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CHEMICAL FUNCTIONALISATION OF CARBON NANOTUBES FOR THE DISPERSION IN POLYMER MATRICES

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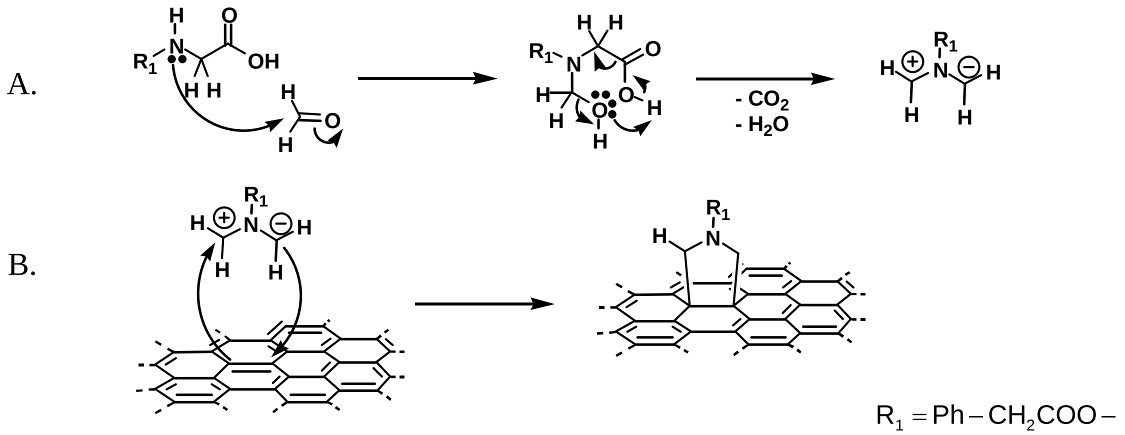
Carbon nanotubes (CNT) and nanofibres (CNF) exhibit unique mechanical, electric and thermal properties [1-2]. Their physical form is not convenient for most applications, demanding their combination with a matrix material. The preparation of a composite requires an efficient dispersion of the reinforcing phase and its good interaction with the matrix. However, the chemical inertness and low surface energy of the graphitic structure of the CNT and CNF makes this process difficult. Thus, the surface modification of CNT and CNF, aiming at the improvement of their interaction with other materials, is becoming an area of increasing importance. This modification can be achieved by attaching functional groups to the CNT/CNF surface [3-4] that will interact strongly with the matrix material, thus originating composites with exceptional structural properties at low reinforcement loads [5,6].

Most functionalization methods involve strong acid treatment of the CNT/CNF, producing extensive nanotube breakage. A class of functionalisation reactions that does not involve acid treatment is the direct addition to the π-electrons of the CNT/CNF [7,8]. These chemical reactions are less aggressive to the CNT/CNF in the sense that they do not induce high nanotube breakage, maintaining the CNT aspect ratio almost unchanged relative to the non-functionalised CNT.

The present work reports the functionalisation of CNT and CNF using two different methods. The first method is based on a Diels-Alder addition reaction (DA) of 1,3-butadiene to the CNT surface, as described in a previous work [9]. The other method is based on the addition of 1,3-dipoles to the CNT surface, generated by condensation of an α-amino acid and an aldehyde [8,10], as represented in Scheme 1.



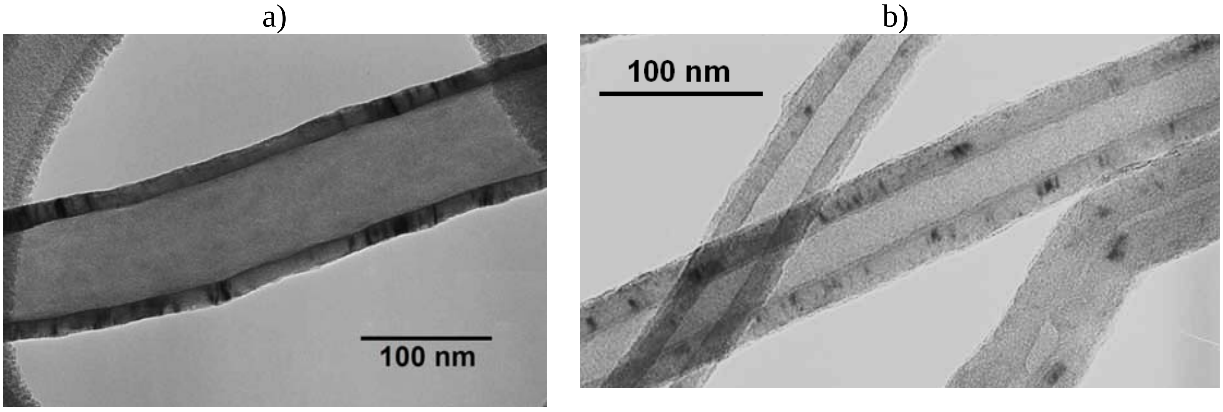
Scheme 1. A. Formation of the 1,3-dipole; B. Addition of the 1,3-dipole to the graphite surface.

The characterisation of the CNT and CNF functionalisation was done by thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS) and electron microscopy. For the CNT and CNF an increase in weight loss was observed after functionalization, measured by TGA under a constant flow of N_2, as shown in Table 1. The XPS spectra confirmed the presence of the amine at the surface of the nanofibres functionalized by the 1,3-dipolar cycloaddition reaction. Transmission electron micrographs of the non functionalised and functionalised CNFs are shown in Figure 1. The CNF functionalised by the DA addition of butadiene, under high butadiene concentration, show a layer of a polymeric product formed at the CNF surface (Figure 1 b). The extension of this layer may be controlled by the reaction conditions.

Table 1. TGA weight loss for CNF functionalized in different conditions.

CNF treatment	Weight loss (%) ± Stand. Dev.
Untreated	2.3 ± 1.2
DA reaction	11.2 ± 2.5
1,3-dipolar cycloaddition reaction	16.7 ± 2.3

Figure 1. TEM micrographs of CNFs: a) non-functionalised, b) functionalised by Diels-Alder addition.



Composites were prepared by mixing the CNF with polymer matrices using melt blending techniques. The analyses of the cross-sections of the composites formed showed that the distribution of the CNF through the polymer matrix was good for the non-functionalised and functionalised CNF in both matrices. The functionalised fibres were well wet by the matrix polymer, while the non-functionalised CNF showed poor wetting by the matrix.

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