

Improving Carbon Nanotube/Polymer Interactions in Nanocomposites

Francis Avilés*, Juan V. Cauich-Rodríguez*, Patricio Toro-Estay**,
Mehrdad Yazdani-Pedram**, Héctor Aguilar-Bolados**

*SCIENTIFIC RESEARCH CENTER OF YUCATAN, AC (CICY), (CENTRO DE INVESTIGACIÓN CIENTÍFICA DE YUCATÁN, A.C., UNIDAD DE MATERIALES), MÉRIDA, YUCATÁN, MEXICO;

**UNIVERSITY OF CHILE (UNIVERSIDAD DE CHILE), SANTIAGO, CHILE

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5.1 Introduction

Surface modification is the act of modifying the surface of a material by generating physical, chemical, or biological characteristics different from the ones originally found. A common way to achieve this goal is through chemical functionalization, which introduces new functional groups on the surface of the “substrate” material. Besides increasing the chemical reactivity of the surface, these new chemical groups need to be carefully chosen to match the surface groups or molecules of a second material that the substrate is aimed to interact with to promote physicochemical interactions. For carbon nanotubes (CNTs), their strong C–C covalent bonding and ring structure not only render excellent physical properties, but also render low chemical reactivity, which causes difficulties in their

interaction with polymer molecules. This creates a need for chemical and physical surface modifications on CNTs to improve their physicochemical interactions with host polymers. The selection of the CNT functionalization method and molecule(s) used strongly depends on the chemical nature of the host polymer, and their selection is a topic addressed in this chapter. Although the mechanical properties of CNT/polymer composites may not compete with those of fiber-reinforced polymer composites, the selection of an adequate CNT functionalization method/bridging molecule could greatly assist in creating proper interfaces that improve the mechanical, thermal, electrical, and multifunctional properties of polymer nanocomposites.

5.2 Carbon Nanotube Functionalization Methods

Chemical (or physical) modifications of CNTs are frequently required to achieve their full potential and exploit their outstanding properties. Chemical modifications of CNTs generally occur at their end caps or defective sidewalls. It is generally accepted that with the loss of π -conjugation, there is also a change from sp^2 to sp^3 hybridization. These modifications may allow a good dispersion into a polymer matrix, improve the polymer–CNT load transfer ability in the resulting composite, and also allow proper CNT characterization in solution. Enhanced interactions between CNTs and a polymer matrix can be achieved in several ways. The most common ones are chemical methods for covalent attachment of different organic groups, but there are also alternatives that use defect-group or defect-site functionalization (such as Stone–Wales defects, sp^3 -hybridized defects, vacancies, etc.), noncovalent functionalization with surfactants, and noncovalent exohedral and endohedral functionalizations. Although physical and other functionalization methods are touched upon herein, this section focuses on chemical modifications through the covalent attachment of functional groups.

5.2.1 Oxidation

Oxidation is undoubtedly the most common functionalization method for CNTs. It can be used as a final treatment to improve the functionality of single-wall (SWCNT) and multi-wall carbon nanotubes (MWCNTs) [1–3], or as the first treatment of a sequence of chemical modifications [4–6]. It is also frequently used to improve the dispersion of CNTs in liquids, organic solvents, and polymers [7,8]. Most of the purification methods used after CNT synthesis employ acids to dilute the metallic catalysts, so a certain degree of oxidation may be inherently conducted even when it is not deliberately attempted [9,10]. For commercial CNTs, this is evident from the physicochemical characterization of the as-received material, showing the presence of oxygen-containing functional groups [11,12]. CNT oxidation can be conducted by physical methods, such as plasma treatments [13], and also by wet-chemical methods [4]. Plasma treatments, such as UV/ozone or oxygen plasma, have the advantage of being gentle to the CNT structure, yielding only minor damage [13–15]. However, the density of oxygen-containing functional groups generated by known plasma

treatments is significantly less than that generated by wet-chemical methods; therefore, a compromise exists between CNT damage and the density of functional groups. In spite of these options, the large majority of works dealing with CNT polymer composites in the open literature have preferred wet-chemical methods to promote covalent bonding, albeit with some CNT damage, which seems unavoidable [12,16,17].

CNT oxidation by means of inorganic acids, such as nitric acid (HNO_3), sulfuric acid (H_2SO_4), or a combination of both, are among the most reported methods to date [12,17–20]. The use of potassium permanganate (KMnO_4), hydrogen peroxide (H_2O_2), ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$), ozone (O_3), and other similar chemical compounds are also effective oxidation methods [4,5,21]. Successful oxidation methods generate carboxyl, carbonyl, and hydroxyl functional groups, typically as part of carboxylic acids, aldehydes, ketones, or alcohols. The relative contribution of each of these functional groups depends on the oxidation treatment employed. Using X-ray photoelectron spectroscopy, Wepasnick et al. [21] examined six common chemical oxidation methods, and concluded that oxidation with KMnO_4 and the mixture of nitric and sulfuric acids are the chemical treatments that yield a higher degree of oxidation (based on O at.%) and generation of COOH functional groups. On the other hand, they report a higher density of C=O groups for treatments using H_2O_2 or O_3 . Concomitant with the generation of moieties upon oxidation is the generation of sp^3 hybridization defects in the sp^2 structure of the CNTs [22,23]. For cases where a high concentration of OH groups is desired, chemical reduction can sequentially be used after oxidation [24,25]. For example, Scheibe et al. [25] report the use of sodium tetrahydroborate (NaBH_4) to convert carbonyl and lactone groups of oxidized MWCNTs into hydroxyl groups. The generation of these new OH groups, however, may be at the cost of reducing COOH groups [24].

