

Functionalization as a way to enhance dispersion of carbon nanotubes in matrices: a review

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Abstract

The past 3 decades of thorough scientific scrutiny of carbon nanotubes (CNTs) revealed that, in spite of their remarkable properties, some technological applications are adversely affected by certain difficulties in handling the CNTs, along with their tendencies, arising out of their graphitic structure, to form agglomerates and exhibit limited interaction with other materials. These issues play a crucial role when CNTs are applied as nanofillers inside matrices, in particular polar ones. In this case, unless several preliminary steps are taken, an efficient and uniform dispersion of the CNTs becomes impossible, thus the nanocomposite cannot exhibit the expected final properties. Unfortunately, a universal procedure does not exist since the problem of the dispersion of CNTs is very complex, and its solution requires an advanced understanding of the properties of the CNTs (e.g. whether the CNTs are single- or multiwalled, size, length, lattice defects etc.) as well as of the matrices used. This review aims to help the reader to select the appropriate dispersion procedure by acquiring fundamental knowledge regarding: (1) the synthesis and properties of pristine CNTs; (2) methods of chemical functionalization and properties of functionalized CNTs; and (3) methodologies for the mechanical dispersion of CNTs. A brief overview regarding chemo-physical characterization techniques is also given to enable a better evaluation of the properties of the CNTs, both before and after functionalization.

Keywords: Carbon nanotubes; Dispersion; Electrical properties; Functionalization; Mechanical properties; Synthesis.

1. Introduction

The continuous development of new/advanced materials with improved properties is a compelling requirement to satisfy human's technological needs in several breakthrough fields, such as biomedicine, sensing, renewable energy generation and storage, environmental remediation processes, robotics, optoelectronics, nanotechnology, and so on [1-10]. In the last several years, intense research efforts had been mounted, focused on the production of nanocomposites, where the performance of polymeric, metallic, or ceramic matrices is enhanced by adding nanoscopic fillers with unusual properties [11-19]. These fillers can be zero-, one-, or twodimensional, and morphologically being spherical, elongated, or planar systems, respectively. In this context, graphitic nanofillers such as graphene, carbon nanotubes (CNTs) and carbon nanofibers (CNFs) play a very promising role due to their specific structural and functional properties (e.g. high aspect ratio, high mechanical strength, high electrical and thermal conductivity, high electron

emission, high optical absorption, low energy-loss, etc.) [20-22]. Among the materials adopted as matrix such as metal matrix composites (MMCs), polymer matrix composites (PMCs), and ceramic matrix composites (CMCs) in research studies, polymers/PMCs are the most studied ones due to simpler processing compared with both ceramics/CMCs and metals/MMCs [23]; moreover, it is also interesting to notice that computational modeling studies largely focus on polymeric matrices as well. Among the three graphitic nanomaterials mentioned, CNTs are considered as excellent fillers due to their high tensile strength, low density, and high electrical and thermal conductivities [22,24]. CNTs-reinforced composites should guarantee excellent properties exploitable in various engineering applications, such as conductive glues/inks, sensors, gas/energy storage devices, light weighted-reinforced materials for applications in extreme environments, and many others [25-30]. However, there is often a significant mismatch between theory and practice as the final properties of the nanocomposites are strongly affected by the fabrication process and, in particular, by the dispersion of the nanofiller in the matrix. Thus, a greater comprehension of the effects induced by different processes is imperative, in particular for what concern the dispersion of the CNTs in the matrix. In fact, one of the main limitations to be overcome is the tendency of CNTs to stick together into bundles (i.e. CNTs exhibit strong Van der Waals forces and little or no affinity for non-graphitic materials), thus limiting the efficiency of dispersion inside the matrix and the interfacial interaction between filler and matrix [31]. For instance, to overcome this issue different functionalization techniques have been widely adopted to improve the dispersion of CNTs in matrices [32,33]. Numerous theoretical studies are increasingly providing a deeper knowledge of the molecular dynamics related to the dispersion and interaction between CNTs and matrices. This allows better understanding of its mechanisms and evaluation of the beneficial effect of functionalized CNTs in composite materials [34-37].

Therefore, the aim of this review is to provide a simply organized and easy-to-refer/consult document describing the science of CNTs, their chemo-structural properties and synthesis, with a particular focus on the different methods of dispersion and/or functionalization of CNTs for the production of novel/advanced nanocomposites. In this article, the principles behind the most diffuse functionalization techniques involving CNTs are critically discussed, and case studies regarding the most innovative concepts in CNTs and CNTs-reinforced composites are provided.

Last, important guidelines are summarized to facilitate the work of novice end-users interested in this field of research and development.

2. Carbon nanotubes: chemistry and structure-related property

Carbon is one of the most abundant elements on earth, and it is found in nature both as native and in numerous compounds. Carbon can exhibit three hybridization forms sp^3 , sp^2 and sp , coordinating with 4 atoms (bond angles 109.5 degree), 3 atoms (120 degree) and 2 atoms (180 degree) respectively. Due to its electronic configuration, the complete ionization of carbon is thermodynamically disfavored, whereas its electronegativity pushes towards the formation of covalent bonds [32]. Carbon is naturally present under two main allotropic forms, namely: graphite (hexagonal structure with hybridization sp^2) and diamond (cubic structure with hybridization sp^3). Furthermore, in the last century, continuous research promoted the discoveries of other allotropic forms: carbynes [38,39], fullerenes (spherical particles) [40], graphene (assumed as single-layer graphite) [41], and carbon nanotubes (CNTs) (tubular structure) [42-45]. To be noticed is the aspect that the curved surfaces in both carbon nanotubes and fullerenes are caused by a mixed sp^2 - sp^3 hybridization of the carbon's orbitals.

Carbon nanotubes can be classified into two main types:

- single-walled carbon nanotubes (SWCNTs) consisting of a single graphene sheet wrapped/wound on itself in a tubular shape;

- multiwalled carbon nanotubes (MWCNTs) in which two or more concentric tubes are formed by graphene sheets coaxially wrapped/wound around each other.

SWCNTs usually have a diameter between 0.7 and 2 nm and a length varying between a few microns and up to a few millimeters. Depending on the direction in which the graphene sheet is rolled up, it is possible to have different chirality (defined by the chiral angle between carbon hexagons and the tubular axis), which, together with the diameter, affects the electrical conductivity of the nanotube [46,47]. In Fig. 1 it is shown that the different chirality of SWCNTs, where an armchair configuration of CNTs always exhibits electrical conductivity similar to that of metals, whereas the chiral and zigzag configurations can be either semiconductors or metal conductors [46].

Multiwalled carbon nanotubes (MWCNTs) can be generally described as multiple concentric tubes (like a Russian doll) of rolled graphene layers. However, in some rare cases, it was found that some structures resemble a scroll of parchment (or a rolled newspaper) [47] where the single sheet of graphene is spirally rolled around itself in a configuration that can be explained by the parchment model where, (sketches for the two models are shown in Fig. 1). Due to van der Waals interaction between graphene layers, the interlayer distance between concentric tubes inside a MWCNTs is the same one found between the atomic layers in graphite, which is approximately 3.4 Å. Even though MWCNTs are formed by several concentric SWCNTs, and as mentioned earlier the electrical conductivity of each individual concentric tube is defined by chirality and diameter, all MWCNTs can be considered metal conductors as a consequence of statistical probability and restrictions on the relative diameters of the individual tubes (at least one of the shells, and thus the whole MWCNTs, is always a zero-gap metal).

From a mechanical point of view, the outstanding properties of CNTs are mainly due to the covalent bonds between the carbon atoms. However, as reported in Tables 1 and 2, MWCNTs tend to exhibit better performances than SWCNTs as a result of the presence of multiple concentric tubes. It is interesting to note that the Young Modulus of SWCNTs mainly depends on the diameter of the tubes, and not on the chirality, with a value of circa 1,000 GPa for a diameter of ca. 1-2 nm, as confirmed by both simulated and experimental results. Another interesting property is the ability of CNTs to resist high levels of plastic deformation without breaking (ca. 16%) [53]. These characteristics combined with a low density make CNTs better reinforcing fillers than carbon fibers [54], even considering that CNTs cost is still quite higher than that of carbon fibers (CFs) (Table 2).

All the properties we mentioned so far refer to the perfect CNTs which do not contain lattice defects. Defects and disorders such as vacancies can be present in the lattice for various reasons related to the synthesis of the CNTs or their reaction with harsh chemical agents. Huge number of defects can severely hinder the performance of CNTs, whereas a limited number of defects might have little or no impact of the chemo-physical performance of the CNTs (especially of the MWCNTs). Limited defects and disorders can be very interesting for the application of CNTs in nanocomposites, especially if coupled with the presence of different chemical groups, because it can lead to improved dispersion in matrices.

