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Toward Greener Chemistry Methods for Preparation of Hybrid Polymer Materials Based on Carbon Nanotubes

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1. Introduction

Recent technological advances and the need for materials with new functionalities and better performance have generated an enormous demand for novel materials. Nanostructures such as carbon nanotubes (CNTs) possess outstanding mechanical, electrical, thermal and chemical properties which make them ideal for a wide variety of current or future applications [1], especially for the preparation of multifunctional *hybrid polymer materials*.

The incorporation of CNTs to polymer matrices have demonstrated to improve the mechanical, electrical, thermal and morphological properties of the produced nanocomposites [2]; however, the full exploitation of CNTs has been severely limited due to difficulties associated with dispersion of entangled CNTs during processing, and their poor interfacial interaction with the polymer matrix. Therefore, significant efforts have been directed toward improving the dispersion of CNTs by means of surface modification either by non-covalent functionalization or covalent functionalization [3].

Most strategies designed to functionalize CNTs involve the use of strong acids as reagents and organic solvents as reaction media, which can become environmental pollution and health hazard problems. Nowadays, the global environmental trends are seeking greener chemistry methods to prepare materials, thus, there is plenty of room for developing environmentally-friendly chemistry methods to functionalize CNTs.

"*Green*" chemistry is based on the use of a set of principles that reduces or eliminates the use of hazardous reagents and solvents in the design, preparation and application of materials [4]. In this context, functionalization of CNTs using microwaves, plasma, and ultrasound waves are strategies very promising for greener production of hybrid polymer materials, due to shorter reaction times, reduced energy consumption, and better yields.

The focus of this chapter will be on the microwaves, ultrasound and plasma assisted functionalization of CNTs as greener chemistry methods to produce hybrid polymer materials. After a brief overview on preparation of hybrid polymer materials containing CNTs, we will present the physical principles, mechanisms and processing conditions involved in the functionalization of CNTs for each of these "*Green*" chemistry methods, and then present our point of view on challenges and opportunities in both the immediate and long-term future.

2. Hybrid polymer materials

In polymer science, we can define a *hybrid polymer material* as a combination of two or more materials mixed at the nanometer level, or sometimes at the molecular level (0.1 – 100 nm) in a predetermined structural configuration, covering a specific engineering purpose. The term *hybrid material* is used to distinguish them from the conventionally known *composites* that are referred as simple mixtures of two or more materials at micro-scale level (> 1 μm).
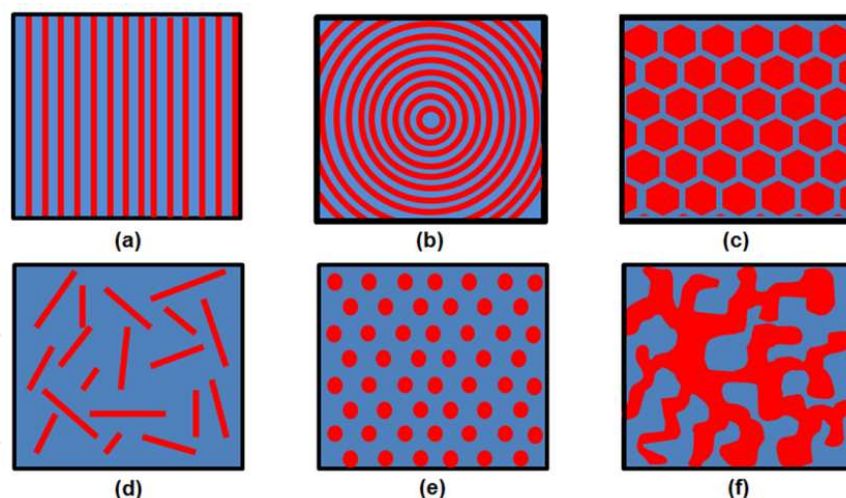

Figure 1. Some examples of structural configurations of hybrids of the composite type: (a) sandwich, (b) concentric cylindrical shells, (c) honeycomb, (d) chopped fibers, (e) particulate, and (f) amorphous blend.

An ideal hybrid polymer material requires an accurate molecular design or structural control of its components in order to obtain synergistic properties. As structural configuration of components moves away from its ideal configuration, the material properties will range from an arithmetic average value (average of the properties of each component) to below of that arithmetic value [5]. Thus, the shape and structural configuration of the components in

a hybrid polymer material play a key role in determining its properties. Figure 1 shows a scheme of hybrids materials composed by two components, in which one of them is arranged so that synergistic properties can be achieved.

The hybrid polymer materials can be classified depending of the nature of interactions between their components. In particular, when structural materials in the form of particles, flakes or fibers are incorporated into polymer matrices, this type of hybrid polymer materials can be classified in (i) *class I* hybrid materials, which show weak interactions between the two components, such as van der Waals, hydrogen bonding or weak electrostatic interactions, and (ii) *class II* hybrid materials, which show covalent interactions between both components such that there is no tendency for the components to separate at their interfaces when the hybrid material is loaded [6].

Hybrid polymer materials containing CNTs have attracted considerable attention due to the unique atomic structure, high surface area-to-volume ratio and excellent electronic, mechanical and thermal properties of carbon nanotubes. Although the incorporation of CNTs to polymer matrices have significantly improved the mechanical, electrical and morphological properties of polymers, there is plenty of room for controlling the structural configuration of the hybrid polymer material, thus, different efforts have been focused in the preparation methods.

3. Polymer-CNTs hybrid materials

3.1. Structural configuration

Since the first ever materials based on polymer-CNTs were reported in 1994 by Ajayan *et al*. [7], several processing methods have been developed for fabricating polymer-CNTs hybrid materials. These methods mainly include solution mixing, *in-situ* polymerization, and melt blending [8].

Because the unique mechanical properties of CNTs, such as the high modulus, tensile strength and strain to fracture, there have been numerous efforts to obtain hybrid materials with improved mechanical properties [2]. Within the structural configurations for this specific application, the "*chopped fibers*" configuration, as seen in Figure 1(d), has been the most desired.

On the other hand, for other unique properties of CNTs such as high electrical and thermal conductivity, the obtaining of multiphase polymer amorphous blends, as seen in Figure 1(f), offers a much higher potential for the development of conductive composites containing CNTs. The selective localization of the CNTs either in one of the blend phases or at the interface of an immiscible co-continuous blend can form an ordered network of conductive phase, creating the so-called segregated systems [9]. In such systems, considerably lower value of percolation threshold compared to "*chopped fibers*" structural configuration can be achieved.

The building of polymer-CNTs hybrid materials with desired structural configurations is potentially promising to develop advanced hybrid materials; however, the full exploitation of

properties of CNTs by means the manufacturing of those desired structural configurations has been severely limited, because difficulties associated with dispersion of the entangled CNTs during processing and their poor interfacial interaction with some polymer matrices.

3.2. Chemical and physical functionalization of CNTs

The efficient exploitation of the unique properties associated with CNTs depends on its uniform and stable dispersion in the host polymer matrix, as well as the nature of the interfacial interactions with the polymer. Thus, obtaining of polymer-CNTs hybrid materials with desired properties has represented a great challenge, because CNTs exhibit strong inter-tube van der Waals' forces of attraction that impede its uniform and stable dispersion in the matrix, in addition to certain properties of the polymer matrix like wetting, polarity, crystallinity, melt viscosity, among others [2, 10].