Oxidation may generate structural damage in the form of vacancies, Thrower or Stone–Wales defects and erosion of the CNT walls [26–29]. It is widely accepted that the functional groups generated by oxidative treatments concentrate on the CNT ends and defective sites, as depicted in Fig. 5.1.

The extent of CNT damage generated upon oxidation depends on several factors, such as the oxidant agent used, its concentration, treatment time, and method employed [12,27,29–31]. In that respect, Avilés et al. [12] proposed a sequential combination of 3.0 M HNO_3 and H_2O_2 (30% v/v), both for 2 h, as an oxidation method that reduces CNT damage. Fourier transform infrared spectroscopy (FTIR) analysis of the MWCNTs oxidized by this method (Fig. 5.2A) reveals the presence of O–H, C=O, C–O, and CH/CH₂ functional groups. The N_2 adsorption–desorption isotherms of these MWCNTs correspond to mesoporous materials with a hysteresis loop toward the end of its cycle [6], and, upon oxidation, the adsorbed volume increases (Fig. 5.2B). The increased adsorbed volume upon oxidation is ascribed to new pores coming from the elimination of amorphous carbon and probably from the elimination of impurity traces. Roughening of the external MWCNT walls and a certain extent of MWCNT damage may also contribute to the increased adsorbed volume. Thermogravimetric analysis (TGA) may also be employed to assess oxidation; as seen from Fig. 5.2C, upon mild oxidation; elimination of amorphous carbonaceous material renders increased thermal stability.

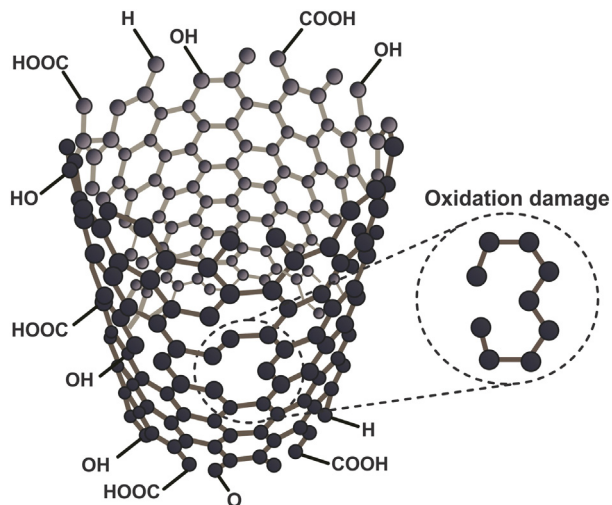


FIGURE 5.1 Schematic of functional groups and structural damage generated by CNT oxidation.

