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Thermal treatment of the carbon nanotubes and their functionalization with styrene

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ABSTRACT

In this work we studied the functionalization of commercially available multiwalled carbon nanotubes (MWCNT) (Nanocyl 3100) with polystyrene by the method so called "*grafting from*". The nanotubes were used as received and oxidized in air at 400 °C. The functionalization was started using thionyl chloride under reflux, followed by a reaction with ethylene glycol which allowed the inclusion of hydroxyl groups. The reaction of those with 2-chloropropionyl chloride led to the generation of the polymerization initiator. Last, the radical polymerization of the functionalized nanotubes, using styrene as the monomer, led to new materials which were studied with thermogravimetric analysis (TGA), Fourier transform infrared (FTIR) spectroscopy, transmission electron microscopy (TEM) and ultraviolet–visible (UV–vis) spectroscopy.

1. Introduction

Since their discovery, carbon nanotubes (CNT) are proposed as reinforcement in polymer composites [1,2]. However, their application is limited by their tendency to agglomerate and poor adhesion with the polymer matrix. Their functionalization with a polymer compatible with the matrix is supposed to resolve both problems. The atom transfer radical polymerization (ATRP) method [3] allows to grow polymer chains from the functionalized nanotubes in a process called "*grafting from*", forming "*polymer brushes*" [4]. Results of CNT functionalized with styrene using this method are reported elsewhere [5,6]. Prior to the functionalization stage, the nanotubes usually are chemically treated with a mixture of concentrated nitric and sulfuric acid, so as to increase the number of carboxylic groups. Unfortunately, the reaction goes easily out of control and the CNT result damaged during the treatment.

In this work, we present the functionalization with polystyrene of commercially available CNT subjected to a previous light thermal oxidative treatment at 400 °C.

2. Experimental

We used multiwalled carbon nanotubes (MWCNT) from Nanocyl (NC3100), fuming chlorhidric acid 37% (Merck), thionyl chloride (Aldrich), ethylene glycol (Merck), chloropropionic chloride (Aldrich), styrene monomer (Merck) cupric bromide (Sigma), N, N, N′, N′, N″- pentamethyldiethylenetriamine (Sigma) and dioxane (Sintorgan).

The MWCNT were divided in two batches: one was used as received and the other was first subjected to a thermal treatment at 400 °C.

Thermal treatment of MWCNT was made in air inside a tubular oven. A heating slope of 35 °C/min was applied until 400 °C. This temperature was maintained for 30 min and then MWCNT were left inside the oven to cool down to room temperature. The nanotubes so treated were dried in vacuum at 120 °C for 3 h.

The polystyrene carbon nanotubes functionalization was made according to the report by Kong et al. [5]. The scheme of the complete process can be seen in Fig. 1.

The polymerized nanotubes, once dried, were studied by thermogravimetric analysis (TGA) in air and nitrogen (SDTA 851 Mettler Toledo), Fourier transform infrared (FTIR) spectroscopy (Nicolet 510P), transmission electron microscopy (TEM) (EM 301 Philips) and ultraviolet–visible (UV–vis) spectroscopy (HP 8453).

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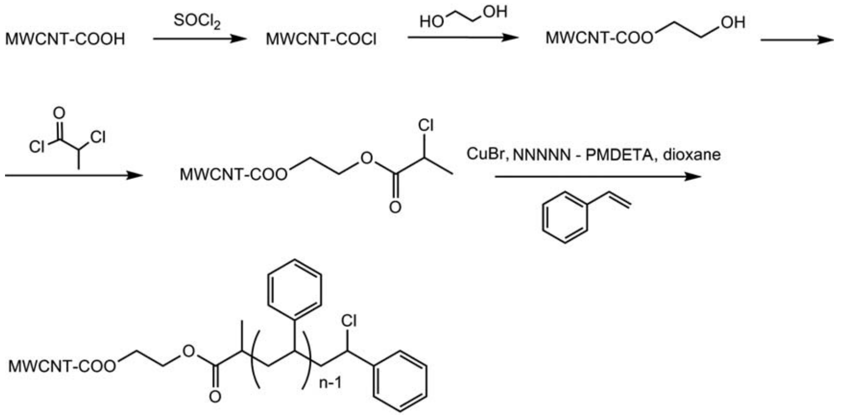

Fig. 1. Scheme of the functionalization process with PS.

