Simple routes for the functionalization of carbon nanoparticles and potencial applications

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The article describes briefly the investigation carried out on carbon-based materials along the past years as well as the current research and aims for the future.

1. Framework

The interest in the field of carbon materials started for M.C. Paiva in the early nineties with the emerging ideas for the development of carbon fibers that could reach the automotive industry. After a brief investigation on the surface characterization of vapor grown carbon fibers produced by J. L. Figueiredo research group, the focus turned into pitch and PAN-based carbon fibers, their surface physical and chemical modification towards strong interfaces with polymers. This was the PhD topic under the supervision of C.A.A. Bernardo, in good collaboration with J. M. D. Tascón and co-workers (Instituto del Carbón, Oviedo, Spain), M. Nardin (Institut des Surfaces et Interfaces, Mulhouse, France) and D. D. Edie (Center for Advanced Engineering Fibers and Films, Clemson University, SC, USA) [2-5]. The research extended to carbon nanotubes in collaboration with Ya-Ping Sun's group, at Clemson University [6], and continued at Instituto de Polímeros e Compósitos (IPC), Universidade do Minho, in partnership with M. Fernanda Proença (Centro de Química, Universidade do Minho), with a long experience in organic chemistry, the synthesis and reactivity of organic carbon-based molecules, in particular heterocyclic compounds. The research carried out and ongoing includes the chemical modification of carbon nanofibers (CNF), multiwall carbon nanotubes (MWCNT), single wall carbon nanotubes (SWCNT), exfoliated graphite and graphene, using covalent and non-covalent approaches. The functionalized carbon nanoparticles showed great stability in water, formed stable polymer aqueous suspensions and were used namely to produce composites with strong interfaces in thermoset resins or thermoplastic polymers, or to anchor metal nanoparticles at their surface. A brief overview of the investigation carried out for the functionalization of sp^2 carbon nanoparticles (CNP) is presented below, as well as some of the outcomes and possible applications. Along the way collaboration work was developed with researchers from different fields, which will be referred along the text and references.

2. Covalent functionalization of carbon nanoparticles

The design of strategies for covalent functionalization of CNP walls aimed at simple reactions that would inflict a low level of damage upon the CNP structure. The use of solvents was avoided whenever possible in order to minimize waste and facilitate their scale up.

The reactions investigated were based on cycloadditions to the π-electrons of the CNP, carried out in solution or under solvent-free conditions, mostly using one-pot procedures. One of the approaches was based on the 1,3-dipolar cycloaddition of azomethine ylides (DCA), generated in situ from *N*-benzyloxycarbonylglycine and paraformaldehyde, under solvent-free. The procedure was carried out to functionalize CNF [7,8], MWCNT [9], SWCNT [10], and graphite nanoplatelets (GnP) [11], in good yield and without relevant structural damage to the CNP, as illustrated by scanning tunneling microscopy in Figure 1a. The cyclic amine (pyrrolidine) formed was observed to be a good anchoring group for silver and copper nanoparticles [10].

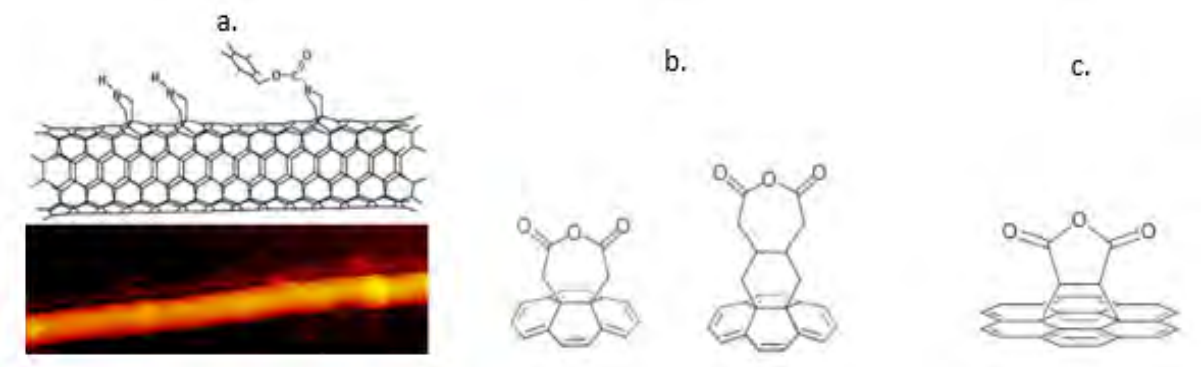

Figure 1. MWCNT observed by scanning tunneling microscopy and schematic representation of the functional groups bonded through the DCA reaction (a); functional groups at the CNP wall identified after DA cycloaddition of 1,3-butadiene (b) and of maleic anhydride (c).