Surface modification of CNTs has been one of the most used strategies in order to improve its affinity with the polymer matrix, and therefore to achieve a better uniform dispersion. These methods have been conveniently divided into chemical functionalization and physical functionalization [3, 11].
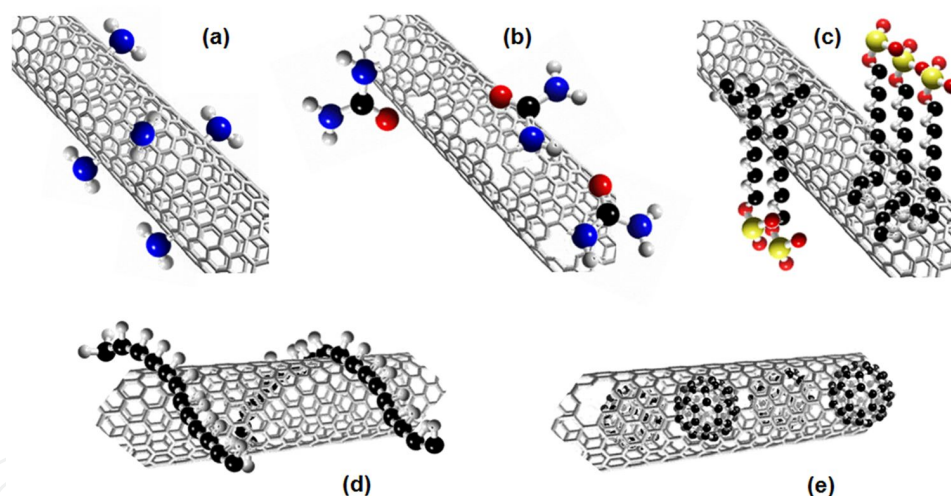

Figure 2. Strategies for chemical and physical functionalization of CNTs: a) covalent sidewall functionalization, b) covalent defect sidewall functionalization, c) non-covalent adsorption of surfactants, d) wrapping of polymers, and e) endohedral functionalization (case for C_{60}).

Chemical functionalization method is based on the covalent linkage of functional groups such as –COOH or –OH on the surface of CNTs. These methods can be also divided in sidewall functionalization and defect functionalization (see Figure 2). The reaction mechanisms that take place at their sidewall include fluorination and derivate reactions, hydrogenation, cycloaddition, and radical (R•) attachment; whilst the reaction mechanisms by amidation, esterification, thiolation, silanization, and polymer grafting (*grafting to* and *grafting from*) takes advantages of chemical transformation of defect sites on CNTs.

Physical functionalization method is based in the formation of non-covalent interactions between molecules and CNTs. These methods include the wrapping of polymer around the CNTs, the physical adsorption of surfactants and the endohedral method (see Figure 2). In the latter, molecules are stored in the inner cavity of CNTs through the capillary effect, where the insertion often takes place at defect sites localized at the ends or on the sidewalls.

In particular, the covalent functionalization of CNTs has been one of the most preferred methods since it allows an efficient interaction between polymer-CNT interface through the functional moieties of the CNTs surface and the available functional groups of the polymer. However, these methods involve rough acid treatment conditions during functionalization which damage the nanotube framework and decrease the electrical conductivity of the hybrid material. In addition, the use acids and organic solvents as the reaction media represent problems of environmental pollution and health hazard.

In this context, the global trend of seeking for "*Green*" chemistry methods is demanding to researchers in the field to develop environment-friendly methods to functionalize CNTs.

4. Greener production of polymer-CNTs hybrid materials

4.1. "*Green*" chemistry: definition and principles

Diverse definitions of "*Green*" chemistry can be found in the literature. According to EPA (Environment Protection Agency) "*Green*" chemistry philosophy speaks of chemicals and chemical processes designed to reduce or eliminate negative environmental impacts, where the use and production of these chemicals may involve reduced waste products, non-toxic components, and improved efficiency. Anastas and Warner [12], who are considered the founders of this field that born in 1990s, define "*Green*" chemistry as the utilization of a set of principles that reduce or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products.

The 12 Principles of "*Green*" chemistry (defined by Anastas and Warner) help us think about how to prevent pollution when creating new chemicals and materials:

1. *Prevention*. It is better to prevent waste to treat or clean up waste after it has been created.

2. *Atom Economy*. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

3. *Less Hazardous Chemical Synthesis*. Synthetic methods should be designed to use and generate substances that possess little or no toxicity to people or the environment.

4. *Designing Safer Chemicals*. Chemical products should be designed to affect their desired function while minimizing their toxicity

5. *Safer Solvents and Auxiliaries*. The use of auxiliary substances should be made unnecessary whenever possible and innocuous when used.

6. *Design for Energy Efficiency*. Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.

7. *Use of Renewable Feedstocks*. A raw material or feedstock should be renewable rather that depleting whenever technically and economically practicable.

8. *Reduce Derivatives*. Unnecessary derivatization like use of blocking group, protection/de-protection, and temporary modification of physical/chemical processes, should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

9. *Catalysis*. Catalytic reagents should be superior to stoichiometric reagents.

10. *Design for Degradation*. Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.

11. *Real-Time Analysis for Pollution Prevention*. Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formations of hazardous substances.

12. *Inherently Safer Chemistry for Accident Prevention*. Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

"*Green*" chemistry is a highly effective approach to pollution prevention since it applies innovative scientific solutions to real-world environmental situations. The preparation of polymer-CNTs hybrid materials can be considered as "*Green*" as more of those principles are applied to the design, production and processing of hybrid materials.

4.2. Greener processing technologies

4.2.1. Microwaves

4.2.1.1. Background and physical principles

Microwaves are electromagnetic waves with wavelengths ranging from 1 mm to 1 m and frequencies between 0.3 GHz and 300 GHz, respectively. 0.915 GHz is preferably used for industrial/commercial microwave ovens and 2.45 GHz is mostly used for household microwave ovens. Since the first ever report of a microwave-assisted organic synthesis in the 80s, it is being further developed and extended to polymer science, in particular in the field of microwave-assisted polymer synthesis and polymer nanocomposites [13].

In polymer chemistry, microwave-assisted reactions present a dramatic increasing in reaction speed and significant improvements in yield compared with conventional heating. These advantages are attributed to instantaneous and direct heating of the reactants, which lead to reduction in reaction time, energy savings and low operating costs. The principles 2, 5, 6 and 11 of '*Green*' chemistry describe these strengths.

How does microwave irradiation lead chemical reactions? When a dielectric material (i.e. molecules containing polar groups in their chemical structure) is placed under microwave irradiation, the dipolar molecules will tend to align their dipole moment along the field intensity vector. As the field intensity vector varies sinusoidally with time, the polar molecules re-align with the electro-magnetic field and generate both translational and rotational motions of the dipoles. These movements generate heat because the internal friction, so a portion of the electromagnetic field is converted in thermal energy.