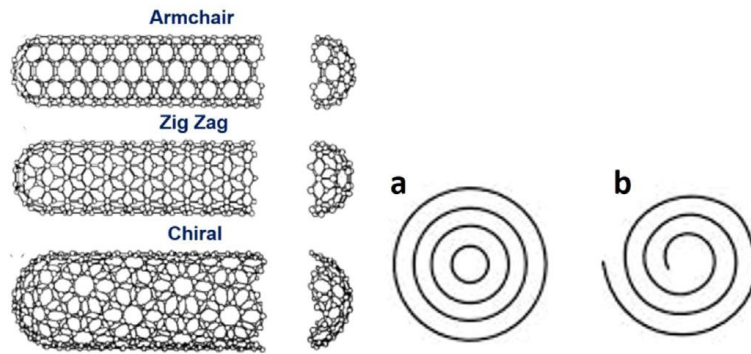


Fig. 1. On the left are shown the three models for SWCNTs structures with different chiralities. On the right, the cross-sectional view of the common Russian doll structure of concentric tubes of MWCNTs (a) and the rare parchment model (b).

Defects can limit the agglomeration of CNTs (decrease in van der Waals forces) enhancing their dispersion inside a matrix and their interaction with polar materials. Therefore, we can say that a limited amount of lattice defects and disorders can be an optimal trade-off between the electromechanical performance of defect-free CNTs and their successful application in nanocomposites. It is interesting to note that, lattice defects can be removed a posteriori by a process of high temperature annealing (above 1700 °C) in vacuum or in the presence of inert gas.

Table 1. Electrical resistivity of different kinds of CNTs in comparison with carbon fibers and amorphous carbon [48-52].

	Electrical resistivity [Ω m]
MWCNTs	$8-20 \times 10^{-6}$
SWCNTs	$<1 \times 10^{-6}$
Carbon fibers	1×10^{-6}
Amorphous carbon	$5-8 \times 10^{-4}$

Table 2. Main mechanical properties and cost of different kinds of CNTs in comparison with carbon fibers [55-57].

	Young Modulus [GPa]	Tensile Strength [GPa]	Density [g/cm^3]	Price [€/kg]
MWCNTs	1,200	150	2.1-2.6	100
SWCNTs	1,054	75	1.33-1.94	130
Carbon fibers	350	2.5	1.75-2.10	21

3. Methods of synthesis of CNTs

Although the discovery of carbon nanotubes is often attributed to the Japanese physicist Sumio Iijima for his article published in 1991 [42], in reality the history of the discovery of nanotubes is much more complex and began much earlier; the concept was developed first in 1954 by Radushkevich and Lukyanovich [58] and second in 1972 by Baker et al. [59]. The method for the synthesis of nanotubes used by Ando [60] described in the article of Sumio Iijima [42] was the electric arc discharge, which belongs to high temperature methodology, together with laser ablation and solar vaporization. These methodologies have in common the high temperature sublimation of graphite which is used as carbon precursor.

3.1. Arc discharge

This method is based on an arc discharge generated between two graphite electrodes placed face-to-face in the instrument chamber (see Fig. 2) [61] under a partial pressure of helium (He) or argon (Ar) (typically 600

mbar). The electric discharge generates a temperature (up to 6,000 °C) at which the graphite sublimates, and the ejected carbon atoms form a plasma. The ejected atoms then deposit on the cathode. While this technique was developed to synthesize fullerene, it was then discovered that the presence of small amount of transition metals in the anode catalyzes the synthesis of CNTs [62]. It should be emphasized that the presence of metal catalyst, such as Fe, Ni, Co or their alloys [63], is always necessary to catalyze the growth of the CNTs, regardless of the deposition technique. At the end of the growth, the metal particles are usually lodged at the tips of the nanotube or at their base, as explained by the tip-growth mechanism and by the base-growth mechanism respectively [64].

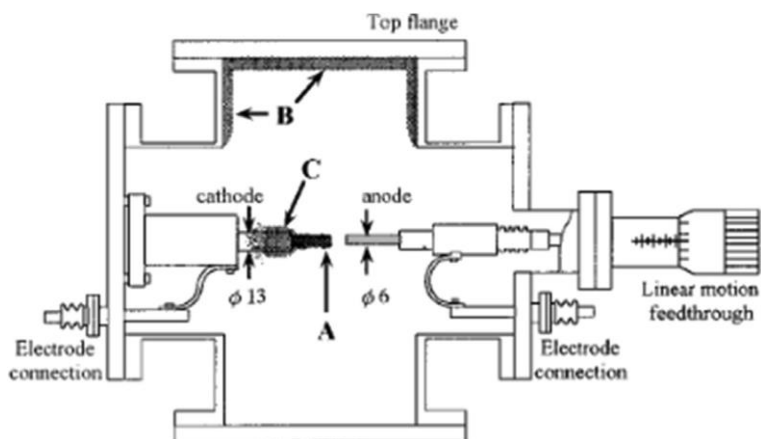


Fig. 2. Schematic representation of a typical arc-discharge apparatus [61].

3.2. Laser ablation

Another method investigated early on is the laser ablation process, which is based on laser-induced sublimation of a mixture of graphite and metallic catalyst (iron [Fe], nickel [Ni], cobalt [Co]). The process is performed in a quartz tube reactor inserted in furnace and heated at 2,700-3,200 °C under helium (He) or argon (Ar) atmosphere. As depicted in Fig. 3 [65], the gas flux promotes the deposition of carbon atoms and catalysts' particles on a collector at lower temperature. By varying both the cooling temperature of the collector and the gas flow rate, it possible to control the growth of the nanotubes [66]. By varying the laser, catalyst composition, growth temperature, nature of gases and gas pressure, the average nanotube diameter and size distribution can be varied [67].

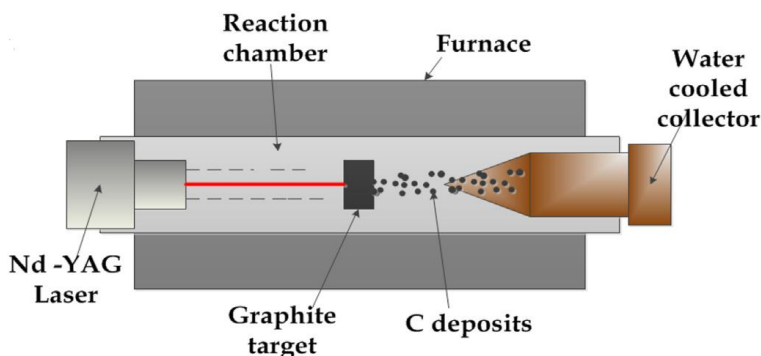


Fig. 3. Laser ablation apparatus for the production of CNTs [65].

3.3. Solar beam deposition

Sublimation induced by solar beam is a particular method investigated in the past involving a solar furnace in which the sunlight is focused on a graphite sample to sublime the carbon. The soot obtained is then condensed in a cold dark zone of the reactor. The sunlight is collected by a flat tracking mirror and is reflected towards a parabolic mirror which focuses the solar radiation directly on the graphite target (as in Fig. 4) [62]. Under clear sky conditions, temperatures of ca. 2727 °C are reached at the solar station and the sublimation process can start. With this technique, initially only fullerenes were produced [68]. However, since 1998 also CNTs were obtained by changing the target composition and adjusting the experimental conditions [69].

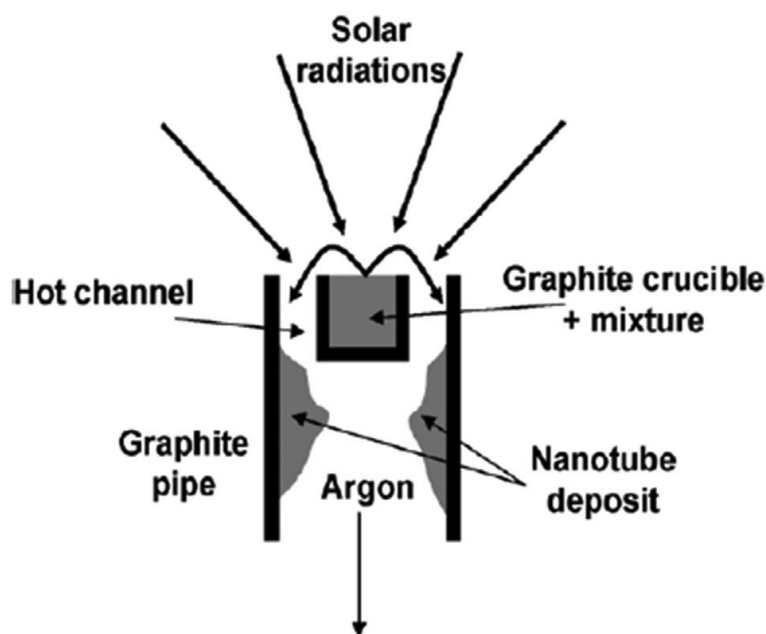


Fig. 4. Schematic representation of principles guiding the solar furnace technique [62].