Another covalent functionalization approach investigated was the Diels-Alder (DA) cycloaddition of 1,3-butadiene. The reaction was carried out on CNF [12] and MWCNT [13] in solution (diglyme) or under solvent-free conditions. It was shown that under the conditions used, the alkene initially formed undergoes a cascade oxidation process, yielding mainly carboxylic anhydride groups as final products (Figure 1b). The DA cycloaddition of maleic anhydride to MWCNT was also investigated. In this case, the hydrolysis of the anhydride was facilitated by the presence of MWCNT. However, the process could be reversed by heating in a high boiling point solvent thus recovering the anhydride form (Figure 1c) [14].

3. Non-covalent functionalization of carbon nanoparticles

In the context of non-covalent functionalization of CNP a selection of symmetrical perylene bisimides (PBI) were prepared by reaction of perylene tetracarboxylic dianhydride and a series of alpha-amino acids [15]. Their ability to adsorb at the MWCNT surface to form stable aqueous suspensions was investigated. The alpha-amino acid plays an important role on the stability of the suspensions, as was observed experimentally and confirmed by theoretical calculations (Figure 2a). It was demonstrated that PBI functionalized with Boc-lysine and phenylalanine led to stable suspensions of CNT in water at a quite low PBI concentration (5 x 10^{-5} M).

A water-soluble pyrene derivative was also prepared in high yield using a simple and low-cost functionalization methodology, easy to scale up. The synthesized pyrene derivative, depicted in Figure 2b, was tested for the stabilization of different types of GnP in aqueous solution [16], at low pyrene concentrations (5 x 10^{-5} M).

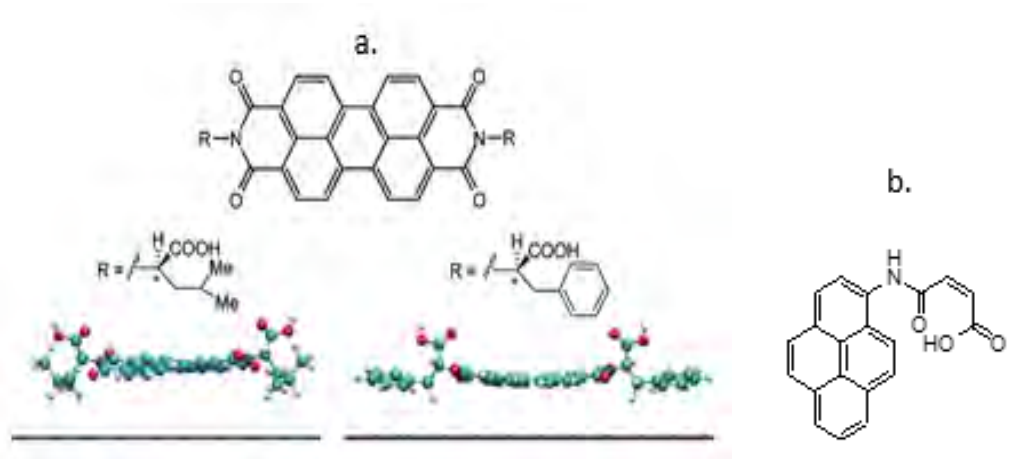

Figure 2. Equilibrium of different PBI geometries on the CNT surface (a); representation of the structure of the synthesized pyrene derivative (b).

4. Carbon nanoparticle-polymer interface

The CNP/polymer interface in a composite is strengthened by strong interactions between the two materials. However, the atomically smooth surface of the CNP will interact weakly with most polymers and the CNT tends to cluster and remain in the agglomerate form, hindering the dispersion and formation of homogeneous composites. The functionalization of CNP by covalent chemistry changes the interfacial energy and, if the functional groups are adequately selected, they may react covalently with the polymer forming a strong interface (Figure 3). Even when low reactivity between the functional groups and the polymer is predicted, the reaction may be favored under specific mixing conditions. For thermoplastic polymers reaction may proceed under melt mixing conditions, at relatively high temperature and viscosity. This was observed for MWCNT and GnP functionalized by the DCA reaction, decorated with a cyclic amine that is thermally stable and reactive in the polymer melt, using poly(lactic acid) (PLA) and polypropylene (PP) mixed with PP modified with maleic anhydride [17-20].