The power absorbed per unit, P (V/m^3) is expressed as [14]:

$$P = 2\pi f\, \varepsilon_0 \varepsilon_r^{''} \mid E \mid^2 \qquad (1)$$

where f is the microwave frequency (GHz), ε_0 the permittivity of free space ($\varepsilon_0 = 8.86 \times 10^{-12}$ F/m), $\varepsilon_r^{''}$ the dielectric loss factor and E (V/m) is the magnitude of the internal field.

The dielectric loss factor is a measurement of the efficiency with which microwave energy is converted into heat, and depends on the dielectric conductivity σ and on the microwave frequency f according to

$$\varepsilon_r^{''} = \sigma / 2\pi f \qquad (2)$$

The degree of energy coupling in the reaction system is expressed by the dissipation factor D, which is defined by the loss tangent $\tan \delta$

$$D = \tan\delta = \varepsilon_r^{''} / \varepsilon_r^{'} \qquad (3)$$

where $\varepsilon_r^{'}$ is the relative dielectric constant and describes the ability of molecules to be polarized by the electric field. Thus, the dissipation factor defines the ability of a medium at a given frequency and temperature to convert electromagnetic energy into heat.

Therefore, the absorbed microwave energy into dielectric material produces the molecular friction, which leads the rapid heating of the reaction medium and the subsequent chemical reactions. The dramatic rate enhancements of these reactions have been explained by means of very well-known Arrhenius law:

$$k = A\exp[-E_a / RT] \qquad (4)$$

Some authors have suggested that, the microwave dielectric heating increases the temperature of the medium in a way that cannot be achieved by conventional heating (superheating), so the rate enhancements are considered essentially a result of thermal effects, although the exact temperature reaction has been difficult to determine experimentally [15]. Other authors, however, suggest that the microwave energy produces an increase in molec-

ular vibrations which could affect anyway the pre-exponential factor A, and also produce an alteration in the exponential factor by affecting the activation energy [16, 17].

After 50 years of research, microwave chemistry is still a research field in expansion and also seems it as green technology; however, some questions regarding microwave heating mechanisms remain unsolved. The microwave-assisted production of polymer-CNTs hybrid materials is a recent field of research, in which additional questions have emerged. Beyond to give an overview on microwaves-assisted preparation of hybrid materials, this section is addressed under one of those questions: how could microwave energy be controlled to prepare more efficiently these hybrid materials? As discussed below, the answer to this question is still not understood.

4.2.1.2. Carbon nanotubes-microwaves interaction

Carbon nanotubes have demonstrated to act as highly efficient absorbers of microwave energy, producing heating, outgassing and light emission [18]. Over the past few years, the investigation on microwave heating mechanisms in CNTs has been a focus of interest. It has been proposed that the microwave irradiation might cause heating by two plausible mechanisms [19]: (i) Joule heating and (ii) vibrational heating.

The mechanism of *Joule heating* postulate that the electric field component of the microwave induces the motion of the electrons in electrically conductive impurities present at as-synthesised CNTs such as metallic catalysts, leading a localised superheating at the site of impurities which increase the temperature of CNTs. In addition, another suggested potential source of localized superheating has been the generation of gas plasma from absorbed gases (particularly H_2) in CNTs, introduced during the synthesis phase or via atmospheric absorption.

The sources of superheating in the *Joule heating* mechanism are focus of discussion. It has been argued that the nano-sized magnetic particles should be impacted minimally by microwave irradiation at low frequencies and therefore, plays no significant role in the microwave energy absorption. Paton *et al.* work [18], among others, demonstrated that even with the removal of iron and other catalytic particles, the CNTs still present microwave heating. On the other hand, regarding to gas plasma, it is still unclear if the plasma is directly generated by microwave irradiation or by other superheating effect. Moreover, it is doubtful that plasma be generated under presence of solvents, since their conductivity is higher than air.

Paton *et al.* [18] hypothesized that *Joule heating* mechanism in CNTs can be explained by the motion of free electrons distributed on the surface of the CNTs, induced by the electric field component of the electromagnetic field. This theory was supported by the measurements of DC conductivity of as-synthesised, heat and acid treated CNTs. The microwave energy absorption was significantly increased as the crystallinity and electrical conductivity of CNTs were improved.

Regarding to *vibrational heating* mechanism, Ye [20] described the heating of non-bounded CNTs in terms of non-linear dynamics of a vibrating nanotube. CNTs subjected to microwaves undergo superheating due to transverse vibrations attributed to parametric resonance, similarly to forced longitudinal vibrations of a stretched elastic string. Ye found that

CNTs present a resonance frequency between 2.0 – 2.5 GHz, which is in the region of the frequency of microwaves of the most operating systems used in this field (2.45 GHz). However, the intensity of vibration modes might be attenuated by the presence of impurities, a viscous environment, and highly entangled CNTs.

Both *Joule heating* and *vibration heating* mechanisms help to explain the different obtained results of microwave energy absorption, in the presence of solvents or dry conditions. However, the need of an in-depth understanding of the microwave heating mechanisms is more tangible as microwave-CNTs systems become more complex.

4.2.1.3. Microwaves-assisted functionalization of CNTs

Within the standard procedures to chemically functionalize CNTs is firstly the purification phase. The most common techniques include acid reflux, oxidation and filtration, where most of them involve long processing times or multiple stages, the use of large acid volumes and some cases the structural damage of CNTs [3]. Microwave-assisted purification of CNTs has emerged as promising technique for effective purification of CNTs with minimal damages and significant reduction of the processing times and use of harmful reactants [19].

Purification has been attributed to generation of highly localized temperatures within metallic particles which burst any amorphous carbon coating. During purification phase in conventional techniques, the use of aggressive treatments facilitates the creation of defect sites on sidewall of CNTs, in order to graft desired functional groups; however, in microwave-assisted processes the energy absorbed by CNTs leads the activation of vacancy sites on surface and the subsequent reaction with active functional groups of molecules. At the same time, the microwave irradiation can supply enough energy to reorient any "damaged" sp^3 carbon bonds into sp^2 hybridization, thus leading an increase in CNTs quality.

As described previously, the main goal of functionalization of CNTs in the preparation of hybrid materials is to improve their dispersion degree and interaction with the polymer matrix. Thus, the challenge of microwave-assisted functionalization is to achieve a desired degree of functionalization on CNTs surface, whilst avoiding damages of the structure that could compromise the properties of the final product. A review on recent works in microwave-assisted functionalization of CNTs was published by Ling and Deokar [21], and it is not our intent to duplicate that effort here. Rather, we focus on some "*Green*" key issues that might improve the preparation of hybrid polymer materials through control of microwave energy absorption.

In this context, microwave-assisted functionalization under solvent-free conditions is a promising approach for large-scale functionalization of CNTs and paves the way to greener chemistry, because in the absence of solvents, the CNTs and reagents absorb the microwave energy more directly and so takes full advantage of the strong microwave absorption of such components. In addition, the solvent-free conditions open the possibility to all proposed microwave heating mechanisms, and therefore increase the absorption of microwave energy.

