Chapter 2.
Chemical functionalization and polymer grafting of carbon nanotubes

A great number of interesting carbon nanotube applications are related to polymer nanocomposites. Thus, many efforts have been carried out to enhance nanocomposite preparation methods aiming the production of homogeneous materials with desirable properties. Carbon nanotube surface reactivity and polymer-nanotube interaction have been improved by two main techniques, such as chemical functionalization (by elemental doping and/or functional group attachment) [1-4] and surface polymer-grafting [5-9]. The ability to manipulate carbon nanotubes enables their uniform dispersion in solvents, the subsequent functionalization reactions, and, the compatibilization with polymer, ceramic or metallic matrices for the fabrication of novel composites.

The main methods for modifying carbon nanotubes with polymers are: (i) non-covalent attachment, i.e. polymer wrapping and absorption, and (ii) covalent attachment, i.e. “grafting to”, “grafting from”, and functional groups reactions. In the case of covalent attachment, the resulting grafted polymer on CNTs is generically named polymer brush. Polymer brushes (polymer attached to different surfaces) have recently attracted considerable attention and there have been numerous studies describing their structure and novel properties [10-13]. So far, they have found application in a broad range of fields, such as cleaning, scrapping, applying and electronic contacts, among others [14].

In particular, this thesis considers the effect of chemical functionalization of carbon nanotubes, nitrogen-doping, radical surface functionalization and attachment of polymer chains on MWNTs used as fillers, in polymer composites. Therefore, this chapter reviews the structural and bonding characteristics that describe the chemical reactivity of carbon nanotubes. Additionally, most common chemical modifications of the carbon nanotubes are also described, as well as the preparation of polymer-brushes using carbon nanotubes as
surfaces via covalent attachment of polystyrene by the “grafting from” technique. Thus, this chapter will discuss the background and some basic concepts related to the polymer-grafting technique to functionalize carbon nanotubes, focusing on the nitroxide-mediated radical polymerization method.

2.1. Introduction

Carbon is the only element in the periodic table that is able to bond to itself in an extended network so as to form structures, such as fullerenes and carbon nanotubes. The delocalized $\pi$-electrons donated by each carbon atom in CNTs are free to move in the entire structure, and could give rise to electrical conductivity. In addition, the high frequency vibrations of the carbon-carbon bond provide a significant thermal conductivity in the carbon structures. The C-C strong bond determines the mechanical properties commonly expressed as strength, stiffness and toughness in materials. These fascinating properties promote the development of the carbon nanotube chemistry. This kind of chemistry considers the chemical reaction of carbon nanotubes and fullerenes with organic, inorganic, and organometallic molecules.

There are ways of forming chemical attachments to the walls or ends of carbon nanotubes. Generally, these chemical bonds might be used to join carbon nanotubes to other chemical molecules, such as solvents, polymers, ceramics, metals, solid substrates, or carbon nanotubes. Unfortunately chemical functionalized carbon nanotubes usually exhibit decreased mechanical or electrical properties when compared to as-produced carbon nanotubes.

2.2. Chemical reactivity of carbon nanotubes

Chemical reactivity of carbon nanotubes is due to structural modifications, such as: (i) local electronic structure, (ii) curvature and bending, (iii) superficial defective sites, and (iv) substitutional doping or functionalized sites. In particular, the presence of highly curved tubes (narrow diameter) could be reactive without the presence of defects. However, this type of reactivity only occurs with tubes of less <2nm in diameter.

2.2.1. Local electronic structure and chemical reactivity

Trigonal carbon bonds ($sp^2$-hybridization) strongly prefer a planar configuration with a pyramidalization angle of $\theta_p = 0^\circ$; whereas tetragonal bonds ($sp^3$-hybridization) require $\theta_p = 19.5^\circ$ (Fig. 2.1(b)). It has been observed that small fullerenes (e.g. $C_{60}$, $C_{70}$) exhibit $\sim \theta_p = 11.6^\circ$, thus the more appropriate geometry for them corresponds to tetragonal rather than trigonal hybridization. The chemical conversion of any trivalent carbon in $C_{60}$ to a tetravalent carbon relieves the strain in the whole cage structure. Consequently, reactions that serve to saturate the carbon atoms in fullerene structures are chemically favorable. Fullerene double bonds with higher pyramidalization angles (characteristics of any
structure) are the most reactive. In this case, the C\textsubscript{240} structure is the least reactive of all the fullerenes. Therefore, it can be concluded that the reactivity of fullerenes is primarily due to their spherical geometry and the strain generated by the pyramidalization angles of C-C conjugated bonds.

Carbon nanotubes and fullerenes are both curved structures; nevertheless, they present significant differences. Thus for a curved carbon nanotube (of diameters < 2nm), the carbon atoms are restrained and could be more reactive. In fact, the strain energy of pyramidalization is proportional to $\theta^2_p$. As a consequence, reactions are energetically more probable in fullerenes which are highly curved. Carbon nanotubes can be divided in two regions: the end caps and the side walls. End caps look like fullerene hemispheres with $\theta_p > 9.7^\circ$, ensuring a good reactivity. The sidewalls of narrow diameter tubes (e.g. < 2 nm) could exhibit $\theta_p \approx 6.0^\circ$, representing a lower reactivity region. According to pyramidalization angles, narrow SWNTs reactivity is higher when compared to graphene sheets ($\theta_p = 0^\circ$) [15].

