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Moulay-Rachid Babaa, Jean-Louis Bantignies, Laurent Alvarez, Philippe Parent, François Le Normand, et al.. NEXAFS study of multi-walled carbon nanotubes functionalization with sulfonated poly(ether ether ketone) chains. *Journal of Nanoscience and Nanotechnology*, 2007, 7 (10), pp.3463-3467. 10.1166/jnn.2007.816 . hal-00212083

HAL Id: hal-00212083

<https://hal.science/hal-00212083>

Submitted on 4 Sep 2024

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NEXAFS Study of Multi-Walled Carbon Nanotubes Functionalization with Sulfonated Poly(ether ether ketone) Chains

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Functionalization of multi-walled carbon nanotubes (MWNTs) surface by sulfonated poly (ether ether ketone) SPEEK chains using a direct attachment reaction was investigated. A two step method was performed. MWNTs were oxidized by a nitric acid treatment to generate carboxyl groups on their surface. The grafting reaction of sulfonated groups of SPEEK with carboxyl groups present on the surface of oxidized MWNTs readily proceeds by using hexane diamine as an interlinking molecule. Transmission electron microscopy (TEM) shows that tubes are wrapped by polymer chains. Near edge X-ray absorption fine structure spectroscopy (NEXAFS) at the C K-edge, O K-edge, and N K-edge and X-ray photoelectron spectroscopy (XPS) were used to give evidence of covalent functionalization of MWNTs by SPEEK macromolecules.

Keywords: NEXAFS, Nanotube, Functionalization.

1. INTRODUCTION

Carbon nanotubes (NTs) exhibit extraordinary mechanical^{1,2} and electronic properties.³⁻⁴ Since their discovery in 1991, these materials have attracted much interest for their potential applications in various fields such as composites⁵⁻⁷ and nano-electronics.⁸ However, processing of NTs has been difficult due to their insolubility in common solvents. As a consequence they tend to exist as entangled agglomerates. Considerable research efforts have been focused on the chemical modification of NT surfaces which can provide not only a facility for manipulation by improving the solubility in both organic and aqueous solvent, but also which gives the possibility to control the nature of binding between NTs and adsorbed molecules.⁹ Functionalization of NTs gives a new approach to develop superior composite materials with high mechanical properties. It enables interactions between polymer matrix and NTs to be controlled by using different organic groups,^{10,11} attached to the nanotubes and then facilitate the design of NTs-reinforced composites materials. Covalent attachment

of NTs to polymer chains can improve both the ability to disperse the nanotubes homogeneously throughout the matrix and load transfer from the matrix to nanotubes. The grafting of functional polymers on nanotubes can be a good way to achieve this aim. NEXAFS recently proves to be quite pertinent in monitoring the different steps of carbon nanotube functionalization as it is a local, chemically selective probe and different adsorption and functionalized states can be distinguished.¹²

The functionalization of the pure nanotubes is studied here using NEXAFS at the C K-edge, O K-edge, and N K-edge, respectively. We give evidence of the functionalization of the tube surface with the different molecules involved in the functionalization reactions.

2. EXPERIMENTAL DETAILS

2.1. Materials

Multi-walled carbon nanotubes (MWNTs, CCVD method) were purchased from Nanocyl. The diameter distribution is ranged from 4 nm to 15 nm. Commercially available Poly(ether ether ketone) (PEEK) was a Vitrex®

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PEEK 150 PF kindly provided by Victrex. All the following materials were obtained from Aldrich and used as received: Dimethylformamid (DMF, 99%), 1, 6-hexane diamine (HDA, 99%), N,N'-dicyclohexylcarbodiimide (DCC, 99%), sulphuric acid (H₂SO₄, 95–98%) and nitric acid (HNO₃, 70%).

2.2. Instruments

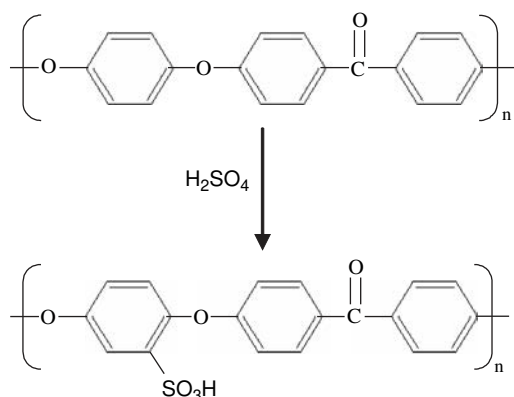
TEM analyses were conducted on a 120 kV JEOL 1200 EX II analytical electron microscope. The nanotubes were dispersed in absolute ethanol before preparing the grids for TEM imaging.