The use of solvent-free conditions involves the use of bulk CNTs, so dealing with the entangled CNTs results more complicated. Although some works have carried out using solvent-

free conditions during microwave irradiation [22-25], a pre-dispersion stage of CNTs with ultrasound in solvent systems is still used. Recently, Ávila-Orta *et al*. [26, 27] developed a method of dispersion of nanostructures in gas phase assisted by ultrasound, enhancing the dispersion of bulk CNTs under solvent-free conditions.
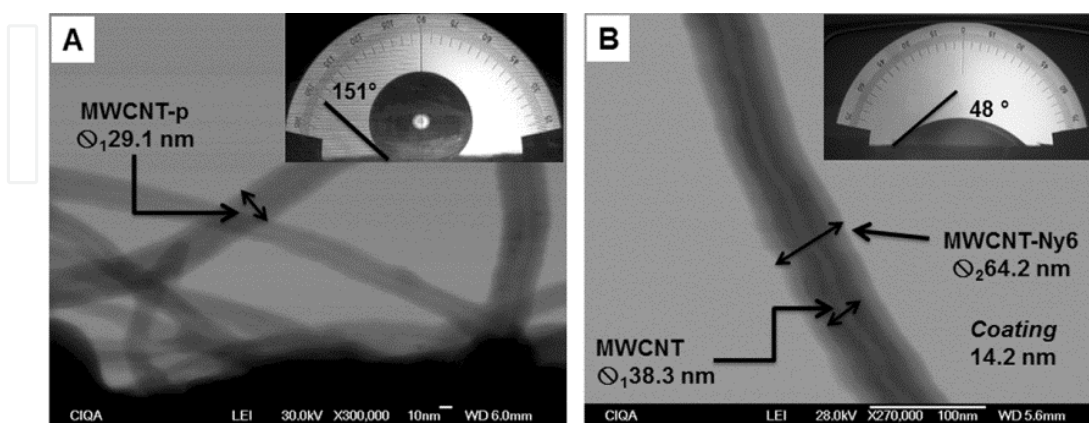

Figure 3. STEM images of MWCNTs. a) pristine MWCNTs (MWCNT-p), and b) functionalized MWCNTs with Nylon (MWCNT-Ny6). [28].
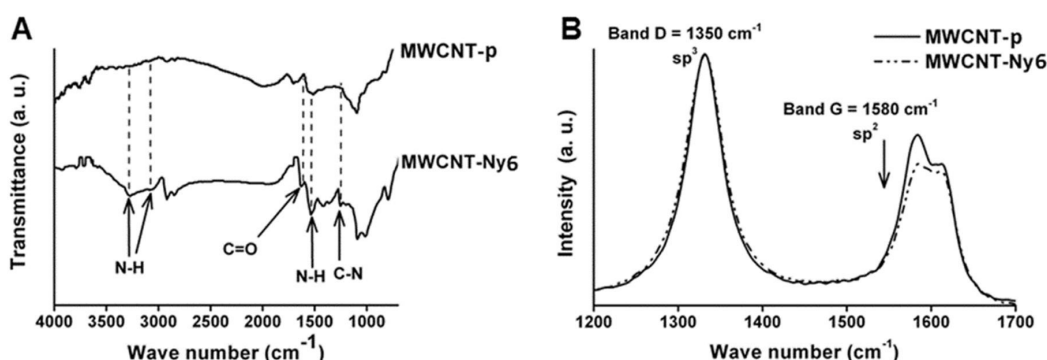

Figure 4. Evidence of the formation and grafting of Nylon-6 on surface of MWCNTs: a) FTIR spectrum, and b) RAMAN spectrum. [28].

González-Morones [28] used the dispersion method developed by Ávila-Orta *et al*. in order to functionalize multi-walled carbon nanotubes (MWCNTs) with Nylon through "*grafting from*" strategy, using ε-caprolactam and aminocaproic acid as monomers. The MWCNTs were previously dispersed into a recipient containing air and then blended with ε-caprolactam powder. The blend was treated for 30 min using a multimodal microwave oven (2.45 GHz) at 250 °C and microwave power of 600 W. Figure 3 shows a STEM image of function-alized carbon nanotubes, in which the average thickness of the polymeric coating was 14.2 nm. The contact angle measurements for pristine and functionalized MWCNTs are also showed in the Figure 3. The reduction in hydrophobic character of MWCNTs-p represented by a decreasing in their contact angle (from 151° to 48°) suggests the presence of a hydro-philic coating. Furthermore, the FTIR spectrum for functionalized MWCNTs shows the

presence of the characteristic functional groups of Nylon-6 (Figure 4a), which demonstrates the formation of Nylon-6 by hydrolytic polymerization; whilst the RAMAN spectrum shows a decreasing in the G band intensity (sp^2), suggesting that Nylon-6 are grafted on the surface of MWCNTs through actives sites created during microwave irradiation.

Although the pre-dispersion stage of CNTs in gas phase assisted by ultrasound reduce the consumption of solvent ("*Green*" principle # 5), after the functionalization by microwaves, it is still necessary the use of organic solvents to eliminate the residual monomer ("*Green*" principle # 8). Thus, in order to boost the advantages of this pre-dispersion phase, the efforts should focus on pathways to increase the conversion of reagents ("*Green*" principles # 2, 6 and 9).

4.2.1.4. Preparation of polymer-CNTs hybrid materials

Some efforts have been performed in the preparation of hybrid materials under solvent-free conditions. Virtanen *et al.* developed a hybrid material with a structural configuration sandwich-like (similar to Figure 1a), composed by two polymer plates (extremes) and a film made up from functionalized CNTs (center) which were joined by microwave irradiation [29]. Lin *et al.* obtained hybrid material from microwave-assisted cured process of epoxy resin containing vertically aligned CNTs [30].
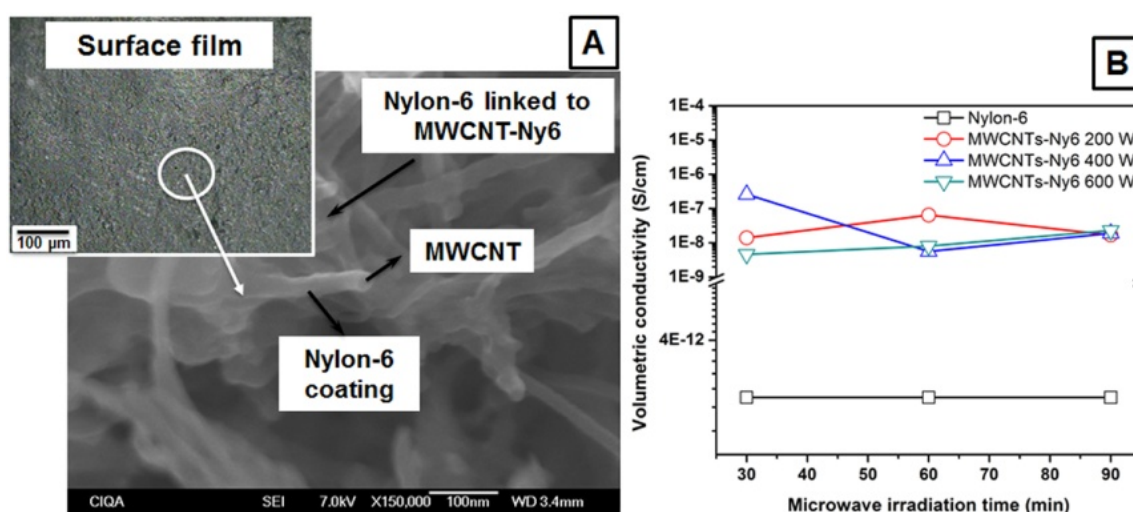

Figure 5. Nylon-6/MWCNTs hybrid material obtained by *in-situ* polymerization assisted by microwaves. a) STEM images of a film made from a hybrid material obtained at microwave power of 600 W, and b) conductivities values of hybrid materials as function of microwave power. [32].