![Fig. 2.1. Diagrams of (a) metallic (5,5) SWNT, (b) pyramidalization angle, and (c) misalignment angles ($\phi$) along C1-C4 in the (5,5) SWNT and its capping fullerene C\textsubscript{60} [15].](image)

### 2.2.2. Effect of bending and curvature in chemical reactivity

Structural bending and curvature in carbon nanotubes are closely related with their chemical reactivity.
Bending of carbon nanotubes results in the formation of kinks and twists. These introduce local strain through conformational deformations [16]. This process has similar effects on the atomic orbitals, such as pentagonal defects. Therefore, bending of carbon nanotubes could be used to increase and control the reaction sites over the nanotube surface. In fact, selective schemes for carbon nanotubes derivatization that allow controlled reactions on specific sites, not only at end caps, would be useful. Experimentally it has been observed that bending of nanotubes can enhance the hydrogenation energy [17, 18], i.e. chemical reactivity, by introducing mechanical deformations. Park et al [19] developed an analytical model to determine the dependence of the chemical reactivity as a function of the local structure of a deformed carbon nanotube (Fig. 2.2).

![Fig. 2.2. The local chemical reactivity (hydrogenation energy) controlled by the carbon nanotube bending angle, that could be induced by mechanical deformations. The model considers only single bonds [19].](image)

SWNTs and MWNTs are strongly differentiated by their curvature. Contrarily to SWNTs that exhibit high curvature radius (i.e. high reactivity), MWNTs possess low curvature radius on the sidewalls. The principal consequences of this fact are:

(i) The chemical reactivity related to the local electronic structure in MWNTs is less effective when compared to SWNTs because MWNTs exhibit low curvature radius on the sidewalls. This means that the MWNTs behave chemically like graphite.

(ii) The chemical reactivity on SWNTs strongly depends on their diameter [20].

### 2.2.3. Defective sites and chemical reactivity

Carbon nanotubes could possess different structural defects. Some of them are described below and presented in Fig. 2.3:

- **A.** Inclusion of five or seven membered rings within the carbon network,
- **B.** sp³-hybridized defects, with R=H and OH groups,
- **C.** –COOH groups introduced by nanotube damage under oxidative conditions, and
- **D.** Open ends terminated with –COOH groups, or even other terminal groups such as –NO₂, -OH, -H and =O.
Defects in carbon nanotubes are important in the covalent chemistry, because they can serve as anchoring groups for achieving functionalization, mainly in the case of MWNTs sidewalls that have higher degree of planarity, and thus minor reactivity. In SWNTs, the curvature is the dominating factor explaining their reactivity. In addition, the chemical reactivity caused by impurities, open ends and dangling bonds (walls partial graphitization) in MWNTs could increase compared to SWNTs, if MWNTs are less perfect.

![Image: The most common defect sites in SWNTs: A) Five or seven membered rings within the carbon framework (inducing bending); B) sp³-hybridized defects (R=H and OH); C) Carbon framework damage by oxidation, which leaves –COOH groups; D) Open ended SWNTs terminated with –COOH, or other terminal groups, such as -NO₂, -OH, -H and =O [4].]

2.2.4. Nitrogen-doping sites and chemical reactivity

Doped-carbon nanotubes exhibit other types of defective sites due to the functional groups added to the carbon network. In particular, several N-based structures have been reported in nitrogen-doped carbon nanotubes (CNₓ), among them: pyridine-like, pyrrolic site, and graphitic-like. These reactive sites are schematic represented in Fig. 2.4. As discussed above, the site number and structural location depend on several factors, as a function of the N concentration. In addition, experimental results have shown that CNₓ nanotubes exhibit a higher reactivity when compared to un-doped tubes [21]. The N-doped nanotubes present higher reactivity towards reactants (like oxygen) due to the introduction of nitrogen species and the structural irregularity of carbon hexagonal rings [22]. The N substitution reactions are also able to create radicals over nanotube surfaces, which can react with suitable reactants. A detail description of the nitrogen-doped carbon nanotube structure and functionality is given in a previous section.
It is worth mentioning that the electrical, mechanical and thermal properties of carbon nanotubes could be modified if defects are introduced in the predominantly hexagonal network. In fact, it has been observed that carbon nanotubes can tolerate a limited number of defects before losing their properties.

### 2.3. Chemical modification of carbon nanotubes

Many of the chemical functionalization efforts have focused on SWNTs because they are characterized by strong covalent bonding and unique and almost perfect 1D structure. Because it was observed that MWNTs could exhibit higher mechanical properties, and several possibilities to chemical modifications (functionalized and doping) in comparison with SWNTs, different chemical functionalization of MWNTs have been carried out. In particular, because this study is interested in the chemical modification of MWNTs, some reports will be quoted.

#### 2.3.1. Types of chemical modification of carbon nanotubes

The chemical modification of carbon nanotubes could be performed by covalent or non-covalent methods. The covalent modification considers the attachment of functional groups on the tube sides with chemical bonds, whereas non-covalent modifications use adsorbed molecules to modify the surface energy of carbon nanotubes. Thus, several mechanisms considering covalent and non-covalent modification can be described (Fig. 2.5):

(i) Cap and sidewall functionalization, taking advantage of their local electronic structure induced by the bonds and curvature (mainly in SWNTs).

(ii) Functionalization in defective sites and open ends, using the chemical group reactivity (Fig. 2.5 (A) and (B)).

(iii) Functionalization in atom-doped sites, using the chemical group reactivity.

(iv) Non-covalent functionalization using surfactants and polymers (Fig. 2.5 (C) and (E)), and

(v) Endohedral functionalization using molecules (Fig. 2.5(E)).
In some cases, these functionalization reactions could induce the loss of the electronic structure in carbon nanotubes. The central dilemma of the functionalization field is to exploit the great potential reactivity of carbon nanotubes with the preservation of basic electronic and mechanical structure.