The NEXAFS experiments were performed at the Bear¹⁷ beamline of the Elettra synchrotron radiation facility (Trieste, Italy). The spectral resolving power ($E/\Delta E$) of incident photons at 400 eV was respectively 800 and 4000 at normal and high resolution, respectively. The X-ray spot area was 0.01 mm². Spectra were recorded in the total electron yield mode in an ultrahigh vacuum chamber. The solid nanotube powder was pressed onto indium metal for mounting on the sample holder. The samples were outgased for 3–4 hours at around 150 °C before the recordings.

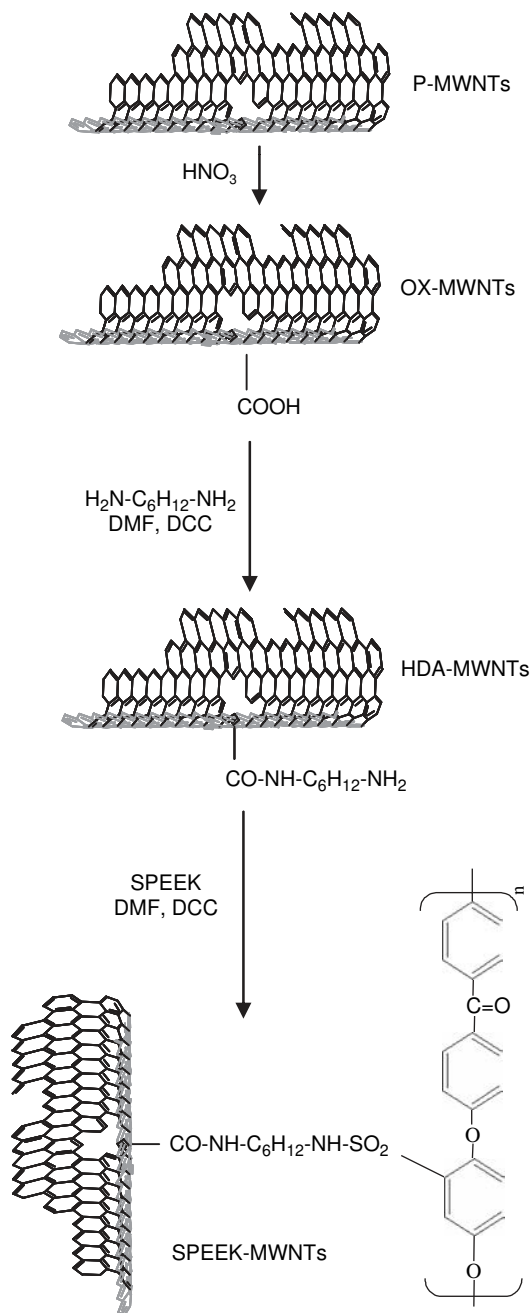
XPS measurements were recorded on a VSW spectrometer equipped with a 150 mm electron analyzer using a channelplate detection mode. A monochromatic Al K α radiation source provided a photon beam at 1486.6 eV. The analyzer was operated in the fixed analyzer transmission mode at a constant pass energy of 44 eV. The experimental resolution including the source and the analyzer was 0.85 eV.

2.3. Functionalization of MWNTs with SPEEK Chains

The synthesis of sulfonated PEEK (SPEEK) was carried out using H₂SO₄ treatment according to the literature.¹³ Typically 20 g of PEEK was dried in a vacuum oven at 100 °C and then dissolved in 500 ml of concentrated sulfuric acid (H₂SO₄, 98%) under vigorous stirring. The sulfonation degree (DS) in this paper is about 70%. The DS



Scheme 1. Schematic illustration of the sulfonation of PEEK.



Scheme 2. Schematic presentation of functionalization reactions.

was estimated by titration according to the technique described elsewhere.¹³ The structure of PEEK and SPEEK are shown in Scheme 1.