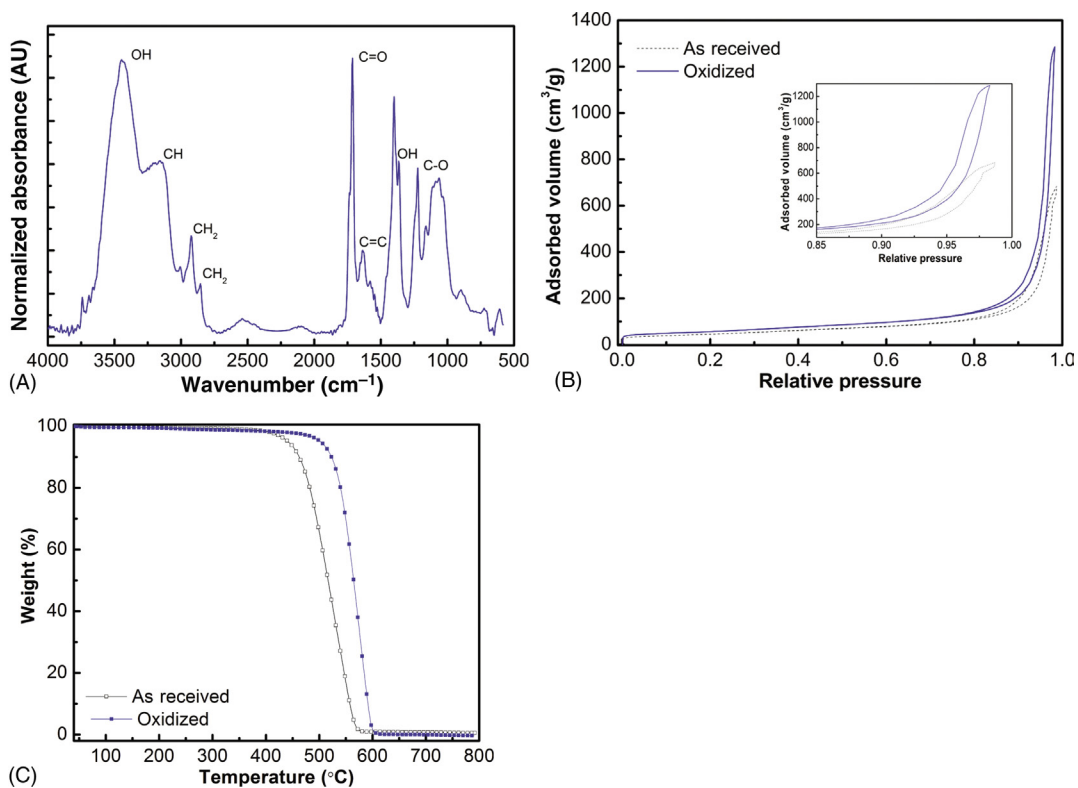


FIGURE 5.2 Characterization of chemically oxidized MWCNTs. (A) Fourier transform infrared spectroscopy (FTIR), (B) adsorption isotherms, and (C) thermogravimetric analysis (TGA).

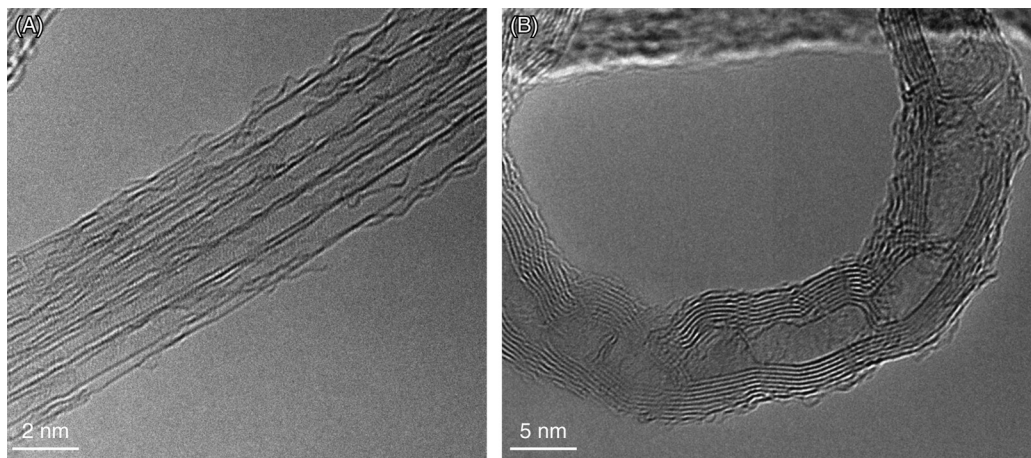


FIGURE 5.3 Transmission electron microscopy (TEM) images of CNTs oxidized under aggressive acid conditions. (A) SWCNTs and (B) MWCNTs.

Other forms to characterize CNT oxidation may employ X-ray photoelectron spectroscopy, UV–Vis transmittance of colloidal dispersions, and quantification of the CNT mobility in solution by zeta (ζ)-potential measurements [6,21,32]. The ζ -potential of CNTs is a strong function of the O/C ratio, pH, and solvent employed [32,33]; ζ -potentials of the order of 30–60 mV have been reported for oxidized MWCNT, depending on the pH and oxidation agent [32,33]; the reported trend is to increase the ζ -potential toward more negative values as the degree of oxidation and/or pH increases.

Oxidations with overly concentrated acids or that are conducted for prolonged time periods may severely damage the surface of CNTs, even causing fragmentation [27,29]. Fig. 5.3 shows transmission electron microscopy (TEM) images of SWCNT bundles (Fig. 5.3A) and an individual MWCNT (Fig. 5.3B), both treated with a 1:1 mixture of H_2SO_4 (99% v/v) and HNO_3 (70% v/v) for 2 h. As seen from this figure, such an aggressive acid condition causes surface roughening, erosion, wall attrition, local bends, wall stripping, thickness reduction (rendering nonuniform wall thickness and diameter), and conversion of part of the graphitic structure of the outermost and innermost layers into disordered carbon, due to the harsh etching action of the acids employed. The situation may be more severe for SWCNTs than for MWCNTs, given their single-layer condition [34]. These defects alter the electronic and vibrational properties of the CNTs, and may greatly impact their mechanical and electrical properties, and those of their polymer composites [22,26].