Table 1
Designation of the samples.

Name	Character
P-MWCNT	Pristine nanotubes
T-MWCNT	Thermal treated nanotubes
PS-P-MWCNT	P-MWCNT functionalized with PS
PS-T-MWCNT	T-MWCNT functionalized with PS

Before FTIR and TGA studies the samples were dried at 120 °C in a vacuum oven for 3 h and then left to cool down under vacuum.

The names assigned to each type of sample can be seen in Table 1.

For TEM observations the samples were diluted in an appropriate solvent: ethanol for the commercial nanotubes and toluene for the functionalized nanotubes. Each solution was sonicated for 10 min and a drop of this solution was put on the grid of TEM.

3. Results and discussion

Fig. 2a and b shows the thermal degradation of all samples, in air or nitrogen atmosphere, respectively. In both cases the gas flux was 40 mL/min and the heating rate of 3 °C/min.

As can be seen in Fig. 2a, the pristine and thermal treated MWCNT remained without any appreciable mass loss until 500 °C while the PS functionalized were degraded in more than 80 wt% for temperatures between 200 and 450 °C. These results could lead to the erroneous idea that the amount of polystyrene added to the nanotubes is enormous. However, the nitrogen degradation (Fig. 2b) shows an organic mass loss of about 10 wt% for the PS-T-MWCNT and 25 wt% for the PS-P-MWCNT.

In nitrogen flux, the PS-P-MWCNT sample lost firstly about 20 wt% of its mass for temperatures in the range of 200–280 °C, that can be attributed to the degradation of ethylene glycol (boiling point at 196 °C) as it was physically attached to the CNT. A second smoother degradation was observed for temperatures between 280 and 480 °C, this can be associated to the polystyrene degradation [6] but the small mass loss (5 wt%) left doubt about the mechanism of degradation. While, the PS-T-MWCNT sample has only a smooth mass loss of 10 wt% in weight from 200 up to 480 °C, indicating a successful functionalization with polystyrene according to the scheme in Fig. 1.

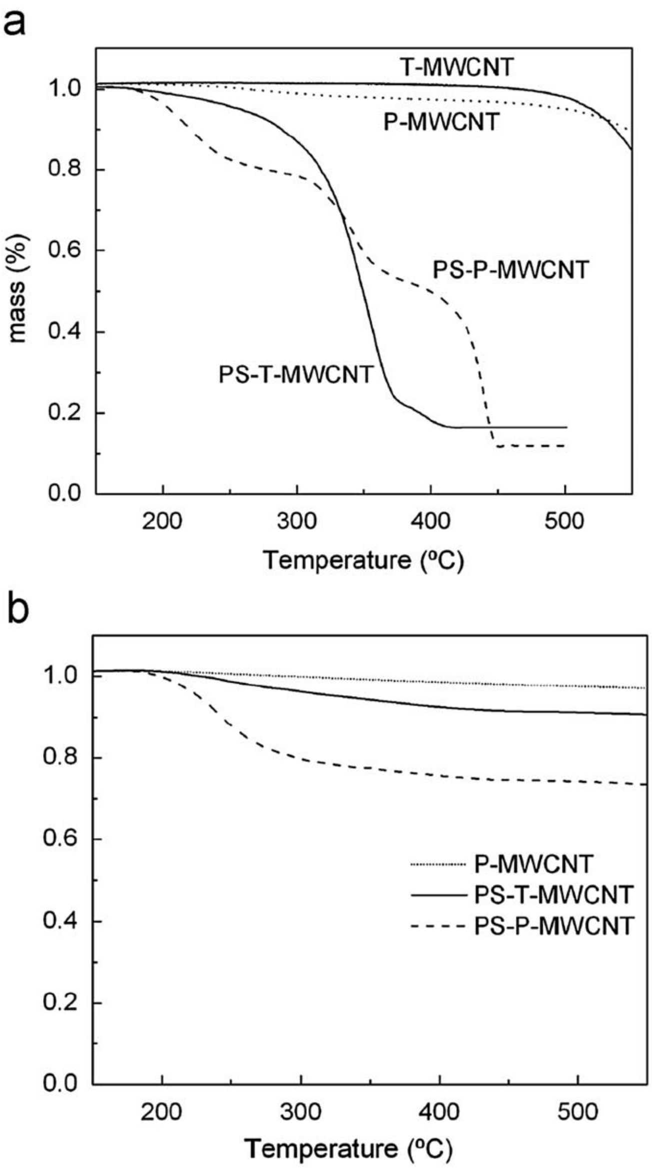

Fig. 2. Thermograms of the different samples: (a) air flux and (b) nitrogen flux.