Because a special interest is placed on one-step processes for preparation of those materials, the combined process of in-situ functionalization of CNTs by "*grafting from*" and in-situ bulk polymerization by microwave irradiation becomes a very attractive approach. In recent years, Dr. Ávila-Orta's group has focused on preparation of hybrid materials with electrical conductivity properties; so a structural configuration with an interconnection between CNTs is mostly desired. The combined process described above has demonstrated to be a good approach to enhance this structural configuration.

In this context, Yañez-Macías *et al.* [31, 32] prepared Nylon-6/MWCNTs hybrid material films with high electrical conductivities (values ranged from 10^{-9} to 10^{-7} S/cm) using this combined process. In that work, the MWCNTs were also previously pre-dispersed using the method developed by Ávila-Orta *et al*. The influence of microwave power on polymerization was studied for 200, 400 and 600 W. Figure 5 shows STEM images of a film made from Nylon-6/MWCNTs hybrid material obtained after 90 min of reaction at 600 W. The image shows as the MWCNTs are interconnected and coated by Nylon-6.

From Yañez-Macías *et al*. work, the microwave power intensity demonstrated to play a crucial role in the hydrolytic polymerization. As microwave power intensity increases the yield of Nylon-6 increases, however, at higher microwave power intensity degradation mechanism occurs. These results show that efficient production of polymer-based CNTs in solvent-free conditions can be boosted through control of microwave energy applied to bulk medium.

4.2.1.5. Future perspectives

Microwave irradiation under solvent-free conditions in combination with a pre-dispersion stage of CNTs in gas phase represents a promising approach to large-scale greener production of polymer-based CNTs hybrid materials. The pre-dispersion stage of CNTs allows increasing the efficiency in the microwave energy absorption and the available surface to their functionalization. However, although great efforts have been developed for in-situ preparation of polymer-CNTs hybrids, it is still required to improve the yield.

The control in the yield of functionalization and polymerization reactions can be performed through an in-depth understanding of the mechanisms of microwave heating and kinetic reactions studies. Since the increasing of microwave power intensity increases the temperature of medium reaction, after further research, an optimum microwave energy supply can be found as function of microwave power intensity. In addition, the use of mono-modal microwave ovens can improve the efficiency in the microwave energy absorption, because the microwaves are only concentered in a reaction volume and are not dispersed around chamber volume like multi-modal microwave ovens.

4.2.2. Ultrasound

4.2.2.1. Background and physical principles of sonochemistry

Ultrasound (US) is defined as sound that is beyond human listening range (i.e. 16 Hz to 18 kHz.). In its upper limit, ultrasound is not well defined but is generally considered to 5 MHz for gases and 500 MHz for liquids and solids, and is also subdivided according to applications of interest. The range of 20 to 100 KHz (although in certain cases up to 1 MHz) is designated as the region of high power ultrasound (*sonochemistry*), while the frequencies above 1 MHz are known as high frequency or ultrasound diagnostics (e.g. the imaging technique using echolocation, as SONAR system to detect or US in the health care).

Since the first report on the chemical effects of high power ultrasound in 1927, when Loomis and Richards [33] studied the hydrolysis of dimethyl sulfate and iodine as a catalyst; the stud-

ies on chemical effects of ultrasound have further extended to several areas such as organic and organometallic chemistry, materials science, food, and pharmaceutical, among others [34].

The use of ultrasound to accelerate chemical reactions has proven to be a particularly impor‐ tant tool for meeting the "*Green*" Chemistry goals of minimization of waste, reduction of ener‐ gy and time requirements ("*Green*" principles # 6, 8 and 11). Thus, nowadays the applications of ultrasonic irradiation are playing an increasing role in chemical processes, especially in cas‐ es where classical methods require drastic conditions or prolonged reaction times [35].
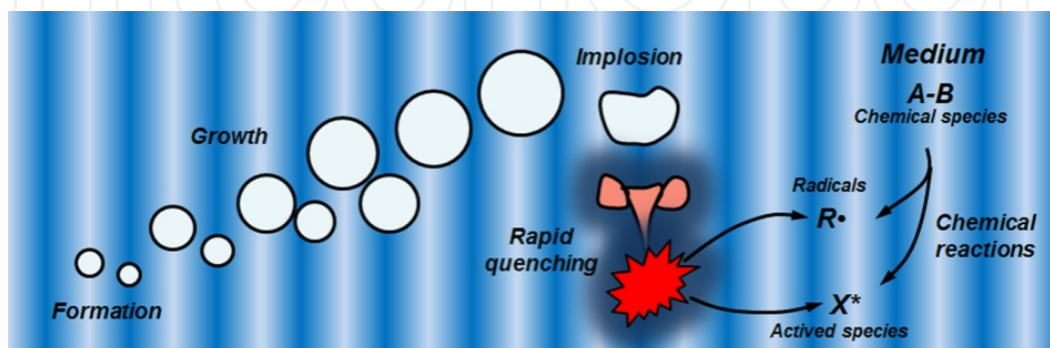

Figure 6. Chemical effects of the high power ultrasound derived from bubble collapse.

The chemical effects of ultrasound in liquids systems are derived from the formation, growth and implosion of small bubbles that appears when the liquid is irradiated by ultra‐ sound waves, phenomenon called "acoustic cavitation" [36]. During bubble collapse, the conversion of kinetic energy of the liquid into thermal energy generates high temperatures (1000 – 10,000 K, most often in the range 4500 to 5500 K) and pressure conditions (~ 500 atm), which lead the formation of free radicals and active species as a result of the heating of the bubble content (Figure 6). On the other hand, the surrounding liquid quenches these portions of the medium in less than 10^{-6} seconds. Thus, the high local temperatures and pressures, combined with extraordinarily rapid cooling, provide a unique means for driving chemical reactions under extreme conditions [34].

A combination between the capability of ultrasonic irradiation to induce chemical reactions and also to achieve a full dispersion of nanostructures in different systems represents a syner‐ gistic approach to produce polymer-carbon nanotubes hybrid materials, because surface mod‐ ification and dispersion of CNTs might take place at the same time; however, unlike microwaves and plasma technologies, there have been very few efforts for exploring it. In this section, we discuss some keys issues associated with the functionalization of CNTs, in order to foster the use of ultrasonic irradiation as greener method for preparation of hybrid materials.