Covalent chemistry also had a positive contribution for interfacial bonding in CNP/thermoset polymers, particularly when the functional groups bonded to the CNP surface participate in the crosslinking reactions during the cure of the resin.

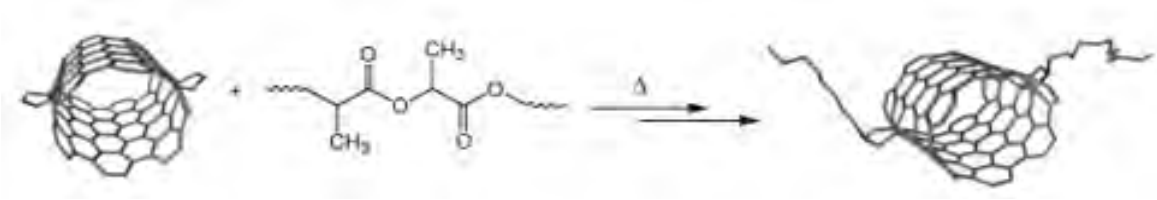

Figure 3. Reaction of a DCA functionalized CNT with PLA yielding the polymer functionalized CNT.

5. Formation of few-layer graphene from bulk graphite and carbon nanotubes

The production of graphene and graphene nanoribbons from graphite and carbon nanotubes, respectively, is a topic of intensive research. We observed that the DCA-functionalized MWCNT could undergo unzipping forming graphene nanoribbons (GNR) during their analysis by scanning tunneling microscopy (STM) [21]. The production of GNR from MWCNT in ethanol was successful [22] and the yield was sufficient to allow the production of composite films with enhanced mechanical properties, using layer-by-layer deposition [11].

Few layer graphene (FLG) was prepared by liquid phase exfoliation of graphite. The procedure was carried out in a dilute solution of the pyrene derivative depicted in Figure 2.b [16] and tested on graphite from various origins. The FLG thus produced was applied as mechanical reinforcement in natural polymer composites produced by layer-by-layer [23]. Composite films with good barrier properties and electrical conductivity were produced from aqueous polymer/FLG suspensions by spray coating [24].

6. Applications

The functionalized and pristine CNP were applied in a range of areas in collaboration with colleagues from different fields and institutions.

In the field of thermoplastic polymer composites the dispersion of CNP was investigated using different techniques in collaboration with J. A. Covas (IPC) [17-20, 25-28]. The characterization of these composites in terms of thermal properties and liquid sensing activity was carried out in collaboration with P. Poetschke (Leibniz Institute for Polymer Research, Dresden) [18, 25-26]. In the aim of Project Inteltex (European FP6 project) electrically conductive thin monofilaments were integrated into fabrics for the production of textiles with sensing activity towards temperature, strain, water, etc. (depending on the polymer) in collaboration with F. Ferreira (2C2T - Centro de Ciência e Tecnologia Têxtil, Universidade do Minho) [30]. Some of the project outcomes are illustrated in Figure 4.

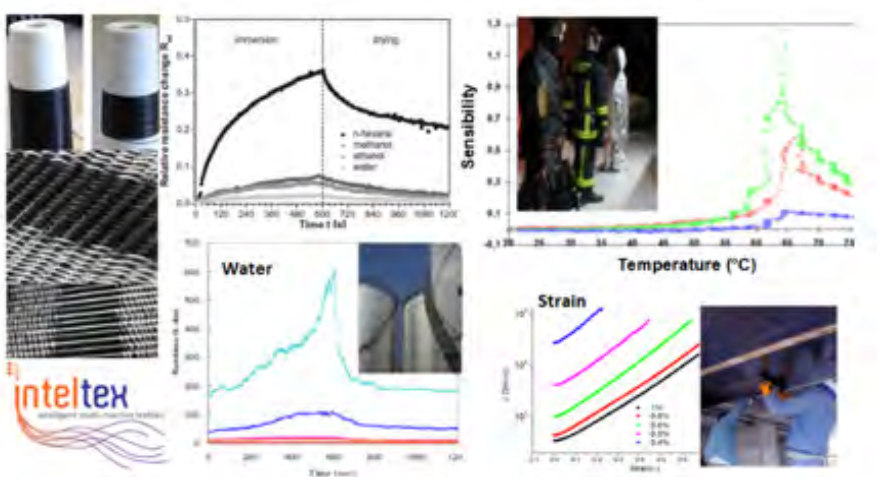

Figure 4. Textiles incorporating electrically conductive composite filaments and their sensing activity.