3.4. Chemical vapor deposition

One of the main concerns related with the high temperature synthetic route is the low production yield and the fact that such high temperature is problematic for industrial production. Nowadays, for large-scale mass production of nanotubes the methodology mostly used is chemical vapor deposition (CVD), either as thermal-CVD or plasma enhanced-CVD, which allows the production of industrial-grade nanotubes at significantly lower temperatures.

Interestingly, CVD is historically the first methodology used by two Russian scientists [58] to grow CNTs as byproducts of the synthesis of carbon nanofibers (CNFs). However, since their research paper was published in Russian in a Russian journal, its diffusion in the global scientific community was limited. As for the high temperature methods, CVD requires the presence of metal particles to catalyze the synthesis. The metal catalyst can be deposited as a thin layer directly on the surface of a substrate (usually silica), where at the temperature of synthesis of the CNTs (600-1200 °C) the thin layer will reshape into nano-agglomerates of metal. Another way is to use a gas carrier to inject the catalyst, along with the carbon precursor, in the form of an organometallic compound [70-72] or a metal oxide [73-75]. At the process temperature the metal compound is reduced to metal atoms which aggregate and react with the carbon to produce CNTs. To be noticed is the fact that the diameter of the nanotube is related to the size of the metal particle catalyzing the growth and that the metal particles remain trapped inside the formed CNTs, either in the tip (far from the

substrate) or at the base (meaning adjacent to the substrate), depending on the strength of adhesion between the catalyst particles and the substrate.

To start the growth of nanotubes the carbon precursor (e.g. acetylene, ethylene, ethanol, methane, camphor ... etc.) [70,76] is carried into the reactor by an inert gas (nitrogen or argon), sometimes along with reactive gases such as hydrogen or ammonia to help in removing amorphous carbon deposited as a byproduct. The silica substrate, where the growth of the CNTs starts, is placed in the hottest region of the deposition system and it is heated up to 600-1200 °C. The thermal cracking of the carbon precursor generates reactive species of carbon which deposit on and interact with the metal particles, thus enabling the growth of the CNTs (see Fig. 5).

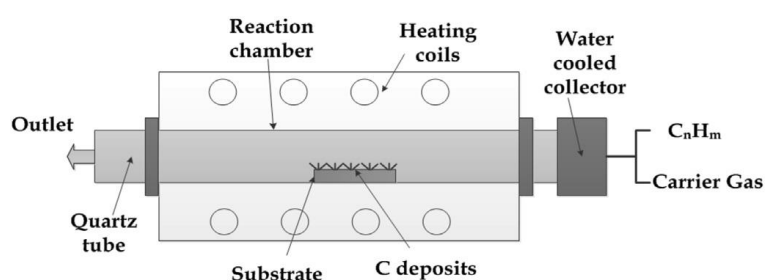


Fig. 5. Schematic representation of a CVD apparatus [65].

The parameters influencing the growth of CNTs are several and numerous strategies have been used to implement the CVD methods towards a selective and efficient production of CNTs, including modifying the reactor set-up (i.e. horizontal furnace, fluidized bed reactor and vertical furnace) and the relative reaction parameters [77].

3.5. Plasma-enhanced chemical vapor deposition

Currently one of the most used production technique of CNTs is plasma-enhanced CVD (PECVD) [78] in which the working temperature is lower than that of thermal-CVD thanks to the use of plasma. The plasma is generally generated by exciting the reacting gasses between two electrodes by using either radio frequency or direct current. Fig. 6 shows the schematic diagram of a typical plasma CVD apparatus. The substrate is placed on the lower electrode, while the reaction gas is fluxed in during the discharge at the upper electrode. The growth of the carbon nanotubes takes place on the nanoparticles of the metal catalyst deposited via sputtering on the substrate.

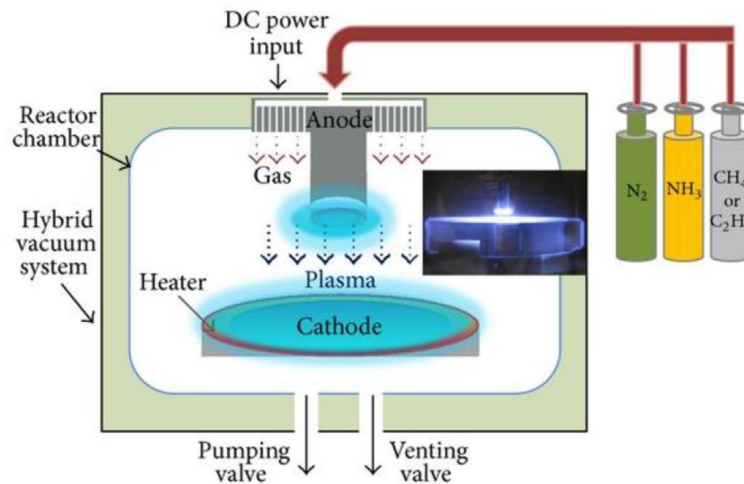


Fig. 6. Schematic representation of principles guiding the Plasma-enhanced CVD [79].

4. Dispersion of CNTs

Dispersion, as defined by the International Union of Pure and Applied Chemistry (IUPAC), refers to a system in which distributed particles of one material are individually dispersed in a continuous phase of another material [80,81], but the term also indicates the procedure with which such particles are dispersed. Dispersion is a key aspect for improving the performance of composite materials. The dispersion of nanotubes into matrices is difficult for three main reasons: (1) CNTs are agglomerated due to van der Waals forces; (2) because of their chemical inertia, the CNTs do not interact with other materials; (3) because of their low density, the CNTs tend to occupy a large volume into the matrix [12,82-84].

Depending on the synthesis method, length, and structure (SWCNTs or MWCNTs) the CNTs can assume different forms of agglomeration. In particular, the MWCNTs commercially synthesized in fluidized bed reactor, generally have larger dimensions and more defects. Their harboring higher quantum of defects and disorders such as vacancies means that they are found in the form of big agglomerates with a structure like 'combed yarn' or 'bird-nests'. Instead, smaller and less defective CNTs tend to intertwine less, agglomerating into less interlocked structures which therefore make them more dispersible. On the other side, some evidence points toward the fact that SWCNTs are more difficult to disperse than MWCNTs, due to higher van der Waals binding of the agglomerates [85]. In any case, type of CNTs (single-wall or multiwall), aspect ratio, length, defects and disorders, synthesis procedure, all contribute to determine the agglomeration level and strength, thus rendering it impossible to draw clear conclusions about the difficulty in satisfactory dispersion.

By analyzing the scientific literature, several dispersion methods have been proposed by numerous researchers. They are based on two different approaches, which often can be combined: mechanical dispersion, or chemo-physical treatment followed by mechanical dispersion (Fig. 7). Mechanical dispersion is based on the utilization of various techniques capable of dispersing CNTs in solvents or solid matrices, namely: ultrasound sonication, mechanical milling, high energy stirring. On the other hand, when mechanical dispersion is preceded by chemo-physical treatment, the dispersion is enhanced by chemical or physical bond between CNTs and chemical agents.

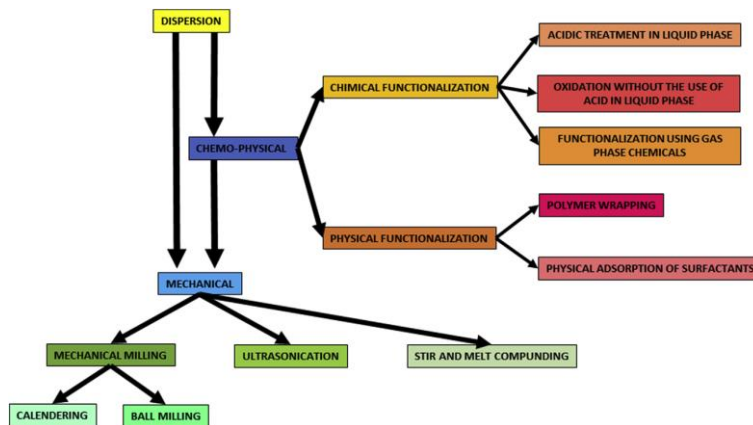


Fig. 7. Schematic summary of the principal dispersion approaches for CNTs.

In the following paragraphs the various types of dispersion methodologies are described.

4.1. Mechanical dispersion

4.1.1. Ultrasonication

Ultrasonication is an effective method widely exploited to disperse fillers (such as CNTs) in liquids having a low viscosity. Usually, this technique is commonly used to separate CNTs agglomerates in solution, but it could also be used effectively in presence of polymers, surfactants, and other compounds. Thus, for this reason, ultrasonication is commonly added to other dispersion techniques [86-90]. This technique can be performed either by using ultrasonic bath or by using an ultrasonic sonotrode (generally named probe or horn sonicator). In general, standard laboratory bath sonicators run at 20-23 kHz (power < 100 W), whereas commercial ones have an adjustable amplitude ranging from 20% to 70% (power 100-1500 W). The probe is usually made of an inert metal (e.g. titanium) and the exchangeable tips diameters range between 1.6 mm and 12.7 mm.