4.2.2.2. Mechanisms for ultrasound activation

The studies on sonochemistry have demonstrated that the ultrasonic irradiation differs from traditional energy sources (such as heat, light or ionizing radiation), so it has been used as a source of alternating activation to assist chemical processes, such as in synthetic methods for

obtaining organic molecules and macromolecules and inorganic [37, 38], extraction of natural and synthetic products [39], and medicine [40]. The enormous local temperatures, pressures as well as the heating and cooling rates generated during bubble collapse provide an unusual mechanism for generating high-energy chemistry. However, despite chemical effects of ultrasound have been studied for many years, the mechanisms underlying these effects are too complex and not well-understood.

It has established that during bubble cavitation, three sites for chemical reactions can be identified [41]: i) the interior of the bubble, ii) the interface region at around the bubble surface, and iii) the liquid region outside the interface region (Figure 6). In the interior of a bubble, volatile solute is evaporated and dissociated due to extreme high temperature, where depending of the nature of the system, different free radicals and excited species are generated. Those chemical species with a relatively long lifetime can diffuse out of the interface region and chemically react with solutes or the bulk medium; whilst in the interface region, in addition to high temperatures due to the thermal conduction from the heated interior of a bubble, the presence of relatively short lifetime species such as OH• and O• can lead more interesting chemical reactions.

When a solid material is present in a cavitation medium, the high speed of the liquid jet generated during bubble collapse produces a violent impact on solid surface, in which some material can be removed (e.g. ultrasonic cleaning processes). On the other hand, from a chemical point of view, the shock waves emitted by the pulsating bubbles and the liquid flow around the bubble enhance a mass transfer toward the solid surface during bubble collapse, so the free radicals and the active species generated are available to induce different chemical reactions on solid surface.

4.2.2.3. Ultrasound-assisted functionalization of CNTs

One of the most common methods to functionalize CNTs is acid treatment at elevated temperatures. In this process, functional groups such as hydroxyl (-OH), carboxyl (-COOH), and carbonyl (-C=O) can be introduced into a carbon nanotube network through their physical defects and sites with imperfections. In particular, electron-spin-resonance (ESR) studies on the acid-oxidized CNTs demonstrated that sites with unpaired electrons are generated on CNTs surface, and are significantly increased when acid-treatment functionalization is assisted by high power ultrasound. Moreover, Cabello-Alvarado *et al*. [42] reported the ultrasound-assisted functionalization oxidation of MWCNTs using H_2SO_4/HNO_3. The MWCNTs were subjected to ultrasonic radiation by 8 hours at 60 °C, obtaining similar results to those reported using high temperatures H_2SO_4/HNO_3 mixture [43].

Ultrasound-assisted acid-treatment functionalization is an ideal alternative for reducing reaction conditions and increase rates of reaction, but the use of strong acids as reagents does not contribute largely to "*Green*" chemistry. However, the high speed of the liquid jet generated during bubble collapse can be strong enough to disperse the CNTs agglomerates and also rupture some covalent carbon-carbon bonds of CNTs, and so, generates those sites with unpaired electrons or "active sites" and subsequently induces desired chemical reactions with the surrounding molecules (Figure 7). As proof of this, in 2006, Chen and Tao reported the functional-

ization of SWCNTs with polymethyl methacrylate by "*grafting from*" [44]. In that work, SWCNTs were irradiated by ultrasound in methyl methacrylate monomer and polymer grafted CNTs were obtained by *in-situ* sonochemically initiated radical polymerization.
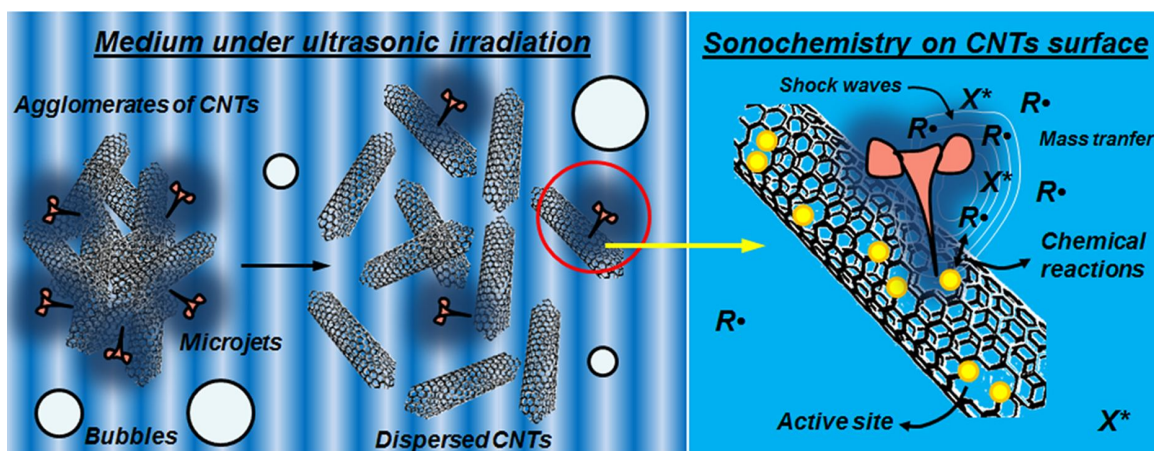

Figure 7. Scheme of the activation mechanism of the CNTs surface treated with ultrasound.

However, the damages of the sp^2-carbon network derived from rupture of carbon-carbon bonds trends to reduce both mechanical and electrical properties of CNTs. Therefore, further research on new pathways to preserve such properties is required. In this context, recently Gebhardt *et al.* [45] developed a novel covalent sidewall functionalization method of CNTs that allowing preserves the integrity of the entire σ-framework of SWCNTs in contrast to classical oxidation. The reductive carboxylation of SWCNTs under ultrasonic treatment resulted in a highly versatile reaction with respect to electronic type selectivity, since functionalization occurs preferentially on semiconducting CNTs. Also, the degree of functionalization can be controlled thought handling of external variables such as pressure.

The emerging on new pathways on ultrasound-assisted functionalization methods could displace to conventional acid treatment methods of CNTs and therefore, opening the possibility for more efficient and greener chemistry methods.

4.2.2.4. Preparation of polymer-CNTs hybrid materials by sonochemistry

The preparation of polymer-CNTs hybrid materials assisted by ultrasound is a feasibility approach since ultrasound has influence on the dispersion of the CNTs and activation of their surface, thereby facilitating interaction between the polymer and the CNTs. In addition, the sonochemical activation can lead polymerization reactions, so offers more attractive features such as low reaction temperatures and short reaction times compared with conventional methods.

Thus, the obtaining of polymer-CNTs hybrid materials by *in-situ* bulk polymerization assisted by ultrasound represents a viable method to exploit all these features: i) a full dispersion of CNTs can be obtained in monomer solution, at same time that ii) the effects of bubble collapse activates the surface of CNTs and lead the *in-situ* functionalization with monomer

molecules, in which also iii) the polymerization is started sonochemically. Park *et al*. reported the preparation of poly(methyl methacrylate) (PMMA)-MWCNTs nanocomposites with AIBN and different content of MWCNTs [46]. The molecular weight of polymer matrix increased as MWCNTs content was increased due to generation of initiator radicals on CNTs surface. Kim *et al*. prepared polystyrene-MWCNTs nanocomposites without any added initiator, in which an electrical percolation threshold less than 1 wt% was obtained [47].