2.3.2. Homogenous dispersion of carbon nanotubes

There are important and practical aspects of nanotube composite preparation, such as disentanglement of bundles, separation-purification, and dispersion-solubilization of samples, prior to chemical reactions and polymerization [15].

Synthetic chemistry primarily takes place in solution. Thus, disentanglement and uniform dispersions of carbon nanotubes in several solvents have to be carried out in order to proceed with chemical reactions. Dispersion becomes difficult because SWNTs and MWNTs are extremely resistant to wetting and are difficult to separate due to strong van der Waals interactions. Nevertheless, it is possible to wet carbon nanotubes, i.e., thus favoring disentanglement and dispersion when using ultrasonic procedures in acids or solvents. In addition, surface modification (introducing dangling bonds and defects) could also be used to attach polymers covalently. Intercalated molecules play the role of disrupting and compensate the loss of van der Waals attractions between carbon nanotubes. In general, it was observed that ionic, covalent, non-covalent functionalization and polymer wrapping procedures could be effective when using uniform carbon nanotube dispersion.

Fig. 2.5. Some functionalization possibilities of SWNTs: (A) Defect-group functionalization, B) covalent sidewall functionalization, (C) non-covalent exohedral functionalization with surfactants, (D) non-covalent exohedral functionalization with polymers, and (E) endohedral functionalization with, for example, C_{60} [4].
Another important aspect of nanotube chemistry is the level of purity of the starting materials that was already commented in previous sections. Additional investigations related to the separation of carbon nanotubes by length, diameter and chirality could be useful. In fact, the control of extent, selectivity and localization of the chemical reactions, as well as the appropriate characterization and development of materials is desirable and could be established by the correct purification and separation of as-produced nanotube samples.

2.3.3. Chemical reactions of dispersed carbon nanotubes

The section is divided into covalent, non-covalent and other types of reactions (endohedral) with carbon nanotubes. Among the covalent functionalization methods two main strategies are employed: modifications based on surface-bound carboxylic acids on carbon nanotubes and direct sidewall modification. The covalent attachment of polymers (i.e. polymer-grafting) on the nanotube surface will be discussed in section 2.4.

2.3.3.1. Covalent functionalization

Several covalent reactions with carbon nanotubes are originated in the chemistry of graphite, HOPG, and recently in the chemistry of fullerenes. In this context, many types of chemical reactions using carbon nanotubes have been investigated [1, 2, 15, 24]. Among them, oxidation, reduction and addition reactions have been performed to functionalize carbon nanotubes. In particular, the oxidation with their subsequent functionalization and the radical reactions approaches will be described in detail.

2.3.3.1.1. Oxidation reaction and subsequent functionalization

The first reports related to the chemistry of SWNTs and MWNTs involved reactions under oxidizing conditions. The most common oxidation agents are KMnO₄/H₂SO₄, K₂Cr₂O₇/H₂SO₄, OsO₄, oxygen gas, and ozone. Other oxidation protocols deal with UV radiation, in addition to other physical modifications.

In the first steps of oxidation, the strong oxidizing agent intercalates reversibly in the nanotube bundles; using longer oxidation times, the reactant disorders and exfoliates the ropes into individual tubes. Finally, the extremely aggressive reagents can disrupt the aromatic ring system of the SWNTs and MWNTs.

In particular, concentrated acid solutions (HNO₃, H₂SO₄, HCl, among others, and their mixtures) produce functionalized sites (such as, carboxylic, sulfuric, anhydride, quinone, ketone, ester and hydroxyl, etc), defects in the hexagonal lattice, open ends, and impurity states at the Fermi level of the nanotubes. Furthermore, strong acid treatments with the aid of sonication, produces damage on the surface and results in the cutting of the tubes. In addition, the temperature rise in acid reactions increases the velocity and extents of structural damage within carbon nanotubes.

It is noteworthy that the oxidation rate is strongly dependent on the structure of the carbon layers, i.e. diameter and cristallinity.
First of all, various researchers observed that thinner tubes are more quickly consumed when compared to the thicker ones, because of their greater helical strain due to the narrow tube diameter.

In second place, less organized parts within carbon nanotubes appear to be more reactive when compared to highly crystalline regions. In general, functionalization of carbon nanotubes by oxidation takes place preferentially at end caps and defective sites [25].

**Subsequent functionalization after oxidation**

The literature presents numerous reaction protocols related to purification (see previous section) and functionalization of carbon nanotubes using acids. Usually in nanotube chemistry, the acid treatment is seen as a preliminary step to increase the carbon nanotube chemical reactivity by the introduction of functional groups labile for posterior modification. These modification steps consider several kinds of chemical reactions, predominantly at nanotube ends and defective sites (Fig. 2.6). Thus, this kind of nanotube chemistry is named, by some authors, end and defect-site chemistry.

Most of the carboxylic acid functional group react with thionyl chloride for activation with the subsequent reaction with amines (-NH₂), alkyl amines, aniline derivatives, phenyl groups, etc. The ionic functionalization of the carboxylic acid groups in carbon nanotubes by octadecylamine has been reported and could form SWNTs-carboxylate zwitterions (SWNT-COO⁻\(\text{NH}_3\)(CH₂)₁₇CH₃) [2].

![Fig. 2.6](image)

*Fig. 2.6. Scheme of common covalent functionalization routes used to derive SWNTs at the ends and defect sites. As produced nanotubes are treated with an oxidative protocol to generate functional groups that react with SOCl₂ followed by amide or ester linkages. Amine and oxygenated functional groups are also effective sites for coordination to metal complexes and ions [1].*
Many efforts have been devoted to make carbon nanotubes biologically compatible. Thus, several water soluble molecules and macromolecules have been attached to acid functionalized-carbon nanotubes, as peptide nucleic acid, DNA, etc.