Ultrasonication is based on the cavitation mechanism, which consists in the formation of high energy bubbles which collapse within the liquid and generate a wave-shock providing high energy local shear necessary to disentangle CNTs bundles [91]. However, the main drawback of using sonotrode is that the high energy can easily damage the CNTs structure. In some cases ultrasonication can lead to a reduction in the length of the CNTs [85,92,93]. Fig. 8 [94] reports the Raman spectra of CNTs before and after sonication (different sonication times are investigated). Results demonstrated that after ultrasonication, the increment of signal at 1286 cm^{-1} attributable to disordered $\text{sp}^3\text{ C}$ in CNTs has been registered, suggesting the generation of defects in the CNTs lattice. In extreme cases, the graphene layers of CNTs can be completely destroyed. As aforementioned in this article, too much structural damage can badly affected the electrical and mechanical properties of CNTs, thus negatively influencing the performances of the final composites.

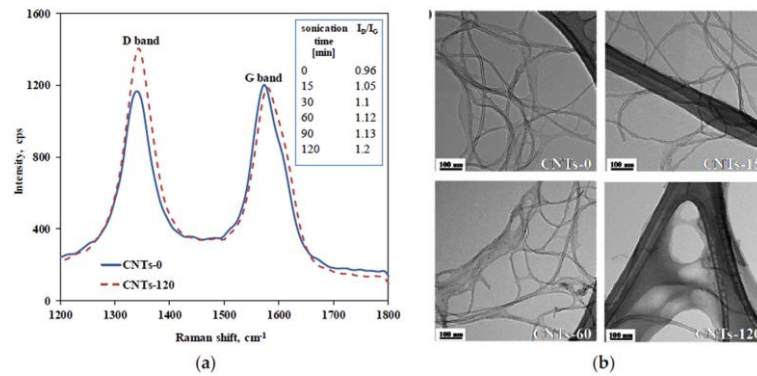


Fig. 8. a) Raman spectra of pristine CNTs and after 2 min and 120 min of ultrasonication and b) representative TEM micrographs of CNTs before and after ultrasonication [94].

4.1.2. Mechanical milling: calendaring

The calender, commonly known as three roll mills, is a machine tool that employs the force created by rollers to mix, disperse or homogenize viscous materials. Interestingly, the use of a three-roll machine has recently provided good results for the dispersion of nanoreinforcement in materials [95]. This dispersion method exploits shear forces rather than compression forces during the process and provides the CNTs dispersion without structural damages. A calendaring machine consists of three adjacent cylindrical rollers (i.e. the feeding and the apron rollers rotate in the same direction, whereas the center roller rotates in the opposite) running at different velocities (as in Fig. 9). The material is introduced in the system by a hopper directly between the first and the second roller. The material is then transported by the second roller into the gap between second and third roller where the filler is dispersed. At the exit, the material that remains on the central roller moves through the third roller towards a metal drain tip. The third roller tends to spin faster than the other two and the material is subjected to a greater shear force. This milling cycle can be repeated several times to ensure the desired dispersion degree.

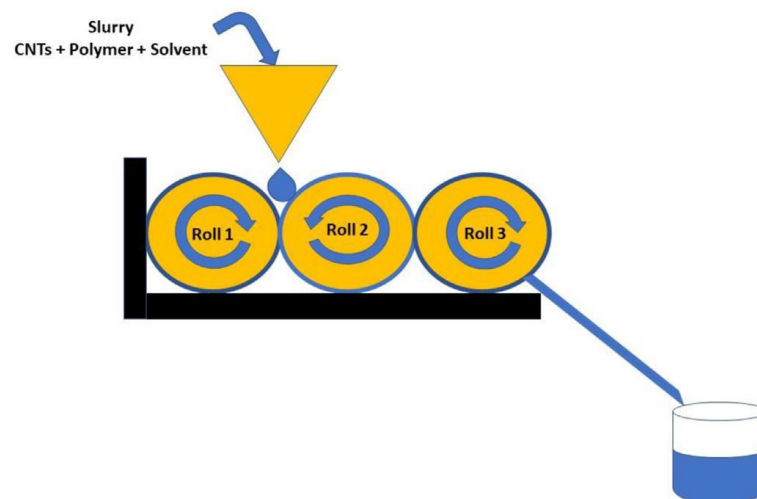


Fig. 9. Schematic of the three roll mill machine used for the calendaring process.

The employment of calendaring to disperse CNTs in a polymer matrix has become a very promising approach to achieve a relatively good carbon nanotubes distribution and dispersion [96-98]. However, there are several concerns about using this technique: for example the minimum gap is about 1-5 mm, which is larger than the

typical dimension of single CNTs. Due to this, calendaring can better disperse the large agglomerated bundles of CNTs into small ones rather than disperse individual CNTs. In addition, the feeding materials should be in a viscous state, thus this technique could be used in presence of thermoplastic matrices for heated systems [99].

4.1.3. Mechanical milling: ball milling

Mechanical milling, or grinding, is commonly used to reduce the physical size of particles to extremely fine powder. In ball milling, the materials to be ground are placed in a proper container together with milling balls. The rotation of the cylindrical container generates the kinetic energy necessary to move the sample and the milling balls, also known as charge materials. Subsequently, the collision between the sample and the milling balls generates high enough pressure to favor crack propagation and fracture, leading to the breakage of the sample [100]. The higher the impact energy, the smaller the fragments produced. The typical motion of balls inside the container is shown in Fig. 10 [101]. Different materials, including ceramic, flint pebbles and stainless steel, are used as balls.

Ball milling has been used for a variety of applications related to CNTs: such as to obtain amorphous carbon or onion-like particles from the breakdown of its structure [102,103]. In some cases the nanotube length was reduced and, simultaneously, the primary agglomerate morphology was altered from loosely packed to compact [104]. With this technique it is also possible to carry out some chemo-mechanical reactions, as shown by Flahaut et al. [75], where an in situ amino functionalization of CNTs was made while using ball milling. Mainly this technique is used to form metallic composites by grinding metal particles and CNTs to form composite powders but it is possible also for other matrices [104]. The mechanical alloying is used primarily for pure Al and Al alloys matrices [15,102,105-108]. Moreover, different alternative processes of ball milling could be used on the basis of either the material and/or the purpose of the process (e.g. high energy milling (HEM)) [15,109,110].

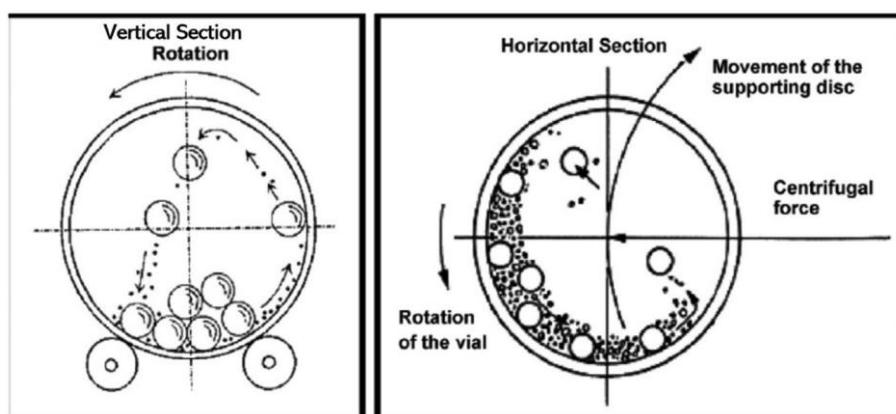


Fig. 10. Schematic representation of the balls motion during the milling process. On the left: vertical configuration (conventional ball mill). On the right: horizontal configuration (planetary ball mill) [101].

4.1.4. Stir and melt compounding

Stirring is a common technique for dispersing particles in liquid systems and can also be used to disperse CNTs in a polymer matrix. The results of the dispersion depend on the size, shape of the propeller and on the mixing speed. Intense agitation of CNTs in a polymer matrix can bring to a relatively good dispersion [12,111]. However, MWCNTs are more easily dispersed than SWCNTs using stirring, even if MWCNTs tend to re-

agglomerate. Indeed, Schmid and Klingenberg [112] suggested that in a fiber suspension agglomeration is mainly caused by elastic interlocking mechanisms and frictional contacts, occurring even without attractive forces between fibers.

During stirring, sliding and Van der Waals forces seem to have a smaller effect on the dispersion; however, agglomeration becomes spontaneous under static flow. In the case of heavily agglomerated CNTs, however, to obtain a fine dispersion in the polymer matrix higher shear forces are required, that can be obtained by using a high speed shear mixer.

