manufacture of succinic anhydride. US patent 3957830, 1976.
- [28] Wang DA, Chen BL, Ji J, Feng LX. Selective adsorption of serum albumin on biomedical polyurethanes modified by a poly(ethylene oxide) coupling-polymer with cibacron blue (F3G-A) endgroups. *Bioconjug Chem.* 2002, 4:792-803.
- [29] Crisci AJ, Tucker MH, Lee M, Jang SG, Dumesic JA, Scott SL. Acid-Functionalized SBA-15-Type Silica Catalysts for Carbohydrate Dehydration. *ACS Catal.* 2011, 1: 719-728.
- [30] Bulletin # 101, Dimethyl Sulfoxide (DMSO) Physical Properties, Gaylord Chemical Corporation **2005**: 19-20.
- [31] W. E. Tenhaeff. "Synthesis of reactive and stimuli-responsive polymer thin films by initiated chemical vapour deposition and their sensor applications. Ph. D Thesis 2009.
- [32] G. Mishra, S. L. McArthur. Plasma Polymerisation of Maleic Anhydride: Just what are the right deposition conditions? *Langmuir* 2010, 26(12): 9645–9658.
- [33] Heistner K, Frey S, Ulman A, Grunze M, Zharnikov M. Irradiation sensitivity of self-assembled monolayers with an introduced "weak link". *Langmuir* 2004, 20: 1222-1227.
- [34] Wang DA, Chen BL, Ji J, Feng LX. Selective adsorption of serum albumin on biomedical polyurethanes modified by a poly(ethylene oxide) coupling-polymer with cibacron blue (F3G-A) endgroups. *Bioconjug Chem.* 2002, 13(4):792-803.]
- [35] Pietrzak R, Grzybek T, Wachowska H. XPS study of pyrite-free coals subjected to different oxidizing agents. *Fuel* 2007, 86: 2616-2624.
- [36] Kozłowski M. XPS study of reductively and non-reductively modified coals. *Fuel* 2004, 83: 259-265.
- [37] Zydział N, Hübner C, Bruns M, Barner-Kowollik C. One-Step Functionalization of Single-Walled Carbon Nanotubes (SWCNTs) with Cyclopentadienyl-Capped Macromolecules via Diels-Alder Chemistry. *Macromolecules* 2011, 44: 3374-3380.