Nanoparticles (e.g. Au, Ag, etc) [26] and quantum dots (CdSe, TiO$_2$, etc) have been bound to oxidized-carbon nanotubes in order to alter the optical and electronic properties of carbon nanotubes. Furthermore, coordination complexes of Ir, Pt and Pd, among others, have been synthesized by metal coordination in an $\eta^2$ fashion to the carbon-carbon double bond in fullerenes. For SWNTs and MWNTs, the oxidized functional group appears to be a favorable mode of bonding of metals by complexation [1].

Finally, the addition of a long-chain hydrocarbon might render the acid functionalized-carbon nanotube soluble in organic solvents (such as chloroform (HCCl$_3$), dichloromethane (CH$_2$Cl$_2$), benzene (C$_5$H$_6$), toluene (CH$_3$-C$_6$H$_5$), carbon disulfide (CS$_2$), etc.), when using octadecylamine (CH$_3$(CH$_2$)$_{12}$NH$_2$), alkyl-aryl amine 4-dodecyl-aniline (4-CH$_3$(CH$_2$)$_{13}$C$_6$H$_4$NH$_2$), among others. In addition, the functionalization of carbon nanotubes with polymers has also been carried out and will be discussed in following sections.

In summary, it could be mentioned some important aspects in the oxidation and subsequent functionalization of carbon nanotubes.

- The oxidation of carbon nanotubes could be successfully used in purification and exfoliation steps. Nevertheless, this technique is difficult to control and reproduce.
- The oxidation produces an improved solubility and an increment in the chemical reactivity of carbon nanotubes due to the creation of defects and functionalized sites on their surfaces. Nevertheless, it also produces dramatic structural damages with the tendency to destroy nanotubes.
- There are several chemical functionalization routes reported for carbon nanotubes using oxidation process. However, the functionalized carbon nanotubes predominantly exhibit the molecular attachment on defective sites and the end-caps. This could be a disadvantage for some applications, such as the nanocomposite preparation, among others.
- The induced structural damage affects seriously the mechanical, electronic and thermal properties of carbon nanotubes, thus affecting their possible applications.

To sum up, even though the oxidation of carbon nanotubes results in functionalized carbon nanotubes, this aggressive technique induces structural damage. Thus, a more effective and less aggressive method, such as the direct covalent functionalization, is preferred in nanotube functionalization processes.

2.3.3.1.2. Reduction, addition and other reactions

There are several chemical processes able to modify carbon nanotubes by direct covalent functionalization. This method takes advantage of the nanotube chemical properties without the use of acids. Fig. 2.7 shows several chemical processes, such as nitrene addition, hydrogenation via Birch reduction, alkylation, arylation [27] and 1,3-
dipolar cycloaddition, among others. In particular, fullerene and carbon nanotube chemistry has shown that their structural properties favor addition reactions. In fact, efficient addition reactions take place with very reactive species, such as arynes, carbenes or halogens (i.e. iodine, bromine, etc) [15].

Chen et al [28] tested the reactivity of SWNTs using photolabeling of \( [\gamma^{32}\text{P}] \)-benzophenone-ATP or \( [\gamma^{32}\text{P}]2\text{N}_3\text{ATP} \) solutions. Their results indicate that the radioactive probes become attached to the nanotube, but the mode of addition remains unknown. Further reactions were carried out using dichlorocarbene (electrophilic reagent) that adds to deactivated double bonds. Birch reduction conditions were applied to hydrogenate benzenoid rings of SWNTs. These reactions are schematically present in Fig. 2.8. References of functionalized SWNTs by the addition of nucleophilic carbenes have also been reported [15]. In this case, each added group is bound to one covalent bond of the tube (no cyclopropanation occurs), thus introducing a negative charge to the nanotube.

Fluorination was chosen during the initial studies of functionalization of carbon nanotubes because of the efficient chemical transformations of graphite. Margrave et al [29] reported the first extensive sidewall functionalization of SWNTs with F (Fig. X). Covalent C-F bond was detected by IR vibrations with stoichiometries of CF\(_x\) (\(x<0.4\)) or CF\(_2\). It was also shown that fluorine substituents on SWNTs can be displaced using strong nucleophiles as Grignard, alkyllithium and metal alkoxides.

2.3.3.1.3. Radical reactions

Several radical reactions have been performed with carbon structures (carbon black, fullerenes and carbon nanotubes) with organic peroxides and nitroxides. Experimental results reported addition of radicals to carbon structures using ESR [30, 31].

Donnet and colleagues [32] have studied the carbon black interaction with AIBN radicals. After characterization, it was found that the paramagnetic susceptibility of untreated and AIBN treated carbon black are almost the same. In addition, ESR results revealed that both samples are temperature independent. Finally they conclude that the observed reaction of free organic radicals with carbon black corresponds to chemical reactions and not to free radical coupling. The same authors, in another study, found that peroxides and carbon black can form macroinitiators labile to initiate in situ radical polymerization.

Several simulations were proposed to study the interactions of carbon nanotubes and radicals. In particular by molecular dynamics, the collision of benzene radicals with a SWNT has been considered by Ni and Sinnot [2]. Radical collisions at higher energies could create defects within the SWNTs walls, but also produce the scattering and adsorption of radicals or heavy fragments of radicals.

Peng et al [3] synthesized SWNTs and fluorinated-SWNTs and reacted them thermally with organic radicals from lauroyl and benzoyl peroxides. They reported the SWNT covalent sidewall attachment.