Extrusion is a popular technique for dispersing CNTs into polymers such as in most thermoplastics, where thermoplastic pellets mixed with CNTs are fed into the extruder hopper. The twin screws rotate at high speed creating a high shear flow, resulting in the dispersion of the CNTs agglomerates, and mixing with the molten polymer. This technique, commonly used for thermoplastic matrices is particularly useful for producing CNTs/polymer nanocomposites with both high and low filler content [113].

4.2. Functionalization

Carbon nanotubes surface properties can be modified by attaching 'chemical functionalities' (functionalization treatment) to their surface, which results in a good strategy to overcome the dispersion problems by improving the solubility, compatibility, and processability of CNTs [32,114-117].

According to the literature, the functionalization of CNTs can be grouped into two main categories:

- chemical or covalent functionalization, in which new chemical groups are chemically bonded to the carbon atoms of the tubes;
- physical or non-covalent, in which various macromolecules are physisorbed or wrapped around the tubular structure.

4.2.1. Chemical functionalization

4.2.1.1. Acidic treatment in liquid phase.

Among the different types of chemical functionalization of CNTs, wet functionalization via acidic oxidation is one of the most commonly adopted [118]. It serves the dual goal of introducing new chemical groups and removing metal particles (trapped catalyst) and amorphous carbon. This is especially true when nitric acid is used to remove residual metals and to introduce oxygen-containing groups (mainly carboxylic acid) as reported in Fig. 11a.

Aviles et al. [120] demonstrated that performing the process in presence of small concentration of nitric acid (HNO_3) improves the presence of O-containing groups without damaging the structure of CNTs. Consequently, the functionalization with HNO_3 enhances the dispersion of CNTs in polar solvents. It must be emphasized that process parameters, such as temperature and reaction time play significant roles. As demonstrated by Rosca et al. [121], for long time treatment (1-2 days) in concentrated HNO_3 (%v > 60%) could strongly damage the structure of CNTs, covering their surface with amorphous carbon. On the contrary, a temperature of 111 °C for 6 h leads to an efficient elimination of both metal impurities and amorphous graphitic platelets. Sulfuric acid (H_2SO_4) is less used than nitric acid as it does not generate a significant oxidation of the external lattice. However, sulfuric acid in combination with hydrogen peroxide (i.e. piranha solution, $3\text{H}_2\text{SO}_4: 1\text{H}_2\text{O}_2$) exhibits a good functionalization performance by introducing both carboxylic functionalities and hydroxyl groups without causing damages to the CNTs' structure. As shown in Fig. 11b the piranha solution generates an oxygen radical (reactive oxygen species [ROS]) that interacts with the carbon

in sp^2 hybridization state leading to the formation of a double bond with oxygen, which subsequently reacts with H_3O^+ to finally create hydroxyl groups on the surface of the CNTs. The functionalization with piranha solution guarantees a good dispersion in both polar and non-polar media [17,118]. Furthermore, by performing this treatment at temperature over $70^\circ C$ it is possible to cut the tubes [122]. The treatment with sulfonitric acid (i.e. $3H_2SO_4:1HNO_3$) for 8 h at $70^\circ C$ can produce a high number of defect thus distorting the CNTs [123]. A study shows how the rise in temperature (from $60^\circ C$ to $140^\circ C$) with this treatment increase the presence of carboxylic ($-COOH$) functional groups [124]. The wettability of CNTs after sulfonitric treatment was also studied in literature. One study in particular [125] was performed on vertically aligned (VA) CNTs and showed how the interaction with water was enhanced by the presence of carboxyl and sulfonic groups introduced after 6 h of treatment. As proved by the experiment, the acidic treatment can reduce the contact angle between water and VA-CNTs from 176° (hydrophobic) to 25° (hydrophilic). Obviously, the increment in wettability is due to the extended presence of O-containing functionalities on the surface. The effect on the dispersion in water after different acid treatments is an important way to evaluate the effectiveness of the treatment and the degree of interaction with the matrix. Furthermore, the use of sonication, via ultrasonic bath, during acidic treatment of CNTs can significantly promote the grafting of a great number of polar groups, while guaranteeing a continuous disentanglement of CNTs bundles during the process [126]. At the end of acid oxidation in general it is necessary to neutralize the reaction solutions containing the treated CNTs. Once neutralized, the CNTs are washed several times with distilled water to remove acid and salt residues adsorbed on the surface and are then recovered through filtration or centrifugation.

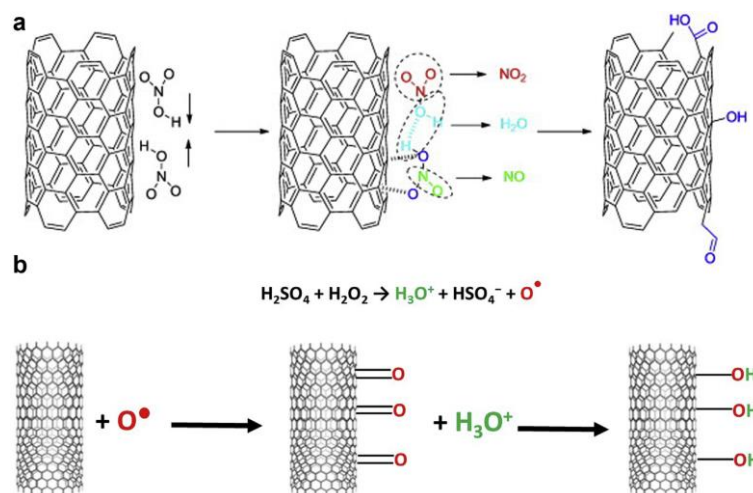


Fig. 11. a) mechanism of oxidation of nitric acid [119]; b) mechanism of oxidation of piranha solution.

4.2.1.2. Oxidation reactions without the use of acid in liquid phase.

The literature suggests several oxidation processes not involving acids. In comparison to acidic treatments, this process allows to introduce a lower oxygen content with lesser damaging of the honeycomb lattice. In this context, Wepasnick et al. [123] tried to analyze the degree of CNTs oxidation by comparing oxidizing chemical agents such as $KMnO_4$ (potassium permanganate), $(NH_4)_2S_2O_8$ (Ammonium persulfate) and H_2O_2 (hydrogen peroxide) with HNO_3 and HNO_3/H_2SO_4 . The study successfully demonstrated that even a non-acidic treatment is sufficient to decorate the surface of CNTs with polar functional groups as shown in Table 2. In detail, the use of $KMnO_4$ is a good technical solution to introduce a high number of carboxylic groups and functionalities. On the other hand, $(NH_4)_2S_2O_8$ can only create carboxyl, lactone and phenolic acid groups on lattice defects existing beforehand, hence it does not guarantee a high oxygen content [123]. It should be

noticed that these studies suggest that, by avoiding the use of strong acids, it would be possible to have more 'environmental-friendly' approaches. While most studies focus on low pH treatments, currently there is not much knowledge regarding the structural alteration of graphitic materials under basic conditions. Both Datsyuk et al. [118] and Kim et al. [127] have studied the treatment of MWCNTs with an $\text{NH}_4\text{OH}/\text{H}_2\text{O}_2$ (ammonium hydroxide/hydrogen peroxide) mixture, which generates epoxy groups with little damage to the external lattice of CNTs. Peng and Liu [126] showed that H_2O_2 in contact with CNTs for 1-6 days reacts with amorphous carbon at the surface of CNTs forming -OH groups (hydroxyl groups) while removing the disordered carbon. Table 3 reports the comparison between different oxidation processes.

Table 3. Comparison of different oxidative processes: different chemical groups formed on the surface in function of oxidant used.