Grafting reaction was carried out in two steps. First pristine MWNTs (P-MWCNTs) were oxidized using HNO₃ treatment. Such treatment is known to eliminate metallic particles issued from the synthesis procedure but also to generate functional groups in the surface, particularly carboxylic groups.¹⁴ Secondly, oxidized MWNTs (OX-MWNTs) were dispersed in DMF by ultrasonication for 2 hours. Hexane diamine (HDA) and DCC were simultaneously added. The mixture was heated at 40 °C and

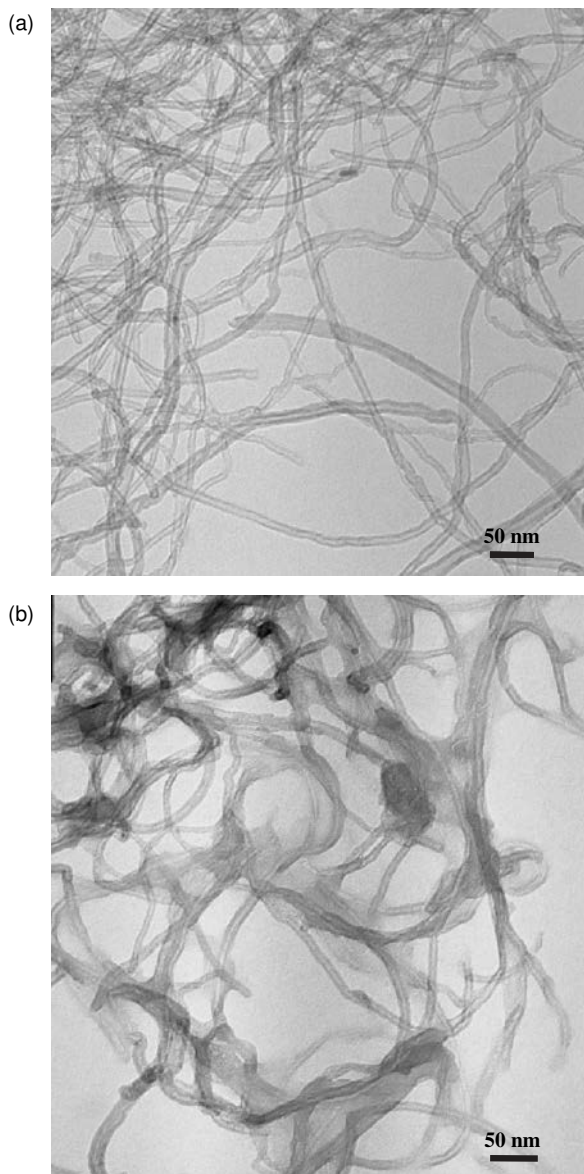


Fig. 1. TEM images of (a) pristine MWNTs and (b) SPEEK-MWCNTs.

stirred for 24 h. After washing and filtration, functionalized MWNTs with HDA (HDA-MWNTs) was stored in the oven at 100 °C during 24 hours. Grafting reaction of SPEEK was carried out in the same conditions. The reaction take place between amine functions of HDA-MWNTs and sulfonate functions presents on SPEEK. The different steps are represented schematically in Scheme 2. SPEEK functionalized MWNTs are designated by SPEEK-MWNTs.

Table I. Relative intensity of the resonances in the 288–292 eV energy range.

Contribution	Energy	Assignment	P-MWCNT	OX-MWCNT	HAD-MWCNT	SPEEK-MWCNT
A	287.5	(Bz) ₂ -C=O π^*	0.164	0.157	0.146	0.191
B	289.0	C=O π^*	0.078	0.107	0.137	0.313
C	290.5	1s $\rightarrow \sigma^*$ C-O	0.193	0.221	0.265	0.390

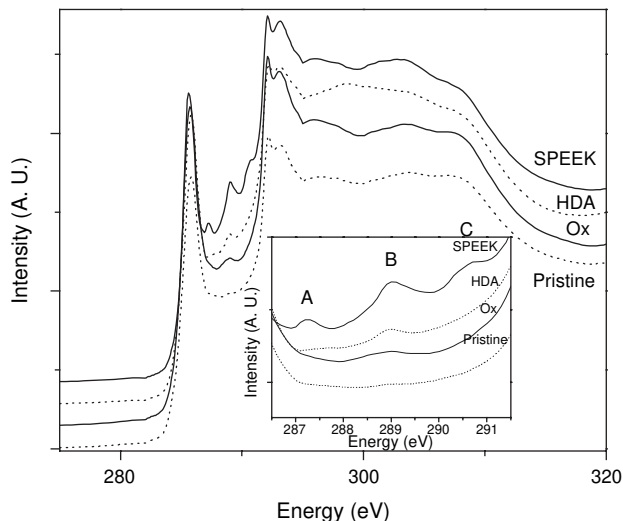


Fig. 2. C K-edge NEXAFS spectrum of MWNTs, OX-MWNTs, HAD-MWNTs, and SPEEK-MWNTs.