It has been also shown that nanotubes can coherently transport spin-polarized electrons over long distances (250 nm) [33]. In this context, Gallani et al [34] performed the grafting of TEMPO radicals to cut and polished SWNTs that were treated with oxalyl chloride.
Shaffer et al [8] suggested that in solution polymerization systems of benzoyl peroxide, carbon nanotubes and monomer, the grafting mechanism involves growing polymer radicals attaching themselves to the defective and oxidized carbon surface of the nanotubes, although the small molecule initiators may also directly attack the nanotubes. Both effects have been observed in radical reactions with fullerenes and carbon black.
These authors followed the radical attachment and the PmPV association by ESR. The authors observed that the radicals are either very weakly coupled, or not coupled. The explanation is related to finite size on the radical conductivity that could interfere and prevent the coupling, but also because of the steric impediments of the polymer chain.

Some other radical addition reactions with carbon nanotubes involve perfluoroalkyl and aryl radicals produced photochemically or by electrochemical reduction.

Therefore for carbon nanotubes, the chemical interaction with radicals, i.e. the fixation of molecular free radicals on carbon nanotubes, could be interpreted using two hypotheses:

(i) It could be assumed by trapping radicals already present on the surface (nanotube scavenging properties); and,

(ii) It could be proceeded by a chemical reaction of radicals with surface functional groups that could produce a stabilized radical.

In summary, the direct covalent functionalization of carbon nanotubes preserves the nanotube structure, and could favor a homogeneous and extended coverage of functionalized sites over the nanotube surface. In particular, radical reactions could be used to prepare further carbon nanotubes derivatives, such as polymer-grafting, and specifically the controlled radical polymer-grafting carbon nanotubes.

2.3.3.2. Non-covalent functionalization

Non-covalent functional carbon nanotubes can be prepared by: (i) adsorption of surfactants, amines, and molecules with large p-systems; and (ii) complexation with organometallic compounds or wrapping of polymers (Fig. 2.5 (C) and (D)). One of the main advantages of non-covalent functionalization is the conservation of the carbon nanotube electronic structure [1].

First of all, surface-active molecules, such as sodium dodecylsulfate (SDS) or benzylalkonium chloride, form stable suspensions of carbon nanotubes. The micelles formed contain carbon nanotubes in the hydrophobic region. If the hydrophobic interior of
the amphiphile contains an aromatic group, a strong interaction with the nanotubes is formed because of the \( \pi^* - \pi \) stacking interactions. Similar immobilizations on carbon nanotubes were observed with the hydrophobic part of proteins, anilines and amines. Evidence of these functionalizations is found by changes in solubility and electronic properties. Presumably donor-acceptor complexes are formed between surfactants-carbon nanotubes because of the curvature [4].

Interestingly, the suspension of purified carbon nanotubes with polymer solutions forms “molecular complexes”. Polymer wrapping around carbon nanotubes enhances solubility and modifies carbon nanotube and polymer properties. A range of polymers, mostly ionic polymers, are capable of coating SWNTs and MWNTs. Among them, polystyrene, poly(methyl methacrylate), poly(vinyl pyrrolidone), poly(styrene sulfonate), etc. It was observed that polymers, such as polyethylene glycol (PEG) and polyvinyl alcohol (PVA), are ineffective in wetting carbon nanotubes. Association and disassociation of polymers from carbon nanotubes can be controlled by varying the solvent polarity.

2.3.3.3. Other functionalization types
Endohedral functionalization takes advantage of the storage capacity of carbon nanotubes. Some of the molecules that can be inserted using the capillarity properties of carbon nanotubes are metals (for example, gold and platinum) and metal salts. The incorporation of fullerenes or metafullerenes has also been carried out (Fig. 2.5 (E)). The encapsulated fullerenes tend to form chains organized by van der Waals forces [4].

2.4. Polymer-grafting of carbon nanotubes

Polymer brushes refer to an assembly of polymer chains that are tethered to a substrate by one end. The substrate includes wafers, particles (such as carbon black, fullerenes and carbon nanotubes), and polymer backbones. The grafting of polymers onto a surface can be made by (a) “grafting from” the surface method, in which the polymerization is initiated from initiating groups (typically free radicals) introduced onto the substrate; (b) “grafting onto” the surface method, in which a polymer chain that is growing is trapped by the surface, rendering a covalent bond between the polymer and the surface, and, (c) polymer reactions with functional groups on the surface, in this approach a polymer exhibiting terminal functional groups reacts with other functional groups that are present on a specific surface.

Several studies have demonstrated the effectiveness of all these techniques when grafting polymers with solids. In the “grafting from” method, radical, cationic and anionic polymerization can be performed onto the desired surface. In addition, higher degree of surface functionalization is possible, but multiple synthetic steps must be carried out on the nanotubes, and polymer characterization is only possible for the grafted chains that are cleaved on the nanotube surface. Conversely, the “grafting to” method suffers from the low polymer loadings due to steric repulsion between grafted and propagating polymer chains. However, this technique allows the characterization of polymer chains prior to grafting. Furthermore, in both “grafting from” and “grafting to” procedures, a broad distribution of molecular weights and composition of the polymer chains are expected, if the polymerization proceeds by an uncontrolled method [35]. Additionally, polymer reactions
with functional groups present on the surface experience low chain polymer attachment due to steric repulsion; fortunately, the molecular weight, and a well defined polymer structure can be controlled [36].

In summary, the “grafting from” method is preferred over other methods, because of their possible advantages, such as higher degree of functionalization, that could be related to surface coverage, and the control of polymer molecular weight and the control of polymer weight and composition.

2.4.1. Polymer-grafting of carbon black and fullerenes

Polymer-grafting has been carried out in carbon structures, such as carbon black, fullerenes, and carbon nanotubes. Previous, studies performed using carbon black and fullerenes constitute the pioneering work that evolved in the polymer grafting on CNT surfaces.