However, structural defects are active sites for recombination, and have been experimentally and theoretically identified as key locations for further functionalizations [35,36]. It has even been proposed that the control of defects in CNTs could lead to tailored electronic and structural properties, and even control of the CNT geometry [37]. Therefore, the compromise between the generation of a high density of oxygen-containing functional groups and the preservation of length, hybridization, and structural properties of CNTs

must be customized depending on the application. For the mechanical and electrical properties of polymer composites, preserving CNT length and structural properties may be the decision driver; however, for applications, such as functionalization with biomolecules, producing a higher density of functional groups may overcome the general desire of structural preservation.

5.2.2 Silanization

One of the most common techniques reported to modify hydrophilicity and improve the chemical compatibility between CNTs and polymer matrices is silanization [24,38,39]. Silanes were originally developed as coupling agents to improve adhesion between organic resins and inorganic surfaces, and are also used as coupling agents for conventional polymer composites made of glass and carbon fibers [40,41]. Organofunctional silanes typically contain organic and inorganic moieties in the same molecule, and therefore they work as coupling agents for polymer composites. Silane-coupling agents are organosilane compounds that have at least two different reactive groups bonded to a silicon atom in a molecule; one of the reactive groups (e.g., methoxy, ethoxy, or acetoxy group) is reactive with the surface of the inorganic material (e.g., glass, carbon, metals, and silica). The other end of the molecule (e.g., epoxy, vinyl, methacryl, or amino group) is reactive with the organic material or synthetic resin, acting in this way as a chemical bonding agent. Therefore, in this functionalization method, the silane-coupling agent is expected to create a bridge at the interface between the CNT and the polymer matrix. A very small amount of an organofunctional silane may not only improve the interfacial strength, but also result in its retention over time. For the case of CNTs, although CNT silanization might be possible directly over as-produced CNTs, it has been mostly achieved by taking advantage of the hydroxyl and/or carboxyl groups previously produced during the CNT oxidation process [24,38,42,43]. Therefore, an oxidation treatment normally precedes CNT silanization. The choice of an adequate silane as a CNT surface treatment is instrumental for the correct compatibility with the polymer matrix and promotion of surface bonding. The selection of a specific silane for a polymer composite is based on matching the organofunctional group of silicon with the resin polymer type to be bonded (Fig. 5.4). For example, CNT functionalization by amino-based silanes (such as 3-aminopropyltriethoxysilane) are adequate for epoxy resins [39,44]. Another silane used for CNTs that matches the functional groups of most epoxy resins is 3-glycidoxypropyltrimethoxysilane [7,45]. 3-Isocyanatopropyltriethoxysilane has been used to strengthen the chemical interface of polyimide and polymethyl methacrylate MWCNT composites [46,47]. A general schematic of possible chemical reactions occurring during MWCNT silanization for three different silanes is depicted in Fig. 5.4. The silanes in this figure are 3-methacryloxypropyltrimethoxysilane (MPS), 3-aminopropyltriethoxysilane, and 3-mercaptopropyltrimethoxysilane (MPTMS), where ethanol or methanol can be produced as by-products.

For example, for polyester or vinyl ester resins, MPS has been reported to promote chemical bonding with MWCNTs, especially when the MWCNTs have been previously

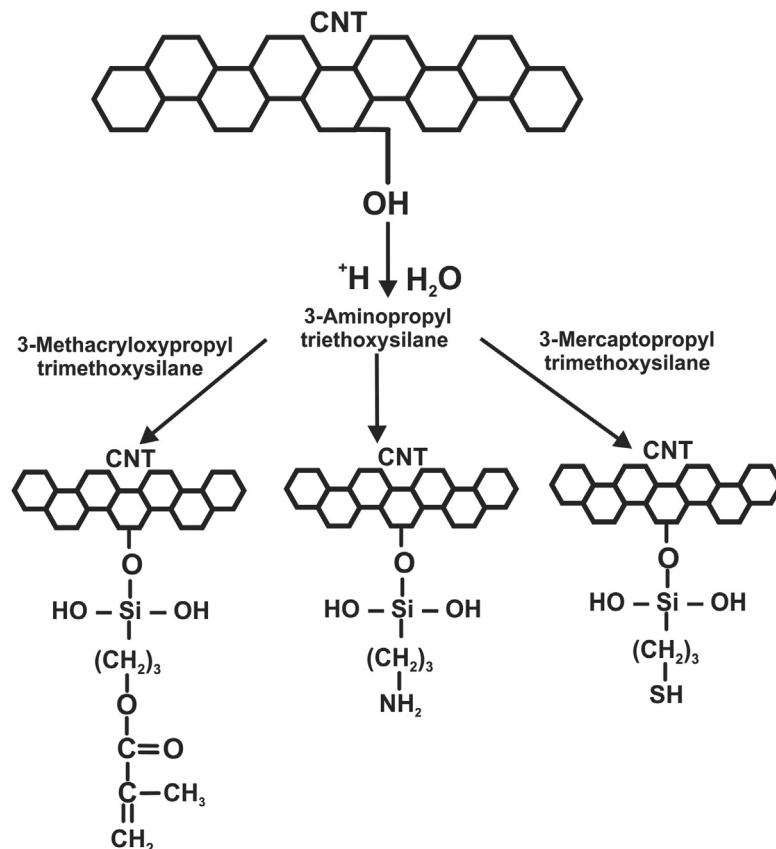


FIGURE 5.4 Different types of silane-coupling agents used for CNT functionalization (after oxidation).