Composites with functionalized MWCNT were produced for testing sensing activity in a collaboration with P. K. Bhatnagar and P. C. Mathur (Department of Electronic Science, University of Delhi South Campus, Índia) [29].

Electrically conductive composite filaments were produced at IPC for application in 3D printing of conductive parts for aerospace applications, such as represented in Figure 5a [25]. The 3D printing was then carried out by Ugo Lafont's team (European Space Research and Technology Centre, Noordwijk, The Netherlands).

Thermoset polymer nanocomposites with electrical and thermal conductivity are under investigation in a collaboration project with Bosch Car Multimédia, Portugal, (project iFactory and ongoing project Factory of the Future) for the development of electrically conductive adhesives (ECAs) for PCB bonding (Figure 5b) [31]. The ECAs developed presented a shelf live larger than 6 months at temperature of -20 °C.

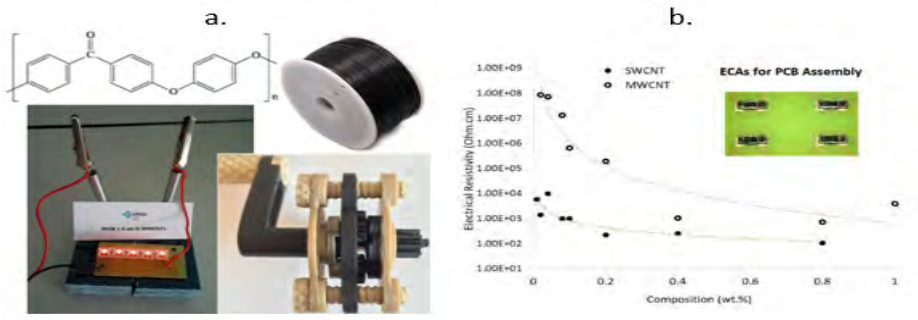

Figure 5. PEEK/MWCNT/GnP conductive filaments produced for 3D printing of complex parts (a); testing ECAs for PCB bonding (b).

In the field of electrochemistry the investigation of the effect of electrode modification with functionalized and pristine CNP, on the electrochemical response was carried out in collaboration with F. Bento and D. Geraldo from Centro de Química, group of Sustainable Chemistry: New Methods and Materials (Figure 6) [32-34].

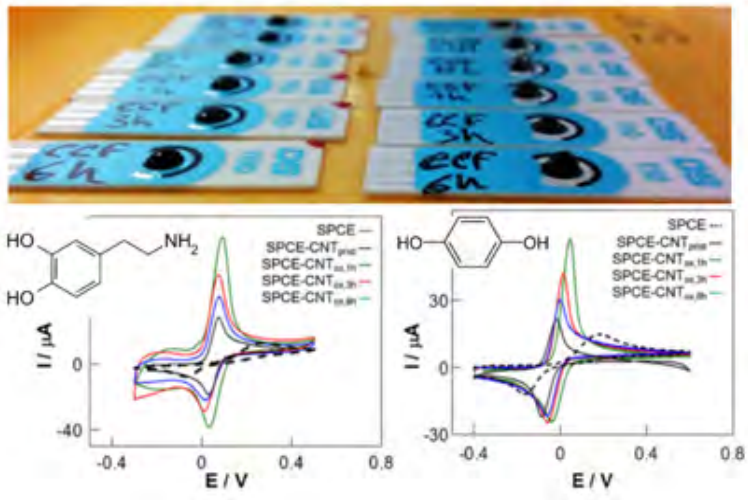

Figure 6. Testing the response of electrodes modified with functionalized MWCNT.

CNP play an important role in the biomedical field to act as mechanical reinforcement and allow electrical stimuli that may enhance cell growth in tissue engineering. In collaboration with N. M. Alves (Instituto de Investigação em Biomateriais, Biodegradáveis e Biomiméticos, I3Bs, Universidade do Minho) and J. F. Mano (formerly at I3Bs) films with enhanced mechanical properties were produced using layer-by-layer techniques, formed by natural polymers, GnP and GnR [11, 23, 35]. In a collaboration with R. F. Silva (CICECO – Aveiro Institute of Materials, Universidade de Aveiro) MWCNT functionalized by the DA reaction were used for tissue engineering with promising results [36].

Finally, the application of aqueous suspensions of MWCNT and SWCNT prepared via non-covalent functionalization, in cementitious matrices, was investigated in a collaboration with R. Fangueiro (2C2T, Universidade do Minho) and S. Rana (formerly at 2C2T) [37, 38].

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