Carbon black

A permanent radical concentration [37], as well as a strong radical trapping behavior has been observed in carbon black [32, 38] and also both properties have been used to graft polymers onto its surface [36, 39, 40]. Polymer-grafting with carbon black has been achieved using the “grafting from”, “grafting onto” and “polymer-reactions with functional groups on the surface” techniques. The radical cationic and anionic polymerization by azo-[41] or peroxyester [42], acylium perchlorate [43] and potassium carboxylated [44] groups introduced on the carbon black surface are examples of “grafting from” technique. Additionally, it has been reported that free radical polymerization of vinyl monomers in the presence of carbon black (“grafting to” method), leads to the grafting of polymers onto the surface of carbon particles, but the percentage of grafting is less than 10%. This is because carbon black preferentially traps low-molecular-weight initiator fragments rather polymer radicals [45, 46].

Furthermore, it has been observed that, when carbon blacks are treated with conventional free radical initiators (benzoyl peroxide (BPO), or 2,2’-azobis(isobutyronitrile) (AIBN)), the corresponding radicals are bound on the surface forming polycondensed aromatic rings and quinonic oxygen groups on the surface [32, 47]. The free radicals formed on the carbon black surface by the addition of initiator radicals were considered to be stabilized by polycondensed aromatic rings. In most of these cases the increase of the number of surface radicals after the treatment with the initiators has been confirmed using Electron Spin Resonance (ESR) [32, 47]. From these studies, it is concluded that the polycondensed aromatic rings and quinonic oxygen groups of carbon black act as a strong radical trapping agents for polymer radicals.

Using the radical trapping behavior of carbon black, Hayashi et al [36] have reported the “grafting to” reaction of carbon black with polystyrene chains polymerized in the presence of (thus, end terminated) a nitroxide (TEMPO) at temperatures above 100°C. This reaction is summarized in Figure 2.9. The in situ polymerization experiments of the authors confirmed that carbon black traps more low-molecular-weight initiator fragments than growing polymer radicals. This behavior could be explained by the stability and the steric hindrance of the growing polymer radicals. They also found that polymers having
hydroxyl terminal groups could be grafted onto the carbon black surface in the presence of ceric ions, as depicted in Fig. 2.10. Complementary results by them determined that PEO could be also grafted onto carbon black without inducing gelation or crosslinking. This behavior revealed that radicals formed were not reacted with two carbon black particles.

![Fig. 2.9. Surface grafting onto carbon black by trapping polymer radicals formed by decomposition of TEMPO-polystyrene [36].](image)

![Fig. 2.10. Surface grafting onto carbon black by trapping polymer radicals formed by redox reaction of ceric ions with polymer containing hydroxyl groups [36].](image)

**Fullerenes**

Early studies on radical polymerization of vinyl monomers in the presence of C\(_{60}\) report very low yields of polymer formed in solution, or even complete inhibition [48]. From these cases, it has been suggested that for the case of styrene the free radicals are trapped by fullerene, and the resulting fullerene radicals do not propagate but instead can terminate. Nevertheless, there are pieces of evidence that if the polymerization is carried out in the presence of a large excess of initiator, the radicals undergo multiple additions on the fullerene surface, changing their nature sufficiently to not inhibit polymerization [49]. Other authors have reported on the grafting of polymer chains on fullerenes. Krusic et al [50] shown that free radical species can efficiently couple to the surface of C\(_{60}\), resulting in a highly functionalized fullerenes. Mehrotra et al [48] reported that in the presence of C\(_{60}\), the polymerization of vinyl monomers (methyl acrylate, methyl methacrylate, acrylonitrile, cyanovinyl acetate, vinyl acetate, 2-cyanoethyl acrylate, styrene and N-vinylpyrrolidone) in solution was inhibited, yielding 15% or less of polymer product. Therefore, it was concluded that the C\(_{60}\) intercepts the initiating radicals in the polymerization reaction. Furthermore, it was observed that monomers with high reactivity could form fullerene-based radicals by their addition to fullerene surface and continue the polymerization process. In fact, functionalization of fullerenes with well-defined polymers by living polymerization techniques (e.g. anionic polymerization, nitroxide mediated free radical polymerization, and atom-transfer free-radical polymerization) has been reported recently. With these living methods, both the architecture of the polymer-grafting on fullerenes surfaces and even more the architecture of the same polymer chains can be well-controlled [51]. As consequence, many kinds of polymer-grafted fullerenes have been reported, among them: side-chain polymers, main-chain polymers, dendritic fullerenes, star-shaped polymers and fullerene end-capped with polymers.

As can be seen, there are several experimental reports in the polymer-grafting of carbon black and fullerenes, by both the “grafting to” and the “grafting from” techniques. Furthermore, these techniques have been successfully applied to covalently bond polymer...
Chemical functionalization and polymer grafting of CNTs

chains using controlled radical polymerization. The free radical polymerization is possible by the chemical interaction of particle surface with the radicals and also by the polycondensed aromatic rings structure formed on the surface. The radicals stabilized on the surface of these carbon structures could in turn initiate the growth of polymer chains, forming an initiator.

2.4.2. Polymer-grafting of carbon nanotubes by “grafting from” technique

The first synthesis of polymer-grafted multiwalled carbon nanotubes were reported by Jin et al in 2000 [5]. Since then, the number of papers has increased enormously. In most of these papers, the polymer-grafting of multiwalled carbon nanotubes have been achieved by either of the already mentioned techniques: “grafting from”, “grafting to”, and “polymer reactions with functional groups at nanotube surface” techniques. The advantages cited for the “grafting from” technique make interesting to consider it in the polymer-grafting of carbon nanotubes. Thus, in the next section, some of the experimental results in “grafting from” method applied to MWNTs will be described.