chemically oxidized [43]. For this case, a more detailed schematic of a possible chemical reaction occurring during MWCNT silanization is depicted in Fig. 5.5A. The oxidized MWCNT surface contains (hydrophilic) hydroxyl groups that act as reaction sites (Fig. 5.5A). The MPS contains a trimethoxy group that after hydrolysis also forms hydroxyl groups and methanol (Fig. 5.5B). The hydroxyl groups on the CNT and silane condense to covalently bind a methacrylate group (hydrophobic) on the MWCNT surface (Fig. 5.5C). The methacrylate group (also an ester), matches the chemical structure of several polyester and vinyl ester resins that may be used as matrices for polymer composites. Similar chemical reactions have been proposed for other silanes, such as those shown in Fig. 5.4 [24,38].

It is important to point out that the reaction proposed in Fig. 5.5C rests upon the OH groups present on the (oxidized) CNT surface, but other chemical reactions based on the COOH groups of the CNT are also possible [42]. If needed, additional OH groups can be generated by reducing the COOH groups of the oxidized CNTs [24]. The silanization

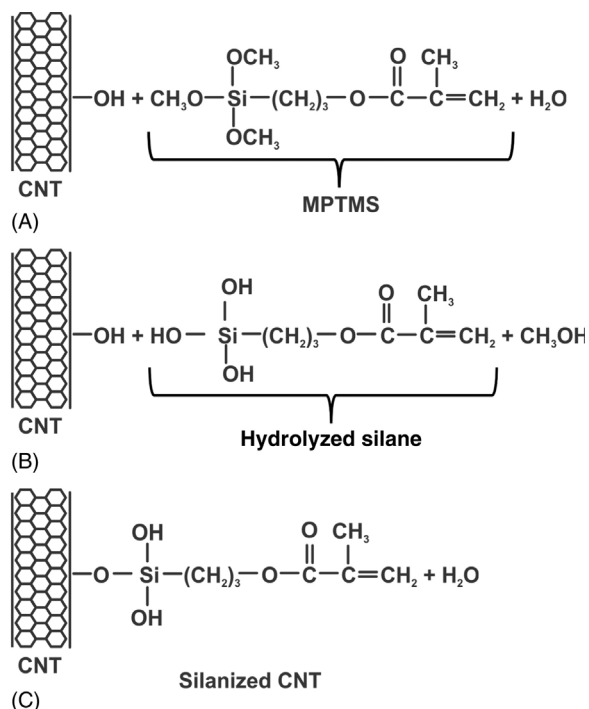


FIGURE 5.5 Schematic representation of a CNT silanization process using 3-methacryloxypropyltrimethoxysilane (MPS). (A) Hydrolysis of silane in presence of oxidized CNTs, (B) reaction between the hydrolyzed silane and the oxidized CNT, and (C) silanized CNT containing functional groups affine to vinyl ester or polyester resins. *MPTMS*, 3-mercaptopropyltrimethoxysilane.

process for CNTs was inherited from the large knowledge accumulated for engineering fibers, such as glass and carbon fibers [40,48]. Although the general procedure used for CNT silanization may be similar to that of conventional (micron-size) engineering fibers, several parameters need to be adjusted for the correct and homogenous silanization of such nanostructures. First of all, for CNTs, the use of ultrasonic waves (or other effective form of dispersion) is highly recommended to achieve homogenous coverage of individual CNTs [6,49]. The concentration of silane in the solution is also quite different to that employed for conventional micron-size fibers. This is because the surface area per unit weight of CNTs is about 2–3 orders of magnitude higher than that of conventional carbon fibers. While conventional engineering fibers use typical silane concentrations (weight of silane with respect to fiber weight) around 0.03–5 wt.% [41,50], successful silane concentrations for MWCNTs have reported the use of 1–2× the weight of silane with respect to the MWCNT weight [6,7,24,44]. On this issue, Avilés et al. [6] reported that the use of MPS at concentrations ranging from 3.5 wt.% to 1000 wt.% (10×) improves the interfacial strength of vinyl ester matrix composites. Based on TGA measurements, they estimated the weight of incorporated silane on the surface of the MWCNTs, finding a decrease in the amount of