Oxidation process	O%	Functional groups introduced	Time	Temperature [°C]	Comments	References
NH ₄ /H ₂ O ₂	2.5	-COOH; -OH	5 h	80	Functionalization not very effective, neutralization required at the end of the process with an acid solution (e.g. HCl)	[118]
H ₂ SO ₄	3.9	-SO ₃ H	15 min	60	Sulfonic acid functional groups can be detrimental in cementitious matrices. The treatment does not guarantee a uniform functionalization of the CNTs. Neutralization is achieved by rinsing with a strong base (e.g. NaOH) solution. Neutralization can lead to the formation of salts which must be removed by further rinsing with deionized water.	[120]
(NH ₄) ₂ S ₂ O ₈	4.5	-OH; -COOH	4 h-24 h	RT	Long reaction times, with little yield of functional groups.	[123,128]
H ₂ O ₂	4.5	-C=O; -OH	4-6 days	70-65	The instability of H ₂ O ₂ requires addition of fresh solutions of peroxide at least every 24 h.	[123,126]
O ₃	4.7	-C=O	1 h	25	The use of a gas requires a closed system to recycle ozone.	[123,129,130]
H ₂ SO ₄ /H ₂ O ₂	7.1	-OH; -COOH	15 min-9 h	RT-70	The piranha solution is very aggressive and gives excellent functionalization results. High reactivity of the mixture can be hazardous for the operator. As per the sulfuric acid, neutralization is needed at the end of the treatment. Neutralization can lead to the formation of salts which must be removed by further rinsing with deionized water.	[118,120,131]
HNO ₃	7.9	-COOH; -C=O	15 min-48 h	RT- 150	Temperature and reaction time can be tailored depending on the sample used and results required. Stirring or sonication can be used. When heating the acid vapor can be refluxed using a condenser. Carboxylic groups are formed	[118,120,121,123,124,132,133]

					on the surface of the nanotubes. Neutralization with base and several washes are required to remove acid residues from the surface of the CNTs.	
H ₂ SO ₄ /HNO ₃	8.8	-COOH; -OH; -SO ₃ H	1-15 h	RT-60	This treatment can be adapted using simultaneous dispersion techniques (e.g. sonication). Functionalization is homogeneous and severely damages the CNTs.	[120,123e125,127,132,134]
KMnO ₄	9	-COOH; -C=O	5 h	150	Some authors claim this technique to be "green", however, to remove permanganate residues a washing with strong acids (H ₂ SO ₄) is often required	[123]

4.2.1.3. Functionalization using gas phase chemicals.

An alternative method to oxidize CNTs consists in fluxing an oxidant gas or vapor through CNTs powder. This method guarantees a substantial reduction in waste production and a more homogenous functionalization with respect to acidic treatments. Xia et al. [135] developed a gas-phase route for the oxidation of CNTs by means of HNO₃ vapor treatment. It is a more efficient way to introduce oxygen-containing functional groups on CNTs surface (21%) rather than conventional treatment with liquid HNO₃ (7.9%). In addition, the use of HNO₃ vapor prevents secondary purification steps (e.g. filtration, washing, and drying) required with the liquid treatment. Another interesting oxidant gas is ozone (O₃), which can be fluxed directly on carbon nanotubes at temperature equal or greater than RT. The reaction between O₃ gas and carbon produces two distinct functional groups on the surface of the CNTs (namely esters and quinones) as well as volatile byproducts such as CO₂ and CO [129]. The treatment with O₃ guarantees a stable dispersion of CNTs for days, as demonstrated by Li et al., just by simple sonication [136]. The application of ultra-violet radiation of 28 W/cm² during ozone treatment for at least 2 min, introduces carboxylic acids groups, whose amount is directly related with the exposure time [137]. Another interesting solution is to exploit CO₂ gas both to create functional groups and to eliminate the metallic residues present in the CNTs after the synthesis [138]. Wang et al. [139] explain that a treatment in flux of CO₂ at 900 °C for 1 h is enough to introduced oxygen-containing functional groups that were uniformly distributed on the external surfaces of CNTs. The results revealed that the CO₂ oxidation thinned the CNTs walls and introduced numerous defects [140]. Another way to purify CNTs by eliminating the residual amorphous carbon and the metal particles, is via air treatment [141,142]. As demonstrated by Li et al. [143], the results of the treatments with air are influenced by temperature: for a 20 min treatment at temperature between 480 °C and 650 °C the specific surface area of CNTs is increased, whereas at temperature greater than 700 °C surface area is decreased. The authors explained that at temperature greater than 700 °C the oxygen molecules present in the air first oxidize the amorphous carbon and then attack the CNTs capped ends. The capped ends are more reactive than the lateral walls of the CNTs because in the caps the C-C bonds are slightly weaker due to the radius of curvature (greater bond strain) and the presence of 5-fold and 7-fold rings [143,144]. Andrews et al. [145] show that at 1600 °C time plays a critical role. A 45 min treatment in air reduces the amount of amorphous carbon present on the surface, whereas for briefer treatment (less than 45 min) generated more oxidized sites on the CNTs. A recent article by some of the authors of this manuscript shows that an optimal oxidation and consequentially an optimal dispersion of the nanotubes in polar solvents, is possible when the CNTs are oxidized by a mixture of 2% O₂ and 98% N₂ at 350 °C [146]. Another method to functionalize CNTs is to use plasma functionalization in presence of different gasses (such as but not limited to O₂, N₂, NH₃, Ar, CF₄, CO₂, H₂, F₂) [147]. Plasma can be produced via a variety of methods such as dielectric barrier discharge, corona discharge, pulsed corona, microwave, radio frequency (RF) plasma, etc. [148]. Many studies have been carried out in the literature to modify the surface properties of carbon nanotubes using different combinations of gas and plasma parameters [149]. The main advantage of using plasma is that the functionalization temperature is low (from RT to approximately 600 °C) [149], and the damage of the CNTs is also limited. Moreover, plasma allows nanotubes to be functionalized with complex molecules such as polymers [150] or biomolecules [151,152]. Main disadvantages are the low stability of the grafted functional groups over time, and the inhomogeneous functionalization of the sample's surface [153]. The latter occurs because only the face of the sample exposed to the plasma is functionalized, unless the powder sample is uniformly stirred during the treatment [154].

4.2.1.4. Physical (or non-covalent) functionalization.

As discussed so far, it is clear that functionalization of CNTs by using covalent methods can efficiently introduce useful functional groups onto surface of carbon nanotubes. However, this kind of approach has two major drawbacks: i) the large number of lattice defects produced on the CNTs results in the depletion of their mechanical properties and the disruption of their p-electron system (thus with negative consequences

on the electrical and thermal properties), and ii) the reactants adopted for these processes are dangerous and not environmental-friendly. Hence, many efforts have been put forward to develop methods able in reducing both the cost of the process and the damage to the CNTs structure. In this context, non-covalent functionalization is an alternative approach to tune the interfacial properties of CNTs. Non-covalent functionalizations are based on the physical interaction (physisorption) between CNTs and the chemicals and can be mainly classified as polymer wrapping or physical adsorption of surfactants.

Polymer wrapping consists of a solution of suspended CNTs in the presence of polymers, such as poly(p-phenylene vinylene) [PPV] [84] or polystyrene [156]. The van der Waals interactions and π - π stacking between CNTs and polymer chains containing aromatic rings leads to the wrapping of the polymeric chains around the tubes to form supramolecular complexes (as in Fig. 12) [155,157].

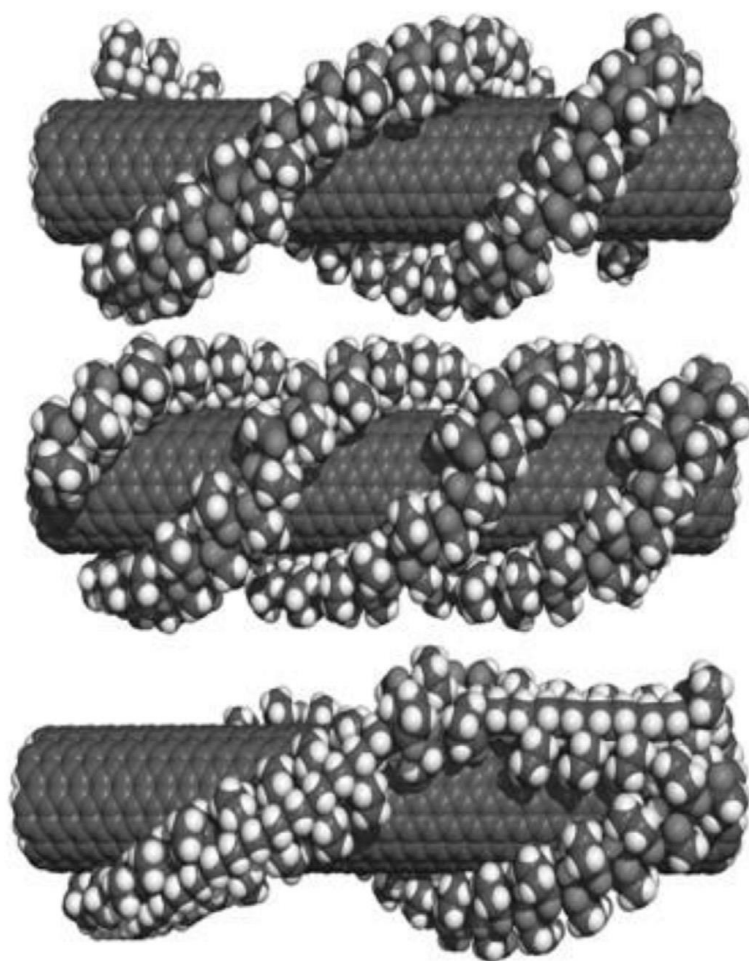


Fig. 12. Examples of polymer wrapping [155].