2.4.2.1. Polymer-grafting using carbon nanotube acid functionalization

Several polymers have been successfully grafted onto MWNTs using the “grafting from” technique. Among them there are: polymethyl methacrylate grafted via emulsion polymerization [6, 7], sterification [52], and other methods [53]; polyethyleneimine-grafted [54, 55]; hyperbranched polyetherketones [56, 57] via Friedel-Crafts acylation in polyphosphoric acid (PPA) [58]; PEO and PS [59]; polyureas, polyurethanes, and poly(urea-urethane) [60]; polyethers [61]; polycetylene [62] and PS [63]. In all of these cases, the carbon nanotubes were chemically functionalized by acid treatment, to introduce initiator molecules by chemical reaction that could be used to carry out in situ polymerization of the different monomers.

The first covalent attachment of polystyrene chains onto carbon nanotubes was reported by Shaffer in 2002 [8]. Polystyrene and some of their copolymers (like poly(styrene-co-hydroxymethyl styrene) and poly(styrene-co-aminomethyl styrene) [64]) had been reported as grafts on carbon nanotubes by either of the three previously discussed methods, namely, “grafting from”, “grafting to”, and “polymer reactions with functional groups at nanotube surface”. In the case of acid functionalized carbon nanotubes, the grafting of polystyrene could be achieved by several reactions, such as esterification [65], amidation [66], acylation [67], Huisger cycloaddition [68], among others.

2.4.2.2. Polymer-grafting using living radical polymerization

Polymer grafting techniques that use direct covalent functionalization methods, such as radical reactions, have been developed in order to avoid the problems associated with the functionalization of carbon nanotubes using acids. These grafting techniques eliminate the need for nanotube pretreatment prior to the functionalization and allow attachment of polymer molecules to pristine tubes without altering their original structure.
The grafting mechanism involves polymeric free radicals that attach themselves to the defective, doped and/or oxidized sites [8, 9] on the carbon nanotube surface, and also radical trapping mechanisms [9] of the CNTs. Both, the polymer “grafting from” and the “grafting to” methods on carbon nanotubes could be performed by radical reactions. In the “grafting from” technique the nanotubes are pretreated with a free radical initiator to give rise to “active” sites where the polymerization can be carried out, whereas in the “grafting to” technique a propagating polymer chain (bearing a free radical) reacts with the tubes directly. An alternative approach includes the use of a “regulator” molecule in addition to the initiator to give rise to a controlled radical polymerization (pseudo-living polymerization) where the free radicals are capped with a nitroxide molecule (the regulator) that is in essence a stable free radical and thus allows the controlled grafting of monomer molecules on the nanotube surface.

The use of a living radical polymerization approach allows a better control of molecular weight and molecular weight distribution of the tethered polymers onto the nanotube surface. Living polymerization methods in addition to the previously mentioned controlled radical polymerization include: anionic, carbocationic and ring-opening metathesis polymerization. All of these methods have been used in the synthesis of polymer brush in a “grafting from” approach, as will be detailed below.

In general, it is known that living free radical polymerization offers a high degree of control over the polymer architecture and is applicable to a broad spectrum of monomers, but there are very few instances where it has been used to graft polymer chains onto carbon nanotubes, for example, Nap et al [69] have considered how the strength and distance of the minimal interaction could be controlled by the choice of polymer chain length, surface coverage, and type of functional end-group; also, how the feed ratio of monomers controlled the quantity of the grafted polymer. Like these, many other factors need to be studied to reach an understanding on the formation of polymer brushes on nanotubes.

Some of the studied systems involved PMMA-grafting on carbon nanotubes. Park et al [70] reported the polymerization of PMMA over carbon nanotubes using 2,2'-azoisobutyronitrile (AIBN) as radical initiator. In this system, the authors have been observed that the induced radicals on the outer wall of the MWNTs by AIBN were found to initiate the grafting of PMMA [71]. Other authors observed that poly(4-vinylpyridine) grafts to single-walled carbon nanotubes (SWNTs) during in situ free radical polymerization of 4-vinylpyridine [72].

2.4.2.2.1. Anionic and cationic polymerization

Anionic and cationic polymerization techniques can be used to graft polymer chains on carbon nanotubes surfaces. Some of the reported results are summarized in the following lines.

Mylvaganam et al [73] reported, with the aid of the density functional theory, that ethylene and epoxide functional groups could be grafted to carbon nanotubes using methoxy radicals and sec-Bu anion as initiators leading to polyethylene- and polyepoxide-grafted nanotubes. The study predicts that both free-radical and anionic functionalization methods are energetically favorable; that the resulting carbon nanotube-radical and the carbon nanotube anion can react with ethylene and epoxide functionalities, respectively; and that the resulting products have free electrons and negative charges on the carbon and oxygen atoms at the free ends of ethylene and epoxide, respectively. Hence, the in situ free-radical and anionic polymerizations can propagate to produce polymer-grafted carbon
nanotube. The cationic functionalization of carbon nanotubes using BF$_3$ as an initiator was found to be infeasible. In addition, polystyrene chains were grafted onto SWNTs via anionic polymerization techniques [74].

2.4.2.2.2 Controlled living radical polymerization
Particularly, the in situ surface-initiated controlled polymerization from the surface of carbon nanotubes was recently reported by several authors using Atom Transfer Radical Polymerization (ATRP) [75] and Nitroxide Mediated Radical Polymerization (NMRP) [35, 76, 77], among others. There exist a limited number of experimental pieces of evidence of these radical polymerization techniques to the polymer-grafting of carbon nanotubes. However, in these works there are some lacks in the demonstration of the polymer covering of the nanotube walls, and even more about the covalent attachment of the polymer chain to the surface.