3. RESULTS AND DISCUSSION

The structure of the samples before and after functionalization is probed with TEM (Fig. 1). The pristine P-MWNTs exhibit a typical structure (Fig. 1(a)). No amorphous carbon impurities are detected. After functionalization (Fig. 1(b)), the tubes (SPEEK-MWCNTs) are wrapped by a layer of polymer.

NEXAFS spectroscopy is then used to investigate the nature of the interactions between functional groups and nanotubes at each step of the process. Figure 2 shows the C K-edge spectral region in MWNTs before and after the successive treatments. The spectra of pristine P-MWNTs is dominated by a sharp C-C 1s $\rightarrow \pi^*$ transition at 286 eV. The excitations between 292 and 315 eV are associated with overlapped 1s $\rightarrow \sigma^*$ transitions. The domain between 287 and 291 eV is particularly interesting in our case since it evidences the chemical modification of NTs by functionalization.¹⁴ We can notice that in the case of OX-MWNTs, a resonance B around 289 eV is exhibited (see inset of Fig. 2). This transition is still present after functionalization with HDA. Specific sensitivity to oxygenated functionalities attached at the surface of the nanotubes were reported; the peak at approximately 289 eV corresponds to C=O π^* resonance¹⁴ in NT-(OH-C=O) or NT*-(OH-C=O) (C* corresponds to the photoexcited carbon atom). In our samples, we assign this peak to the C1s $\rightarrow \pi^*$ transitions of the carbonyl groups. In the case of SPEEK-MWNTs sample, two news π^* resonances occur

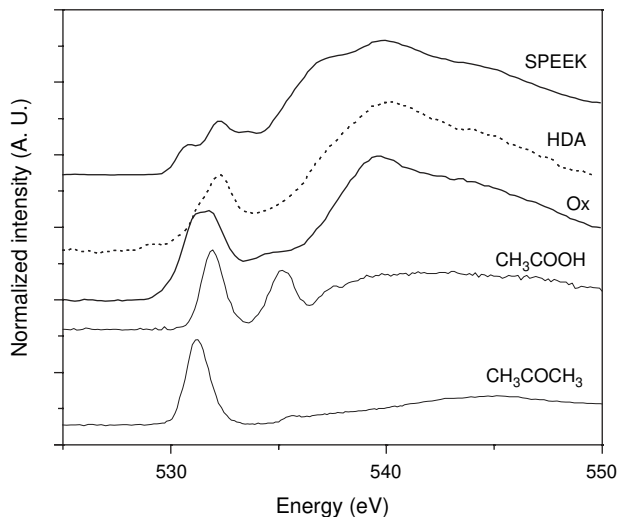


Fig. 3. O K-edge NEXAFS spectra of OX-MWNTs, HAD-MWNTs and SPEEK-MWNTs. Model compounds CH_3COCH_3 and CH_3COOH are also given for comparison.

at 287.5 eV (noted A) and 290.5 eV (noted C). They sign the presence of the SPEEK molecule. The first resonance corresponds to carbonyl linked to benzenic ring and the second one is around the position of the $1s \rightarrow \sigma^* \text{C-O}$ excitation.¹⁴ The absorption line within the domain 280–292.5 eV has been fitted using a set of symmetrical and asymmetrical Voigt functions¹⁵ and the intensities of the absorption line of each of these resonances have been reported in Table I. The reported values are relative to the intensity of the main $1s \rightarrow \pi^*$ resonance at 285.6 eV. Values are only indicative as the threshold energy due to the transition towards continuum states is not known. Nevertheless it could be seen that the intensity of the carbonyl resonance increases as early as the oxidation step whereas the C resonances slightly increase at each subsequent step, and abruptly rises at the polymerisation

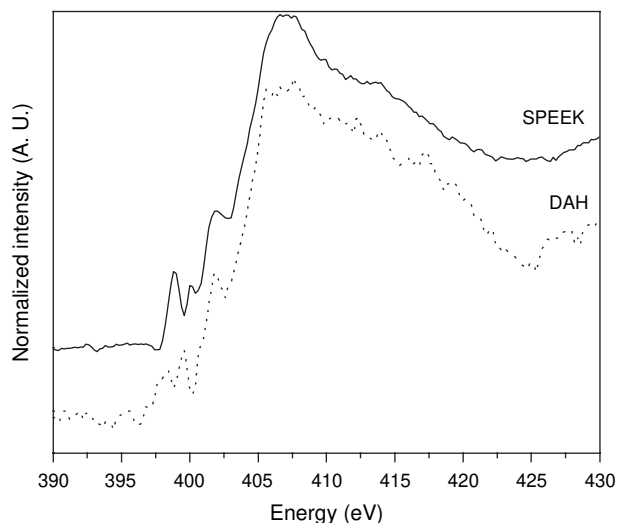


Fig. 4. N K-edge NEXAFS spectra of HAD-MWNTs and SPEEK-MWNTs.