The other approach is based on the use of amphiphilic species such as surfactants (as in Fig. 13). Several studies have been conducted on the effects of surfactants both on the dispersion of CNTs and their final properties [158-167]. Well-known in the literature, surfactants are usually organic amphiphilic compounds, meaning that they contain both hydrophobic groups (their tails) and hydrophilic groups (their heads). Surfactants can be divided into three categories: non-ionic surfactants such as Triton X-100 [161,162], anionic surfactants such as sodium dodecyl sulfate (SDS) [164,165,168], and cationic surfactants such as cetyl trimethylammonium bromide (CTAB) [169,170]. As a result of the physical adsorption of surfactant on the

surface of CNTs the surface tension of CNTs is decreased, and the inter-tube Van der Waals attraction is reduced, thus preventing the formation of agglomerates and bundles.

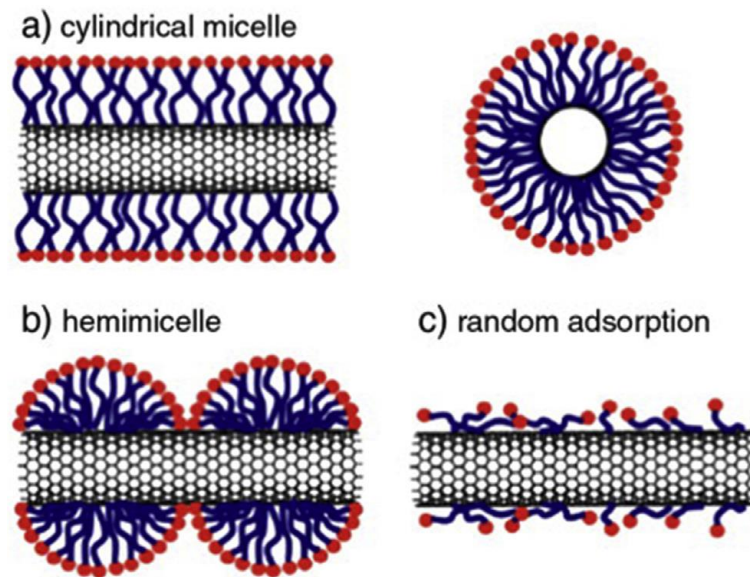


Fig. 13. Models of surfactant-based physical functionalizations [171].

The efficiency of this method depends strongly on the properties of the surfactants; however it must be noted that due to the high surface area of the CNTs, a very large amount of surfactant is required to obtain a good dispersion. The use of large quantities of dispersant (in some cases the amount of dispersant is equal to that of the CNTs used) can hinder the interaction between the nanotubes and the matrix in which they are dispersed. As a consequence, the resulting mechanical, electrical and thermal performances of the composite might be much worse than expected [163,172]. Some researches, in facts, have proved that the dispersing capability of surfactant to CNTs increases with the ratio of surfactant to CNTs, but an excessive concentration level of surfactants has negative effect on the hydration of cement and will cause a marked air-entraining effect [173].

Table 4 summarizes all the main methods of dispersion and functionalization of CNTs shown in this review, with particular attention to the advantages and disadvantages of each one. As previously mentioned, functionalization and dispersion can be combined, reducing, in some cases, the disadvantages of the dispersion methods since changing the surface chemistry reduce the Van der Waals attraction between CNTs, thus preventing reagglomeration.

Table 4. Dispersion technique.

		Advantages	Disadvantages
Dispersion	Ultrasonication	Excellent dispersion of nanotubes. Easy technique that can be coupled with other dispersion techniques	Risk of damaging the structure of the nanotube. If carried out for prolonged periods, it tends to heat the solution
	Calendaring	Useable for dispersion in polymeric matrices. The feeding materials should be in a viscous state	Very long times to obtain an excellent dispersion. Not as effective with low viscosity matrices
	Ball milling	Excellent for mixing nanotubes with metallic or ceramic powders	Risk of damaging the CNTs. Mainly useable for mixing with other powders
	Stir and melt compounding	Excellent for dispersing nanotubes in polymer matrix. Useful for disperse both high and low quantity of CNTs. Commonly used for thermoplastic polymer	Possible re-agglomeration of CNTs after stir in static condition
Functionalization	Acidic treatment in liquid phase	High surface functionalization	Risk of damage the CNTs. Not environmental friendly
	Oxidation without the use of acid in liquid phase	Eco-friendly. Nanotubes are usually not damaged	Low surface functionalization
	Functionalization using gas phase chemicals	Plasma allows to decorate CNTs with more complex functional groups. Allows to remove amorphous carbon from the CNTs surface. Ecofriendly	Little stability of functional groups over time and lack of uniform functionalization over the surface of the sample (unless the sample is stirred). In some cases, high temperatures are required
	Physical functionalization	Allows an excellent dispersion of the nanotubes. No lattice damages	Large quantities of dispersant might be required to obtain an excellent dispersion. Reduced interaction between filler and matrix

5. Characterization techniques

It is important to use the most appropriate characterization technique to evaluate the effectiveness of the functionalization and to characterize the CNTs at the end of the treatment (summarized in Table 5). In addition, the dispersion in polar matrices can be qualitatively evaluated by adding the CNTs in a polar solvent contained in a test tube and observing whether the CNTs aggregate and precipitate and how long it takes.

5.1. Raman spectroscopy

Raman spectroscopy is a non-destructive technique that allows researchers to evaluate the lattice defects and disorders of the nanotubes and their structure. The Raman spectrum, graphically represented as Intensity of the signal (arbitrary units) vs Raman shift (cm^{-1}), of the CNTs can be characterized by the presence of 3 peaks. The D-band at circa 1350 cm^{-1} , arising from the disorder-induced phonon mode (A_{1g}-band), the G-band at circa 1590 cm^{-1} , assigned to the Raman-allowed phonon mode (E_{2g}band) [174] and the Radial breathing mode (RBM) at circa 248 cm^{-1} which is visible only for single or double walled CNTs. The RBM frequency shifts depends on chirality and diameter [175]. The extent of the lattice defects and disorders can be evaluated by the ratio of the intensities of D-band over G-band (ID/IG) [176]. The higher is the ratio the greater is the amount of lattice defects and amorphous carbon. Even though this technique doesn't help when it comes to identify and quantify functional groups introduced on the CNTs, as a rule of thumb, the more chemical groups are covalently bonded to the CNTs the greater is the number of lattice defects.

Table 5. Different techniques used for the characterization of carbon nanotubes.

Characterization technique	It can be used for:
Raman spectroscopy	Detects single and double wall CNTs, determines the amount of lattice defects
Ultraviolet-Visible-Near Infrared (UV-Vis-NIR) spectroscopy	Evaluate the quality of CNTs dispersion in liquid solution
FT-IR and attenuated total reflectance-Fourier transform-infrared spectroscopy A(TR-FTIR)	Purity, typology and semiquantitative analysis regarding the amount of functional chemical groups
X-ray photoelectron spectroscopy (XPS)	Elemental composition, functionalization (covalent and non-covalent)
Thermogravimetric analysis (TGA)	Purity, defects and disorders, presence of by-products, quality control of synthesis and manufacturing processes
Small angle neutron diffraction (SANS)	Morphological analysis of bulk sample
X-ray diffraction	Morphological analysis of bulk samples
Scanning electron microscopy (SEM)	Morphological analysis (diameter and length), agglomeration state
Transmission electron microscopy (TEM)	Morphological analysis of internal structure: diameter, presence and location of metal catalyst, number of layers and distance between them

5.2. Ultraviolet-visible-near infrared spectroscopy

Ultraviolet-visible-near infrared (UV-Vis-NIR) spectroscopy is based on absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible-near-infrared region collected using a UV-Vis spectrometer. UV-Vis spectroscopy is applicable to characterize CNTs [177] in liquid suspensions. As the CNTs are dispersed, the solution will become darker and will absorb more light and hence the maximum absorbance can be used as an indicator of dispersion quality. The ability to monitor liquid solution has the potential to detect the quality of dispersion of CNTs in solution [178]. CNTs show absorption, in aqueous

solution, between 262 and 230 nm respectively in the UV-visible spectrum. This is due to the $\pi-\pi^*$ transitions of aromatic C-C bonds [179].

5.3. X-ray diffraction

This non-destructive characterization method, X-ray diffraction (XRD), is used to obtain information regarding the interlayer spacing of MWCNTs, the structural strain and the impurities contained in a CNTs sample or in a CNTs-nanocomposite. However, carbon nanotubes have multiple orientations compared to the X-ray incident beam. Diameters and chiralities distribution are also observed as well as various number of layers for MWNTs. This leads to a statistical characterization of carbon nanotubes. Due to their intrinsic nature, the main features of X-ray diffraction pattern of CNTs are close to those of graphite and presents two principal peaks: (1) a graphite-like peak (usually between 20 degrees and 30 degrees) that measure the interlayer spacing of graphite layer and can be obtained from its position using the Bragg law; (2) a family of peaks due to the honeycomb lattice of single graphene sheet. Consequently, the X-ray diffraction profile is not useful to differentiate microstructural details between the CNTs and the graphite structure [180] but can help to determinate the sample purity (catalyst, functional groups).