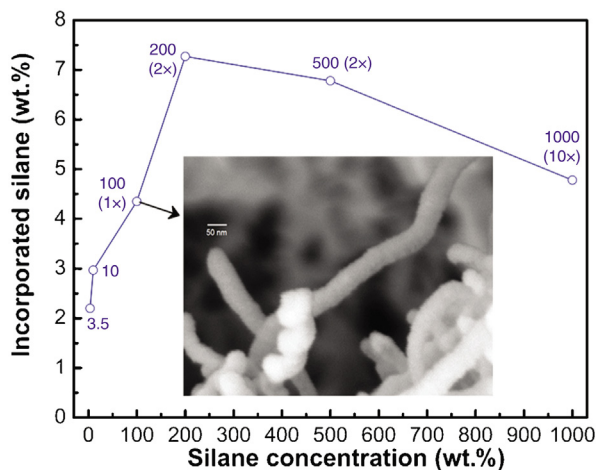


FIGURE 5.6 Concentration of silane incorporated on the MWCNT surface as a function of weight concentration of silane used for MWCNT silanization. Inset shows silanized MWCNTs at 1× silane concentrations.

silane that is effectively incorporated to the MWCNT when silane concentrations beyond 2× (200 wt.%) are used (Fig. 5.6).

Field emission scanning electron microscopy (see inset in Fig. 5.6) showed that for 1× and 2× concentrations, the MWCNT surface is homogeneously covered with MPS, but beyond 2× excess of silane occurs; this means that for concentrations beyond 2×, layers of polysiloxanes may react with themselves, modifying the properties of the interface. This overly formation of polysiloxanes may weaken the strength of the interface and degrade the mechanical properties of polymer composites [6].

5.2.3 Fluorination

Halogenation is very common nowadays for the chemical modification of CNTs. Although chlorination and bromination have been reported as means of halogenation [51], fluorination is preferred to enhance the reactivity of the CNT sidewalls [52,53]. Besides improving the chemical reactivity, fluorination facilitates disentanglement of nanotube bundles and improves processability and solubility [52]. Fluorination improves solubility in solvents such as *N,N*-dimethylformamide (DMF), tetrahydrofuran (THF), and alcohols (such as 2-propanol or 2-butanol), but CNTs treated by fluorination do not dissolve in per-fluorinated solvents, water, diethyl amine, and acetic acid [52]. This type of functionalization weakens the C–F bonds, increases the chemical reactivity of CNTs, and allows further modifications, particularly the attachment of nucleophilic substituents bearing hydroxyl, amino, and carboxylic as terminal groups or even *N*-alkylamino substitutions or alkylation reactions. CNT fluorination can be reverted by a reaction with hydrazine.

Several methods for fluorination exist, such as direct gas, plasma, and hydrothermal fluorination. Direct fluorination can be achieved by a high-temperature reaction (200–250°C) in the presence of hydrogen fluoride [52], as depicted in Fig. 5.7. Similarly,

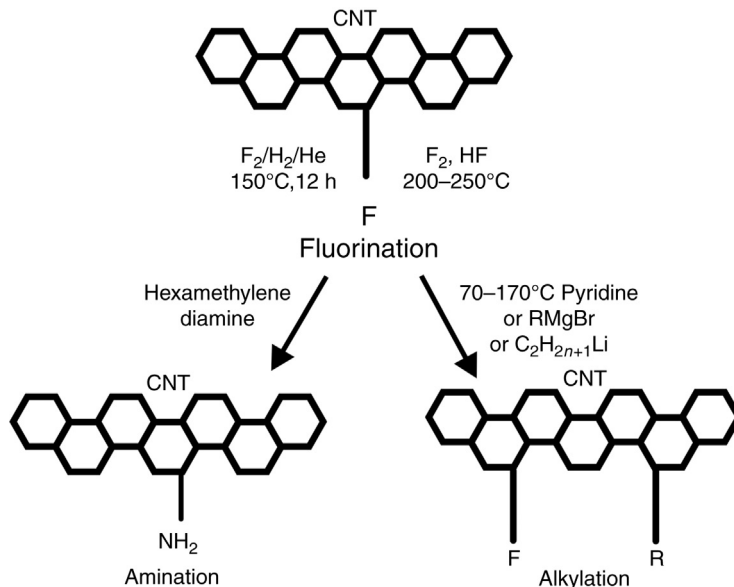


FIGURE 5.7 Common CNT fluorination reactions.

carboxyl-modified CNTs can be treated with a mixture of $\text{F}_2/\text{H}_2/\text{He}$ (2/1/30) at 150°C during 12 h to incorporate F atoms to the CNT surface [54,55]. Fluorine can be identified by attenuated total reflectance FTIR by the presence of a band at $1220\text{--}1250 \text{ cm}^{-1}$. In Zhu et al.'s work [55], Raman spectroscopy showed that the appearance of an sp^3 carbon peak at 1301 cm^{-1} indicates that the sidewalls are covalently modified with fluorine, while elemental analysis showed that up to 20 wt.% of F can be incorporated.