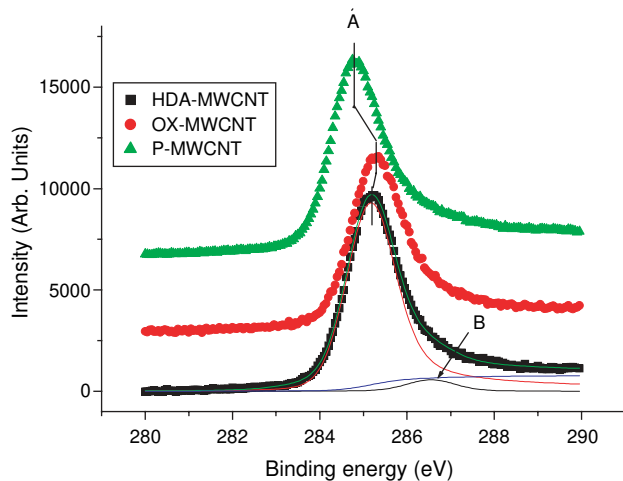


Fig. 5. XPS C 1s line of the functionalized MW-CNTs.

step. By contrast the A resonance increases only at the polymerisation step, as expected.

Figure 3 shows the O K-edge spectra for OX-MWNTs, HDA-MWNTs and SPEEK-MWNTs, respectively. In addition, spectra of CH_3COOH and CH_3COCH_3 model molecules are also displayed. The spectra confirm the presence of oxygen containing functional groups at each step. After oxidation, the strong sharp π^* excitation around 532 eV corresponds to carbonyl groups C=O .¹² By comparison with the O K-edge fingerprints of the carboxylic acid CH_3COOH and the corresponding ketone, we are able to assign the excitation centered at 534.8 eV in OX-MWNTs to the presence of the hydroxyl groups. The broad excitations between 538 and 550 eV are assigned to $1s \rightarrow \sigma^*$ resonances.¹⁴ After functionalization with HDA, the disappearance of the hydroxyl fingerprint (peak at 534.8 eV) signs without ambiguity the attachment of HDA at the surface of the tubes. By contrast, as expected (see Scheme 2) the $\pi^* \text{C=O}$ excitation remains. After secondary functionalization with SPEEK, new π^* resonances are exhibited at more or less 1 eV from the main C=O resonance, probably corresponding to specific oxygen of the SPEEK molecule (C=O , S=O).

The N–K NEXAFS spectra of HDA-MWNTs and SPEEK-MWNTs are given in the Figure 4. The N K edge absorption signal was negligible for the P-MWCNTs and OX-MWCNT samples, respectively. Weak $1s \rightarrow \pi^*$ resonances are observed at 399 eV, 400.1 eV, and 402 eV whereas between 403 eV and 425 eV broad and overlapped $1s \rightarrow \sigma^*$ resonances are exhibited, as expected from the main bz-NH-C=O functionality (Scheme 2). The weak

Table II. XPS results on functionalized MWNTs.

Contribution	P-MWCNT	OX-MWCNT	HAD-MWCNT
C1s (A)	285.2	285.3	284.9
C1s (B)	286.5	286.6	286.1
N	—	—	400.6
N/C	~0	~0	0.11

π^* excitations are probably due to impurities and indicate specific chemical interactions between the nanotube surface and the amide groups.

Some complementary information could be extracted from XPS investigations and the results are shown in Figure 5 and summarized in Table II. The C 1s line exhibits two contributions. The main one occurs around 285.0 eV and is attributed to graphitic C–C, whereas the small contribution B at higher binding energy can be attributed either to the C–O or to the C–N environments. A significant shift of the main contribution by 0.5 eV can be observed. The N1s main line at 400.6 eV is in agreement with a N–C environment in the sp^2 hybridization state of nitrogen.¹⁶

4. CONCLUSION

In conclusion, a functionalization method was successfully applied to graft a SPEEK chain to the surface of MWNTs. TEM observations, NEXAFS and XPS analyses give evidence of functionalization of macromolecules to nanotubes. This approach can be used to facilitate incorporation of nanotubes in polymer matrixes, particularly PEEK. Furthermore, this work demonstrates that NEXAFS spectroscopy is a particularly useful and pertinent technique to characterise the surface chemistry of carbon nanotubes.

Acknowledgments: Th European contract “CANAPE” framework of GDRE-nano.

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