Although the role of CNTs as effective initiators and control agents for radical polymerizations have been recently demonstrated by Gilbert *et al*. [48], the ultrasound irradiation is more widely used as an alternative method of dispersion, but not as a source of sonochemical activation, leaving large areas of opportunities to explore.

Ultrasound technology is also applied in dispersion and preparation of nanocomposites in melt blending; however the concepts of sonochemistry and surface activation of CNTs that address this section might not be applied to such systems, due to cavitation phenomenon is dramatically suppressed and the chemical effects might be dominated by mechanochemical phenomenon different from cavitation [49].

4.2.2.5. Future perspectives

Ultrasound is a viable source of "*Green*" activation in the context of "*Green*" chemistry, since it has demonstrated to promote low reaction temperatures, faster reaction rates and higher yields in functionalization and polymerization processes. Notably, each of these chemical processes require a source of activation that efficiently furnishes the energy necessary to activate the carbon-carbon bonds in the CNTs network, so in order to perform the "*activation*" of the surface of the CNTs, further research on mechanism of interaction between ultrasound-CNTs has to be addressed taking into account factors such as ultrasound power, environmental solvents, temperature and being one of the most important the sonication time. In particular, the use of environmental solvents could be an interesting factor due the solvent is crucial in the process of bubble cavitation.

4.2.3. Plasma

Plasma, the fourth state of the matter, is generated when atoms and molecules are exposed to high sources of energy such as those produced by direct current (DC), alternating current (AC), microwaves and radio frequency (RF). The absorbed energy by such atoms and molecules induces particle collision processes which generate electrons, photons, and excited atoms and molecules. Because of the unique active species present in the plasma, this state of the matter is used in the synthesis [50] and surface modification of CNTs [51].

Regarding to preparation of polymer-CNTs hybrid materials, unlike microwaves and ultrasound technologies described earlier, plasma is mainly used for functionalization of CNTs in order to later use them in the preparation of hybrid materials by *in-situ* polymerization [52, 53] and melt blending [54]. As described before, the surface modification of CNTs leads to improve the dispersion and interactions between CNTs and polymer matrix and represent a critical issue to enhance properties of polymer-CNTs hybrid materials; thus, this section is focused

on the role of plasma-CNTs interactions in the functionalization of CNTs by polymer grafting, in order to exploit more efficiently the unique properties of CNTs (Green principles # 2, 6).

4.2.3.1. Plasma-assisted functionalization of CNTs

The functionalization mechanisms of CNTs by plasma are carried out by both *etching* and *coating* processes [55]. A physical etching process is presented when ions bombard to CNTs leading erosion on CNTs surface and therefore vacancies or "active sites", whilst a chemical etching process is induced by surface reactions between reactive ions and CNTs. Chemical processes are limited to non-inert plasma gases, whilst both inert and reactive gases can produce the physical effects. On the other hand, the coating process results from physical or chemical deposition of the active species present at plasma environment, in which the chemical deposition is induced through the active sites generated from the etching process. A scheme of these mechanisms of functionalization of CNTs is presented in Figure 8.
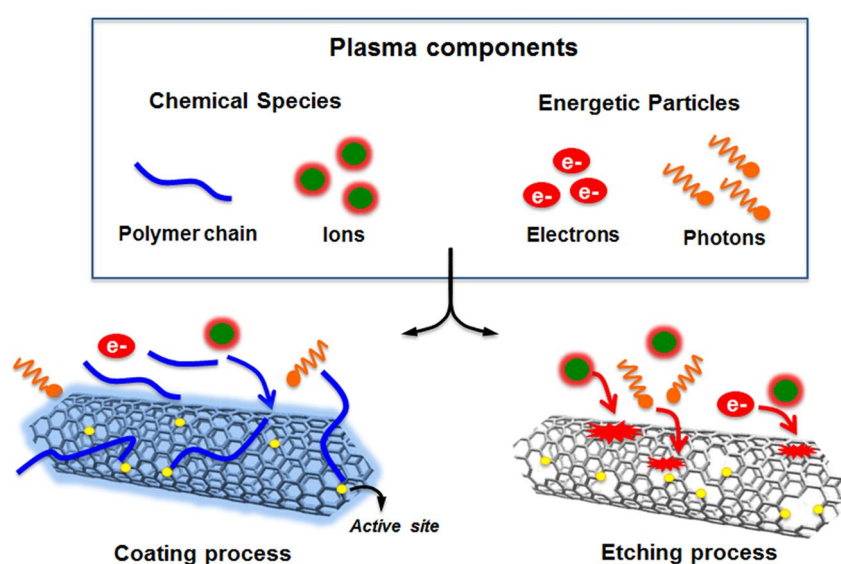

Figure 8. Etching and coating process on CNTs surface.

In order to obtain polymer-CNTs hybrid materials, the functionalization of CNTs with polymers is one of the most preferred strategies to improve the compatibility of CNTs with polymer matrices. In this context, the functionalization of CNTs by polymer grafting occurs when ionized monomers interact with active sites on CNTs surface leading the growth of polymer chains (grafting from/etching process), and also when polymer chains present into plasma environment are physically or chemically deposited on CNTs surface (grafting to/coating process). However, both etching and coating process can occur simultaneously, thus the surface coating can retard the etching process whilst etching can remove the surface coating depending of the plasma gas chemistry.

The surface modification of CNTs based on plasma polymerization presents some advantages compared to wet chemical processes: i) surface modification without altering CNTs bulk properties ("*Green*" principles # 2, 6), ii) large amount of reagents and extreme temperatures

are avoided ("*Green*" principles #3, 5 and 6), and iii) a product with no or very low amount of residual monomer can be obtained ("*Green*" principles # 2 and 8).

Despite these "*Green*" advantages, there are few reports about functionalization of CNTs based on plasma polymerization. Chen *et al*. reported the functionalization of CNTs using the monomers acetaldehyde and ethylenediamine [51]; Shi *et al*. reported the plasma deposition of polypyrrole on CNTs surface [56]; Ávila-Orta *et al*. modified MWCNTs using ethylene glycol as monomer [57]; and more recently, Chen *et al*. reported the preparation of MWCNTs grafted with polyacrylonitrile [58], and Rich *et al*. reported the surface modification of MWCNTs using methyl methacrylate and allylamine as monomers [59].

Because of the structural and chemical character of the polymer coating play an important role on interaction between CNTs and polymer matrix, the structural and chemical nature of the polymer coating obtained by plasma can be controlled through processing parameters. Recently, González-Morones [28] studied the effect of power excitation on chemical nature of the polymer deposited on CNTs surface by plasma polymerization of acrylic acid. In that work, firstly the CNTs were pre-dispersed using the method developed by Ávila-Orta *et al*. [27], then the CNTs were exposed to acrylic acid plasma. It was observed that at low power excitation (20 W) the CNTs surface is partially coated by polyacrylic acid and –COOH groups. At power excitation of 40 W, the polyacrylic acid and -COOH groups are mostly removed since the etching process is favored. Whilst at power excitation of 100 W, the CNTs are partially coated by the polymer and functional groups, thus suggesting a competition between etching and coating process. Figure 9a shows FTIR spectra of the functionalized CNTs at different power excitation. For each case, the solubility in water of the functionalized CNTs is showed in a photograph. A STEM image of the polymer coating on the CNT surface obtained at 20 W is also showed in Figure 9b.