Fluorinated CNTs can serve as a reactive substrate for further chemical modifications. Following CNT fluorination, the reaction with alkoxides (e.g., sodium methoxide in methanol) results in methoxylated CNTs [52]. When these reactions are conducted with lithium hydroxide in methanol, a methoxy derivative is also obtained. Organolithium derivatives, such as methyl, *n*-butyl, *n*-hexyl, and phenyl, can also react with fluorinated CNTs to obtain an alkylated derivative that is soluble in chloroform and THF.

By reacting fluorinated CNTs with methyl, ethyl, butyl, hexyl, octyl, and dodecyl lithium derivatives, or alkyl magnesium bromide (Grignard reagent), partial alkylation can be achieved while retaining F atoms [56] (Fig. 5.7). Li, Na, or K hydroxides in the presence of ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,2-propanediol, 1,2-butanediol, or glycerol yield hydroxyl-terminated CNTs with some remaining atoms of fluorine [57].

5.2.4 Amination

The formation of primary, secondary, tertiary, or even quaternary ammonium salts on CNTs is a common method pursued for different purposes, including solubilization [58], compatibilization with polymeric matrices based on copolyimides [59], heavy metal

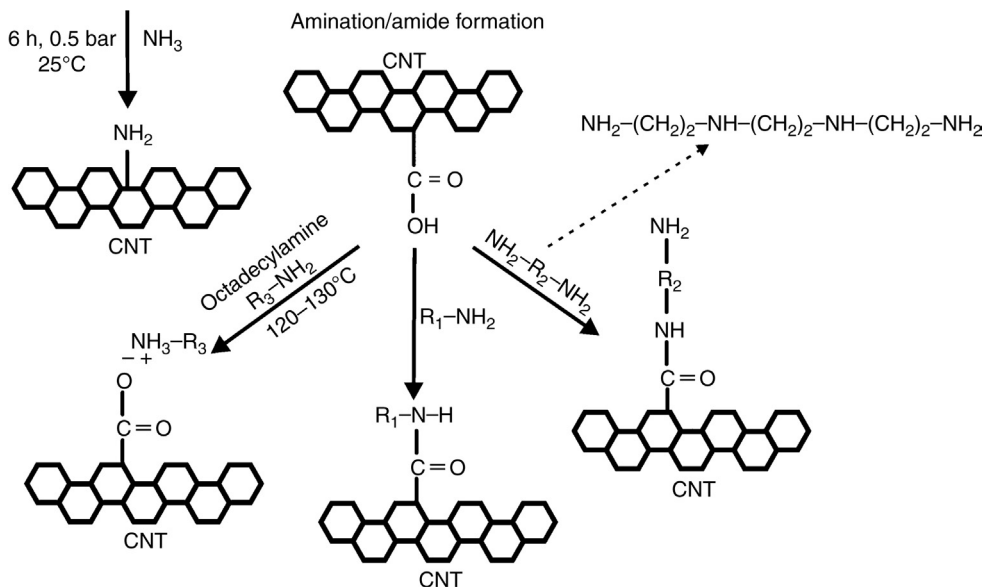


FIGURE 5.8 Typical reactions for CNT-amine/amide formation.

elimination from water effluents [60], crosslinking reactions with epoxy resins [61], and even for delivering genetic material [62,63]. The introduction of amine functional groups has been achieved through a variety of methods comprising gas or liquid phases; identification of amino groups can be achieved by several methods including FTIR, ζ -potential, and TGA. Its quantification by the Kaiser's method or ninhydrin assay (among other techniques) can prove the existence of these chemical moieties. A word of caution is mentioned, as many of these reactions can be reverted (intentionally or unintentionally) during the manufacturing of composites.

Direct amination, as described in Fig. 5.8, has been achieved by ball-mill treatment of MWCNTs in the presence of NH_3 gas flow of 50 mL/min during 6 h at 0.5 bar and 25°C [59,64]. However, oxidation is commonly the first step for the introduction of amino groups. In this regard, CNT amination is achieved after oxidation with nitric acid, combination of nitric and sulfuric acids, or treatments with thionyl chloride to form acyl chloride, followed by subsequent reaction of ethylene diamine [60]. In this case, the linking bridge contains an amide linkage, a hydrolytic unstable moiety, and the end group is a primary amine.

Amine functional groups on the CNT surface are frequently used for improving the chemical compatibilization with epoxy-based composites. For this type of modification not only oxidized CNTs [61,65,66], but also fluorinated CNTs [5,67] can be used. Oxidized CNTs can be treated with triethylenetetramine, diamines ($\text{H}_2\text{N-R-NH}_2$), or hydroxylamines [$\text{HNR}(\text{CH}_2)_n\text{OH}$] in the presence of pyridine to yield amino-terminated or hydroxyl-terminated CNTs, respectively, as shown in Fig. 5.8.

