

REACTIVE CARBON NANOTUBES FOR STRONG INTERFACES IN POLYMER COMPOSITES

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Introduction

Chemical modification of the outer graphene layer of carbon nanotubes is an approach increasingly used to overcome the problem of interfacial bonding with different materials. The effect of functionalization of CNT under different conditions, using the 1,3-dipolar cycloaddition reaction, was studied by X-ray photoelectron spectroscopy. The formation of pyrrolidine groups on the CNT surface was observed, and the reactivity towards four different polymers was studied. CNT surface modification after chemical functionalization was evidenced by Scanning Tunneling Microscopy (STM). After CNT reaction with polycarbonate, polymer coated CNTs were imaged by STM. Composites evidenced excellent CNT/polymer interface.

Experimental

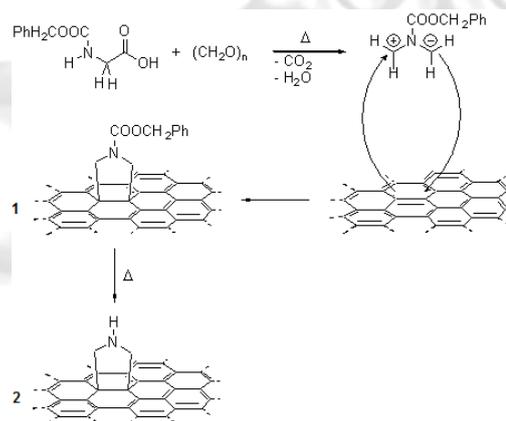
The carbon nanotubes used in this study were NC 7000 from Nanocyl. The chemical functionalization was performed under solvent-free conditions, as described elsewhere [1]. The amino acid used was *N*-benzyloxycarbonylglycine (*Z*-gly-OH) 99%, from Aldrich, and paraformaldehyde, reagent grade, from Sigma. An ethanolic suspension of *Z*-gly-OH, paraformaldehyde (1:5 molar ratio) and CNT was prepared. The suspension was gently heated until the solvent was completely removed. The solid mixture was heated at different temperatures and times in a round-bottom flask. The reaction temperatures were 180, 210, 230 and 250 °C. The resulting nanotubes were washed, filtered and dried.

Thermogravimetric analysis was performed on a Modulated TGA Q500 from TA Instruments. The samples were heated at 10 °C/min under a constant flow of N₂, from room temperature to 800 °C. STM experiments were performed in a UHV chamber (base pressure 3×10⁻¹⁰ Torr) equipped with the variable-temperature, fast-scanning Aarhus STM. The STM images were acquired in the constant current mode. Typical tunneling parameters were 1000-2000 mV and 0.8-1.2 nA for the bias voltage and the tunneling current, respectively, when imaging at the nanometer scale. The Pt/Ir tip was produced by chemical etching. All XPS studies were

carried out on an AXIS ULTRA photoelectron spectrometer (KRATOS ANALYTICAL, Manchester, England). The spectrometer was equipped with a monochromatic Al K α ($h\nu = 1486.6$ eV) X-ray source of 300 W at 15 kV. The kinetic energy of photoelectrons was determined with a hemispheric analyzer set to pass energy of 160 eV for wide-scan spectra and 20 eV for high-resolution spectra, respectively.

Results and Discussion

The surface modification of multiwall carbon nanotubes (CNT) by the 1,3-dipolar cycloaddition of azomethine ylides is a widely used reaction that yields a pyrrolidine cycloadduct at the CNT surface [1]. The approach presented in this work was based on the solvent-free reaction of an α -amino acid, *Z*-gly-OH with paraformaldehyde [2]. Heating the solid reaction mixture generates formaldehyde, by thermal decomposition of paraformaldehyde. *Z*-gly-OH melts in the temperature range of paraformaldehyde decomposition. The 1,3 dipole formed may react with the CNT surface through cycloaddition to originate the tertiary cycloamine **1**. Increasing the temperature leads to thermal cleavage of the protecting group of the original amine leading to the formation of the pyrrolidine **2** in Scheme 1, as reported in previous studies [2]. The product ratio obtained (compound **1** and **2**) varies with the reaction conditions.



Scheme 1. Functionalization of the CNT surface by the 1,3-dipolar cycloaddition reaction.

The pyrrolidine formed at the CNT surface is a reactive group that may react further with other molecules [3]. The functionalized CNT were analysed by TGA and XPS. The quantitative determination of the relative number of nitrogen and oxygen atoms bonded to the CNT surface by XPS provided evidence for the formation of products **1** and **2** and clarified the effect of reaction temperature and time on the pyrrolidine yield.

The nitrogen containing functional groups bonded to the CNT were analyzed by deconvolution of the N1s spectra. All the N1s spectra showed the presence of two different nitrogen containing chemical functions, with binding energies centered near 399 and 401 eV, as depicted in Figure 1B. The lower binding energy component of N1s was identified as the cyclic

amine (pyrrolidine) group **2**. The C1s and N1s spectra of CNT functionalized at 250 °C are presented in Figure 1A and B.