Reversible Addition and Fragmentation Chain Transfer (RAFT)
Hong et al [78] reported the poly(N-isopropylacrylamide) grafting of MWNT via surface reversible addition and fragmentation chain transfer (RAFT) using the RAFT agent functionalized MWNTs as chain transfer. Using the same technique PS chains were grafted from the surface of MWNTs [79].

Atom Transfer Radical Polymerization (ATRP)
The ATRP reaction mechanisms proposed for nanotubes surface polymerization were: first the attachment of polymerization initiators via cycloaddition reaction, or the ring-opening metathesis polymerization (ROMP) [80], and; second the attachment of initiator by the carboxy group generated by chemical oxidation [81]. The polymers growing over nanotubes using this technique until now are principally poly(styrene) [75, 81-85], poly(methacrylate) [86, 87], poly(t-Bu acrylate) [88-90], poly(N-isopropylacrylamide) [91], and poly(acrylic acid) [92], as well as their copolymers [93].

Nitroxide-mediated Radical Polymerization (NMRP)
Nitroxide-mediated radical polymerization has been demonstrated on surfaces, nanoparticles and amphiphiles, and very recently on carbon nanotubes (by Ramirez et al [76]). This technique could be used in both “grafting to” and “grafting from” methods. In the first case, NMRP produces well-defined polymers that are end-capped with thermally labile nitroxide functionalities. Thus, this method could result in the controlled formation of polymer-centered radicals that could be utilized in the functionalization of carbon nanotubes [35, 94]. In the second case, the couple initiator-nitroxide could be attached to the nanotube to form a “macroinitiator”, susceptible of thermal initiation. The opening and closing mechanism for the free radical-controller pair favors the polymer chain growth.

The available literature on the grafting of polystyrene to CNTs using NMRP invariably includes the functionalization of the nanotubes using strong acids to attach the initiator to the nanotube ends and defective sites. Particularly, Ramirez et al [76] attached NMP initiator through carbodiimide or acid chloride chemistry with acid functionalized nanotubes. Adronov et al [35] proposed that polymers could be covalently attached to SWNTs through the radical coupling of the polymer to the nanotube walls. Datsyuk et al [77] synthesized double walled carbon nanotube-polymer brushes by in-situ nitroxide mediated polymerization.
Nitroxide-mediated Radical Polymerization is the less used controlled radical polymerization technique to graft polymer chains on carbon nanotubes; however, the technique is promising because of (i) the successful functionalization without any carbon nanotube surface damage, like in acid functionalized carbon nanotubes, and (ii) the minimal purification and separation problems, (when compared to a technique such as ATRP).

This thesis focuses on the use of the NMRP technique to graft polystyrene on nitrogen-doped carbon nanotubes. Furthermore, great opportunities and applications to this type of polymer brush are envisaged. A detailed review of the NMRP technique is available in several references [95, 96]. A detailed explanation of this technique is out of the scope of the present dissertation.

2.5. Applications of functionalized and polymer-grafted carbon nanotubes

Numerous factors motivate the chemical modification, by functionalization or polymer grafting of carbon nanotubes, most of them are related with their applications. In general, the properties of carbon nanotubes could be differentiated by the intercalation, bonding, or even the doping of molecules with nanotubes.

The grafting of polymers onto carbon nanotubes could allow their assembly onto surfaces for electronic applications, permit the reaction of the grafted nanotubes with host matrices in composites, and finally could enable sensor applications that may require a variety of functional groups bound to carbon nanotubes with specific recognition sites (optical or transport properties) [24].

The polymer composites are the focus of this research. Thus it has to be said that the sidewall functional groups or polymer chains of carbon nanotubes polymer brushes could help the dispersion of the nanotubes in the polymer matrix and improve the mechanical properties of nanocomposites. In fact, the requirements of load transfer efficiency demand that nanotube surfaces should be compatible with the host matrix. In addition, tubes interconnected by chemical bonds could modify (increasing or decreasing) the contact resistance depending on the polymer that is grafted to the surface. Also, the polymer-grafting should avoid the tendency of the carbon nanotubes to form bundles and increase their specific surface area [77].

2.6. Characterization of functionalized and polymer-grafted carbon nanotubes

In general the characterization of carbon nanotubes after chemical functionalization is still developing. Up to now, there are several analytical techniques used to confirm the carbon nanotube chemical reaction, but also, the degree of functionalization.

Functionalized species on the carbon nanotube wall, can be characterized using spectroscopic techniques. Thus, Ultraviolet (UV), Infrared (IR) and Raman Spectroscopy
are used to analyze the changes in the carbon nanotube sidewall structure due to the presence of new chemical bonds.

Thermogravimetric Analysis (TGA) and X-Ray Photoelectron Spectroscopy (XPS) provide information related to the degree of functionalization.

Transmission Electron and Atomic Force Microscopy (TEM and AFM) show the sidewall structure and topological modifications and dispersion effectiveness.

$^1$H NMR is not very informative, because of the traces of iron impurities (catalyst used during the synthesis) and the slow tumbling rates of carbon nanotubes that cause a signal broadening.

2.7. Conclusions

Experimental evidence supports that carbon nanotubes should be considered as a new macromolecular form of carbon with great potential in the development of novel devices. They could be soluble in organic solvents, by modifying the nanotube surface, thus changing their physico-chemical properties. In particular these chemical transformations could consider the surface functionalization by species covalently attached. Covalent attachment is preferred for applications, such as polymer-grafting, the focus of this work. In this study, radical functionalization and controlled radical polymer-grafting are proposed as preliminary stages to elaborate carbon nanotubes-polymer nanocomposites.
References