In air flux, the PS-T-MWCNT started to degrade slowly at 200 °C due to the scission of the ethylene glycol chains covalently attached to the initiator of PS polymerization [6,7]. After that a sudden degradation, commonly associated to a homogeneous material, occurred around 350 °C. This degradation can be associated to two parallel process, polystyrene degradation [7] and CNT degradation by oxidation of the reactivate terminations that were generated during the ethylene glycol chain scission.

On the other hand, the air thermogram of the PS-P-MWCNT sample shows three net degradation processes. The first two processes, at around 220 and 350 °C, are associated, respectively, to the degradations of ethylene glycol and polystyrene as they were physically attached to the CNT. The third degradation process at 450 °C can be related to CNT degradation by oxidation of the reactive terminations remaining after the different polymerization treatments. We believe that the roughness of amorphous carbon formations made possible the physical attachment of polymer chains onto CNT wall.

Air and nitrogen thermograms are coincident and conclusive about the CNT degradation by oxidation of the reactive terminations generated by the ethylene glycol chain scission showing the successful growth of PS chains from the functionalized nanotubes.

FTIR spectra of functionalized carbon nanotubes can be seen in Fig. 3. Note that both spectra show a strong presence of the peaks at 2850 and 2920 $\mathrm{cm^{-1}}$ and a small shoulder at 2950 $\mathrm{cm^{-1}}$ associated to the C–H stretching [5,7] of polystyrene. Also there is a small peak at 1630 $\mathrm{cm^{-1}}$ for both samples, associated to the C=C stretching. For PS-P-MWCNT sample, two small peaks can be seen at 700 and 750 $\mathrm{cm^{-1}}$, associated to monosubstituted aromatic rings, typical for PS [8], while for PS-T-MWCNT sample the same peaks have a 20–30 $\mathrm{cm^{-1}}$ shift to higher wavenumbers. Another very strong characteristic peak for PS is the one at 1451 $\mathrm{cm^{-1}}$, associated to the stretching vibrations of carbon in the aromatic ring [8].

The peak at 1730 $\mathrm{cm^{-1}}$ is commonly associated to the stretching of C=O bonds, these bonds can belong to a carboxylic group in the CNT wall [9] or to a chloropropionic chloride group covalently attached to the polystyrene and CNT wall. The sharpness of this peak in the PS-P-MWCNT sample would indicate the oscillation of this functionality in the carboxylic groups. In the case of PS-T-MWCNT sample, the broadness of this peak would be associated to the oscillation of the same functionality in the chloropropionic chloride group [10].

For the PS-P-MWCNT sample, a strong band around 3450 $\mathrm{cm^{-1}}$ can be seen, associated to the presence of –OH groups [5,8], which confirms the presence of glycol in agreement with the degradation seen around 200 °C in the thermogravimetric plot.

Fig. 4 shows TEM micrographs of the PS-functionalized CNT. Polymer covered homogenously the PS-T-MWCNT sample surface suggesting that the PS grafted to the nanotube wall was also wrapped around by π–π bonds [11] while some polymer was