Within the actions that can be executed in order to increase the efficiency of the plasma polymerization process and achieving some of the "*Green*" principles are the following:

1. *Frequency and power excitation:* An increase in value of these factors will result in an increase in both the level of ionization of the species and polymer deposition rates. ("*Green*" principles # 2, 6 and 8).

2. *Monomer flow rate/pressure:* Low flow rates and pressure lead an increase in the level of ionization of the species. ("*Green*" principles # 2 and 8).

3. *Geometry of the plasma reactor:* Reactors with cylindrical geometry (without corners) distribute homogeneously the generated plasma. ("*Green*" principles # 6, 8 and 12).

4. *Temperature of substrate:* Very low temperatures promote a higher insertion of monomer molecules on CNTs surface with minimal molecular modifications. ("*Green*" principles # 2, 6, 8).

5. *Treatment time:* This factor will depend on desired final structure and morphology. Long treatment times could produce thick polymer coatings or a rugous surface. The later, due to competition between the etching and coating process. ("*Green*" principle # 2).

Another interesting modification to plasma polymerization process includes the pre-treat‐
ment of CNTs with an inert of non-inert gas in order to induce the etching process and the
saturation of the CNTs surface with active sites. Subsequently, the active CNTs are subjected
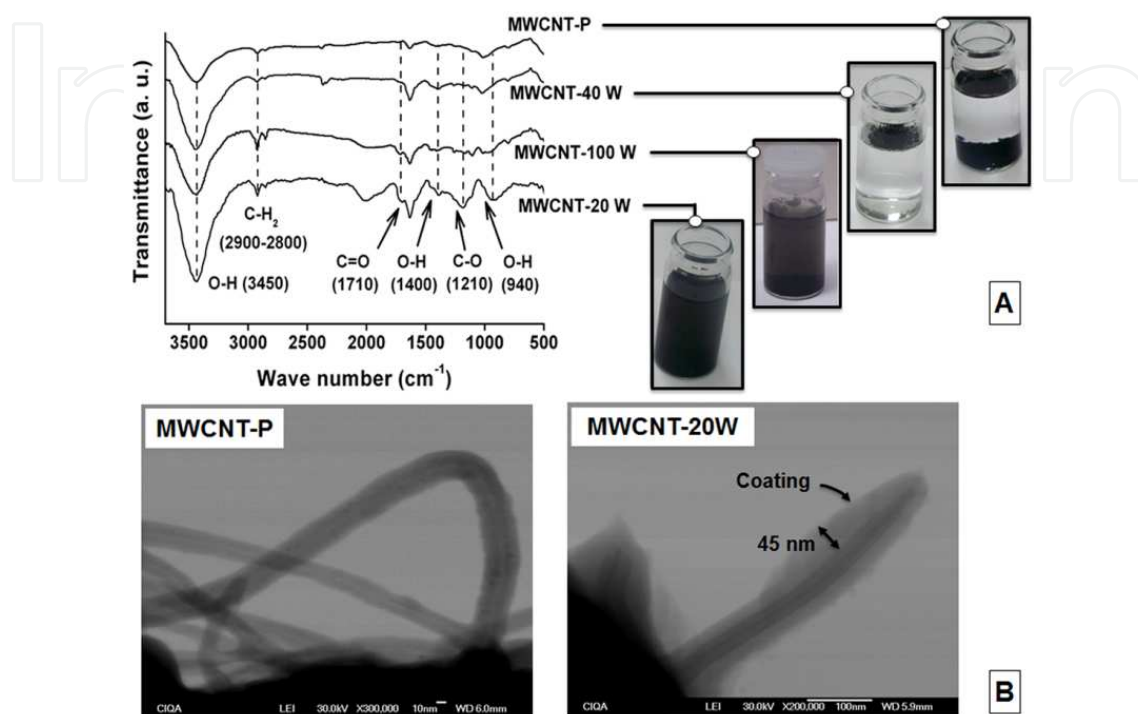to monomer plasma so a better polymer coating can be achieved [58].

Figure 9. Functionalized CNTs with polyacrylic acid by plasma polymerization. a) FTIR spectra and tests of solubility in water. b) STEM images of pristine MWCNTs (left) and MWCNTs functionalized at 20W (right). [28].

Plasma polymerization is a complex process which makes difficult to achieve an efficient
functionalization of CNTs. Due to high number of involved factors, one or two factors have
been only studied.

4.2.3.2. Future perspectives

Plasma-assisted functionalization has demonstrated to be a successful method for creating
environmentally friendly polymer coatings on CNTs surface. The functionalization of
CNTs with desired structural and chemical characteristics can be performed by means of
control of the involved processing conditions; however, there is a need for a complete un‐
derstanding of the interactions between plasma-CNTs which allow controlling successful‐
ly the etching and coating process.

A better understanding of the plasma-CNTs interactions can be enhanced if the efficiency of
the plasma-CNTs interactions is improved. The stages of pre-dispersion and pre-activation
of CNTs should be added previous to plasma polymerization, which allow increasing the
surface area exposed to plasma as well as the interactions with the active species, respective‐

ly. Further research on such issues could launch to plasma polymerization process to large-scale applications.

5. Summary and final remarks

The properties of CNTs and its application in the preparation of polymer hybrid materials have been very active research fields over the last decade. The preparation of polymer-CNTs hybrid materials faces considerable research challenges because their performance depends on the dispersion of CNTs in the polymer matrix and interfacial interactions between the CNTs and the polymer. In order to achieve the maximum performance, the surface modification of CNTs through several functionalization methods is one of the most used strategies to achieve this goal. Nowadays, the global environmental trends provide convincing reasons for exploring greener chemistry methods for functionalization of CNTs, which represent additional research challenges.

Microwave, ultrasound and plasma technology have emerged as promising green approaches since they have demonstrated to reduce the energy consumption, shorter reaction times and increase yields. These greener methods offer a range of energies that are not available from other conventional sources such as thermal, so leave open the possibility to explore more efficient functionalization routes, taking into account the 12 principles of "*Green*" chemistry as a framework.

Despite the progress described within this chapter, there are still considerable research challenges within this field that remain to be addressed. The successful functionalization of CNTs depends on availability of active sites on CNTs surface; however, the mechanisms that generate these sites remain unclear. Therefore, an in-depth understanding of the mechanisms of interaction between microwave/ultrasound/plasma-CNTs is required. For satisfying this need, further studies on correlation between the irradiation conditions and the level of the functionalization are suggested, in order to establish the most efficient and greener conditions for each particular system.

In addition, the incorporation of a dispersion stage of CNTs in gas phase previous to irradiation is highly recommended, because the surface area exposed to irradiation is increased and therefore the interactions with the matter are highly promoted.

As a general statement, the "*Green*" chemistry methods based on microwave, ultrasound and plasma energy can be easily incorporated to emerging fields of nanotechnology, in particular into strategies for preparation polymer-CNTs hybrid materials. However, there are still a number of important research challenges to study.

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