5.4. Scanning electron microscopy

The scanning electron microscopy (SEM) uses a type of electron microscope that produces images and analyzes the elemental composition (SEM-energy-dispersive X-ray spectroscopy [EDX]) of a sample by scanning the surface with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain information about the surface topography and the composition of the sample. SEM imaging cannot achieve resolution better than tens of nanometer. This technique is mostly used for the morphological characterization of CNTs or cross-sections of nanocomposites containing CNTs. With this technology is possible evaluate also the state of agglomeration of CNTs and the defects of CNTs tube structure.

5.5. Transmission electron microscopy

Transmission electron microscopy is a microscopy (TEM) technique in which a beam of electrons is transmitted through a specimen to form a see-through image. The specimen is usually either an ultrathin section of the sample (less than 10 nm thick) or a suspension on a grid. The resolving power (the minimum distance between two points for which they can be distinguished as such and not as one) is about 0.2 nm, that is about 20 times greater the best SEM. Given its great resolving power it is possible to see the different graphitic layers present in the MWCNTs [181]. It is possible to observe the metal catalyst trapped inside the tubes, and in some cases, it is also possible to distinguish functional groups anchored onto the surface of the nanotubes. This technique is used for the morphological characterization of CNTs.

5.6. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive quantitative spectroscopic technique that measures the elemental composition, the chemical state and electronic state of the elements that exist within a material. XPS is very useful to investigate functionalized CNTs by the analysis of the C1s peak in the region from 284.1 to 289.4 eV. The decomposition of the C1s peak could be used to identify and quantify the relative ratio of carbon bond types [182]. XPS technique can give information about the chemical structure of carbon nanotubes. But the most widely used data refers to the structure modification of the CNTs walls due to the chemical interaction with organic compounds or gases adsorption [183].

5.7. Small angle neutron scattering

Small angle neutron scattering (SANS) is used to the determine the atomic and/or magnetic structure of a material. A sample to be examined is placed in a beam of thermal or cold neutrons to obtain a diffraction

pattern that provides information of the structure of the material. The technique is similar to X-ray diffraction but due to their different scattering properties, neutrons and X-rays provide complementary information: X-Rays are suited for superficial analysis, strong x-rays from synchrotron radiation are suited for shallow depths or thin specimens, while neutrons having high penetration depth are suited for bulk samples [184]. This technique is mainly used for the morphological analysis of bulk samples of CNTs [185].

5.8. Fourier transform-infrared spectroscopy

Fourier transform infrared spectroscopy (FT-IR spectroscopy) involves the absorption of infrared radiation with material. Samples may be solid, liquid, or gas. An IR spectrum can be visualized in a graph of infrared light absorbance (or transmittance) vs. frequency or wavelength. Typical units of frequency used in IR spectra are reciprocal centimeters (sometimes called wavenumbers), with the symbol cm^{-1} . Units of IR wavelength are commonly given in micrometers (μm), which are related to wave numbers in a reciprocal way. A typical instrument that uses this technique is a Fourier transform infrared (FT-IR) spectrometer. In CNTs characterization, infrared spectroscopy is often used to determine impurities remaining from synthesis or molecules bonded on the nanotube surface. Numerous works are performed on organic molecules and CNTs: infrared spectroscopy exhibits all the modification of the CNTs structure and reveals the nature of compounds added to the CNTs [186]. However, the spectrum of nanotubes is difficult to visualize, since they tend to absorb most of the radiation incident on the sample. The determination of the functional groups on the surface of the nanotubes (especially if they contain long carbon chains) is complex, however polar functionalities containing oxygen can be detected [187]. This characterization technique must be coupled with one of the other characterization techniques. In particular, IR spectroscopy is complementary to Raman and they are often used together for a more complete characterization of the surface.

5.9. Thermogravimetric analysis

Thermogravimetric analysis or thermal gravimetric analysis (TGA) is a method of thermal analysis in which the mass variation of a sample is measured while the temperature changes. This measurement provides information about thermal stability, thermal decomposition, and thermal oxidation of samples [188]. This technique can be coupled to a mass or IR spectrophotometer to analyze the gases emitted during the thermal decomposition. TGA is mainly used in the study of the thermal stability of CNTs (lattice defects and disorders affects the thermal stability), and differences in the thermal degradation between functionalized and pristine nanotubes can be distinguished.

6. Suggestion for a good dispersion

The mechanism of dispersion is still unclear as of today. In the literature it is assumed that it proceeds by breaking large agglomerates of CNTs into smaller agglomerates. This phenomenon is supposed to occur through two mechanisms, namely rupture (a bulk phenomenon) and erosion (a surface phenomenon). In rupture mechanism, the large agglomerates are broken down into smaller ones in short times, whereas in erosion mechanism, large agglomerates are eroded into smaller ones by removing single nanotubes or small nanotubes bundles from the agglomerate surface, thus needing comparatively longer time [189]. An efficient dispersion of carbon nanotubes inside a matrix plays a key role when CNTs are used as fillers in nanocomposites, hence the dispersion technique used significantly affects the final properties of the composite. Generally mechanical dispersion is used alone or in combination with chemical functionalization. A good approach to successfully disperse CNTs can be summarized in five points:

- Define the structure and dimension of CNTs agglomeration: this is important since the typology of agglomeration can affect the degree of CNTs dispersion. Big agglomerates require long time or high energy for dispersion, with the risk of damaging the structure of CNTs.

- Analyze the chemical properties of the solvent/matrix in which the nanotubes must be dispersed. The agglomerated CNTs can be dispersed directly in some solvents or polymers by directly using mechanical dispersion (such as ultrasonication or high shear stirring), thus obtaining good dispersion and good performance of composite.
- Perform in solution a step of dispersion beforehand by breaking the agglomerates of nanotubes using mechanical dispersion. This step is essential for performing a homogeneous wet chemical functionalization of CNTs. Big agglomerates do not permit the penetration of chemical reactant in the middle of the agglomerate affecting the effectiveness of surface modification of CNTs in that position.
- Functionalize the CNTs to obtain a surface compatible with the medium in which they must be used. It is possible also couple the functionalization with mechanical dispersion methods, e.g. using ultrasonication in a solution with surfactant increasing the deagglomeration of CNTs and their stability in the final solution.
- Disperse the treated CNTs in the matrix by using the most appropriate mechanical dispersion method. This must be chosen not only as a function of the matrix used but also as a function of the properties researched with the use of CNTs. If the mechanical dispersion requires high energy that can damage the structure of CNTs, a loss of mechanical and/or electrical properties of the final composite will occur.

It is important to remember that chemical functionalization can, as already mentioned above, alter the graphitic structure of the nanotubes. This can lead to a decrease in some properties of nanotubes (e.g. electrical conductivity). The functionalization of SWCNTs leads to a more severe reduction in electrical conductivity, while the effects are less severe for MWCNTs. If the functionalization is too strong, the CNTs can be easily dispersed in the matrix or solvent, but this very good compatibilization with the matrix will not show beneficial effects on the final composite performance [190-192]. In addition to the methodologies presented in this article, it is to be noted that several new studies [193-198] are attempting to bypass the mechanical dispersion and chemical functionalization steps of the surface. These techniques plan a direct synthesis of CNTs on the powder with which the composite material is prepared.

7. Conclusion

In this review, an overview of various aspects playing important roles in the optimal use of CNTs as nanofillers in composite materials has been provided. We underlined that it is useful to have a basic knowledge of the way CNTs are synthesized (CVD is the most used technology at industrial scale) and what CNTs' properties can be expected as a consequence. For instance, as shown, single-wall and multiwall CNTs can exhibit significant electric and mechanical dissimilarity, but differences can be also found within the same family of SWCNTs or MWCNTs due to the degree of lattice defects. Lattice defects can be present in the pristine CNTs because of the synthesis methodology used. But defects can also be introduced a posteriori when mechanical or chemical dispersion methods are applied to improve and facilitate the dispersion of the CNTs inside a matrix. As discussed, CNTs tend to be agglomerate in different forms like bundles, combed yarn and bird-nest that must be untangled. Various mechanical dispersion methods can be used for this purpose. However, the mechanical dispersion is often not enough to disperse CNTs, especially inside polar media (CNTs have apolar graphitic structure). Thus, it is necessary to introduce a functionalization step. Several chemical and physical functionalization treatments have been illustrated in this work. All these methods change the CNTs surface, making them more polar and, consequently, more wettable in polar media. Functionalization can also help to produce a chemo-physical interaction with the matrix. However, the functionalization and mechanical dispersion techniques can also significantly damage the CNTs structure with consequent loss of the remarkable innate properties of the CNTs needed in the composite. Therefore, it is necessary a trade-off to minimize the CNTs damage as much as possible while maximizing the dispersion and interaction within

the matrix. In order to help the reader with this endeavor, we have illustrated several characterization techniques to evaluate the damage and the properties of CNTs, both before and after treatments.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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