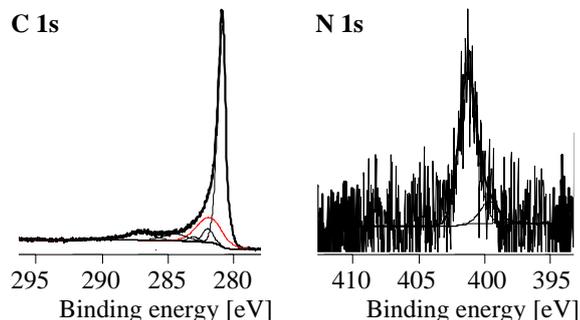


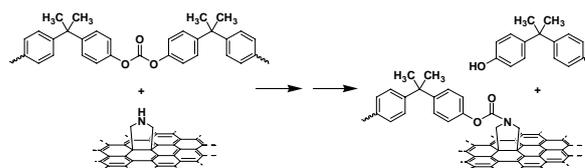
Fig. 1 C1s and N1s spectra of CNT functionalized at 250 °C.

The C 1s spectra of all functionalized CNT presented a similar shape, characterized by a main component peak and a strong tailing to the higher binding energy side, with two main peaks at binding energies 285.7 eV and 286.8–287.1 eV respectively. TGA performed under inert atmosphere provided the weight of organic groups bonded to the CNT surface, presented in Table 1. Table 1 also reports the XPS results for the atomic concentration of N and O formed at the CNT surface under the reaction conditions studied, measured on the wide scan spectra. The XPS data may be used to estimate the weight loss, considering that the organic groups attached to the CNT surface are mainly compounds **1** and **2**, the later formed by thermal decomposition of the former. Within a reasonable approximation, the weight loss estimated from the XPS N and O atom concentration should approach the weight loss measured by TGA, under inert atmosphere. Table 1 presents the experimental results obtained for TGA weight loss and the corresponding estimate from the XPS results.

Table 1. XPS N and O atomic ratio and weight loss results measured by TGA and estimated from the XPS results.

Reaction temp. (°C)	Reaction time (h)	N:C	(O:C) _{org}	w _{TGA} (%)	w _{XPS} (%)
Non-functionalized MWNT		-	0.0035	1.6 ± 0.7	0.8
180	1	0.021	0.0330	19.5 ± 2	22.9
	3	0.016	0.0350	20.4 ± 2	22.2
	6	0.018	0.0375	18.5 ± 1	24.3
210	2	0.020	0.0470	25.8 ± 2	30.3
	7	0.028	0.0235	22.0 ± 2	19.5
230	14	0.020	0.0140	20.7 ± 2	11.7
	3	0.036	0.0235	11.1 ± 1	22.2
	6	0.027	0.0290	21.2 ± 4	22.1
	9	0.028	0.0180	13.7 ± 4	16.6
250	12	0.028	0.0210	13.4 ± 2	18.2
	3	0.020	0.0160	17 ± 2	12.7
	5	0.019	0.0100	14 ± 2	9.2
	7	0.022	0.0100	13 ± 2	10.2

The XPS results showed that, on the lower reaction temperature range the main product formed was **1**; as the temperature increased the concentration of the reactive **2** increased; at 230 °C and above the concentration of **2** dominated even at short reaction times. The reactivity towards different polymers was studied by TGA and XPS. The CNT surface modification after chemical functionalization and reaction with polycarbonate (Scheme 2) was imaged by STM. The polymer coated CNT, showing larger diameter than the original CNT (\varnothing before reaction \approx 10 nm) exhibits a coating, as shown in Fig. 2. Composites of PC/CNT were prepared and the CNT dispersion and interface with PC were studied.



Scheme 2. Proposed reaction between the pyrrolidine at the CNT surface and the carbonate group in PC.

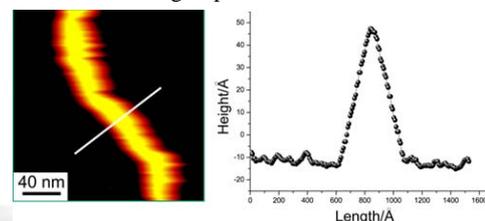


Fig. 2 Ultra high vacuum STM image of a functionalized CNT after reaction with PC in solution

Conclusions

The 1,3-dipolar cycloaddition of azomethine ylides to CNT using Z-gly-OH and formaldehyde was carried out at 180, 210, 230 and 250 °C and the products formed along the reaction length were analysed.

The reaction yield was analysed by TGA and XPS. XPS provided evidence for the formation of a tertiary cyclic amine (**1**) and a pyrrolidine (**2**). The concentration of the two reaction products varied with temperature. At the lower temperature tested the main product formed was the tertiary amine, while at the higher reaction temperature the major product formed was the reactive pyrrolidine functional group.

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