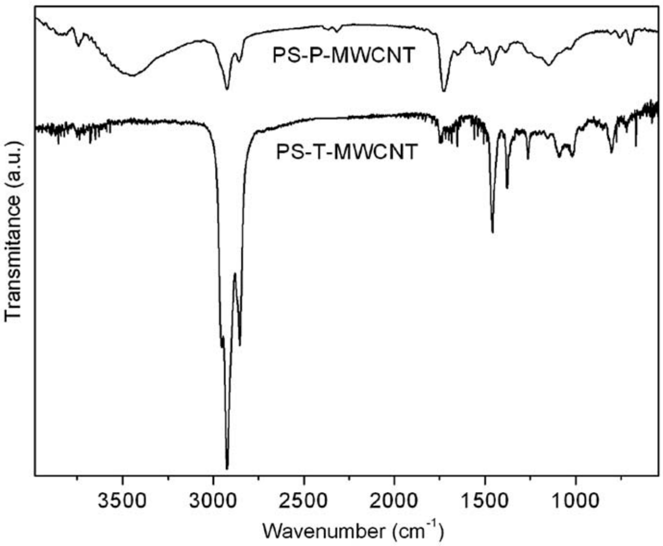

Fig. 3. FTIR spectra of functionalized nanotubes.

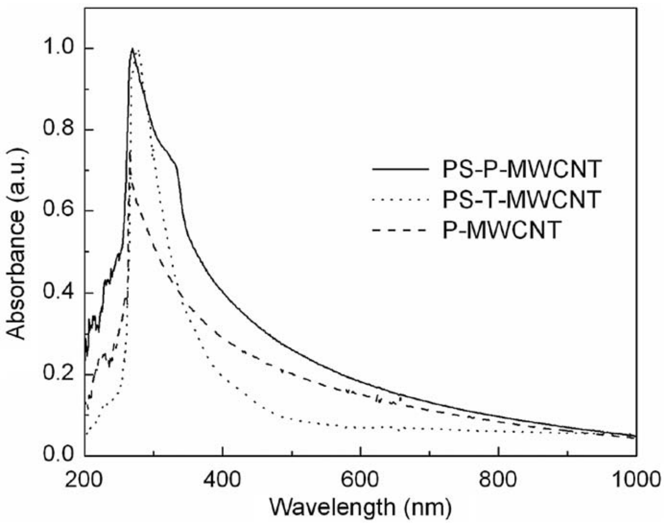

Fig. 5. UV–vis spectra of pristine and functionalized nanotubes.

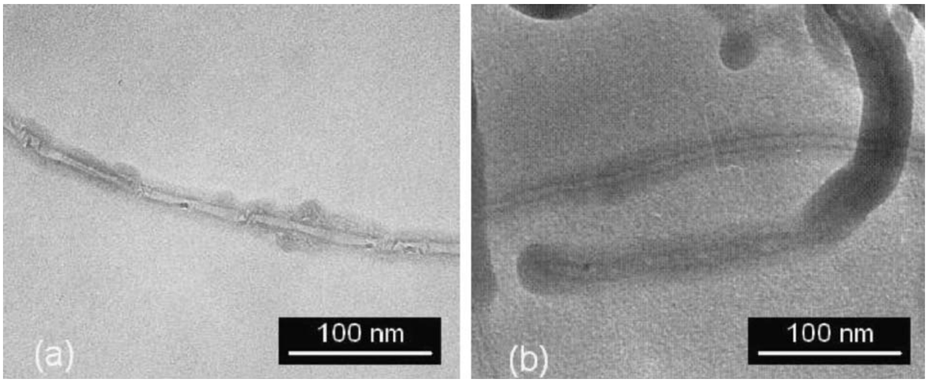

Fig. 4. TEM micrographs of: (a) PS-P-MWCNT and (b) PS-T-MWCNT.

observed around protuberances of amorphous carbon onto the nanotube wall in the PS-P-MWCNT sample.

The UV–vis spectra of the functionalized nanotubes diluted in DMF, with and without thermal treatment, are shown in Fig. 5.

An important peak at 280 nm associated to $\pi \rightarrow \pi^*$ transitions characteristic of aromatic rings can be seen for both functionalized samples [11] confirming the presence of polystyrene. There is also a shoulder at 330 nm, much stronger in the PS-P-MWCNT sample that is associated to $n \rightarrow \pi^*$ transitions of carboxylic groups, which agrees with TGA losses around 200 °C and FTIR spectra results.

4. Conclusions

Carbon nanotubes with a previous thermal oxidation treatment were successfully functionalized with polystyrene applying the "*grafting from*" method. The functionalization appeared homogeneous onto the complete nanotube surface. Besides, with this method there is no need to apply the purification process with a sulfonitric solution.

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