Sun et al. [68] covalently introduced amine groups into CNTs for preparing epoxy composites. This was achieved by using carboxylated (COOH) CNTs, followed by conversion into the corresponding acyl chloride, and finally by the reaction of 1,6-diamino hexane. Amination was proved by using FTIR by the presence of a wide band in the range of 2800–3500 cm^{-1} , bands at 2900 cm^{-1} corresponding to C–H stretching of the diamine, and absorptions at 1640, 1490, and 1300 cm^{-1} , corresponding to amide I, amide II, and amide III, respectively. Further evidence arose from the presence of bands related to N–H bending at 1570 cm^{-1} . In their work, ζ -potential was also used as a method to identify the presence of amino groups on the CNTs. In this case, the ζ -potentials of COOH- and NH_2 -treated CNTs were quite different at any pH value. For COOH-treated CNTs, the ζ -potential was slightly negative and decreased up to -35 mV when the pH increased from 2 to 9. The behavior was opposite for NH_2 -treated CNTs, which present a $+30$ mV ζ -potential at a pH of 2 that decreases to zero as the pH approaches 9. This later behavior was attributed to the presence of amido groups, which protonate via H^+ capture in the aqueous solution. Finally, by using TGA, decomposition of amino groups was also suggested in the range of 200–430°C, while above 440°C, the decomposition of secondary amidocyanogen was reported. By using TGA, a 3.1 wt.% of amino groups was estimated.

Amination has also been achieved by both cycloaddition reactions [62] and also by direct conversion of the carboxylic groups on the oxidized CNTs into amine groups [63] to deliver either DNA plasmids or siRNA.

Soluble octadecylammonium CNT-carboxylated zwitterions (Fig. 5.8) have been obtained by the reaction of nitric acid-oxidized SWCNTs in the presence of octadecylamine in the molten state (120–130°C) [58]. The authors claim that this ionic functionalization was chosen because this method provides a higher yield than covalent functionalization and is a simpler, cost effective, and can be scaled up.

Amide formation can also be achieved through Claisen reaction using oxidized CNTs treated with *N,N*-dimethylacetamide dimethylacetal [69]. Amide formation has also been suggested by the condensation reaction between carboxylic acid and amino-functionalized CNTs [70]. In Hecker et al.'s work [70], the interconnected CNTs were assisted by using carbodiimide-activated coupling using *N,N*-dicyclohexyl carbodiimide dimethyl amino pyridine. Other possible methods for the formation of primary amines on CNTs make use of the halide derivative and its reaction with an excess of ammonia. Similarly, azides, nitriles, and nitrocompounds can be reduced, leading to amine formation.

Aminated CNTs can be further derivatized. Oxidation of amines with H_2O_2 , KMnO_4 , or peroxyacids can lead to hydroxyl amines, amine oxides, nitro compounds, or nitro derivatives. The reactions of aldehydes and ketones with NH_2 -functionalized CNTs can lead to imine formation (Schiff base), which after reduction can result in the production of secondary amines. The reaction with sulfonyl chloride can lead to sulfonamides, a known family of compounds with antibacterial activity. However, in many of these derivatives heat can have a profound effect, such as in the case of Hoffman's elimination, where the ammonium salt can lead to alkene formation. These need to be taken into consideration especially for thermoforming or composite manufacturing at high temperatures.

5.2.5 Other Chemical Modifications

Several organic functional groups other than OH, COOH, F, or NH₂ can be directly introduced to CNTs with specific purposes. Transformation of metallic SWCNTs to semi-conducting type with minimal modification of the electronic structure is reported to be achieved through hydrogenation [71]. Hydrogenation can be achieved by the Birch reaction using ammonia as the reaction medium [72] or by flowing hydrogen gas through a hot tungsten filament [71]. Vinylation was used by Kan et al. [73] for molecular-imprinted polymers with the capability of specific adsorption and recognition of the template molecule. For this, carboxylated MWCNTs were treated with thionyl chloride and then allylic alcohol for the selective copolymerization of methacrylic acid and trimethylolpropane trimethacrylate using dopamine as a template. Nitrenes can be thermally generated on CNTs by microwave activation with *p*-toluenesulfonyl, methylsulfonyl, and trimethylsilyl azides, or even isocyanates, yielding the corresponding aziridine [74]. Furthermore, cyclopropanation of CNTs can be achieved by a reaction with diethyl bromomalonate with sodium hydride (Bingel reaction). Direct addition to the unsaturated π -electrons can also be achieved by Diels–Alder addition to render carboxylic groups on the CNT surface [75]. This type of reaction has been extended to various dienes and dienophiles with the aim of introducing alcohol, amine, carboxylic, epoxy, and ester groups [76]. Sidewall functionalization with 12%–23% dichlorocarbene (nucleophilic carbene addition) has generated SWCNTs that are soluble in both THF and dichlorobenzene [77]. The free radical addition of succinic or glutaric acid acyl peroxides in *ortho*-dichlorobenzene at 80–90°C has been reported to introduce 2-carboxyethyl or 3-carboxypropyl groups on the sidewalls of SWCNTs [2]. The introduction of substituted pyrrolidine rings by 1,3-dipolar cycloaddition of azomethine ylides has been reported by Herrero and Prato [78]. Thiol- or mercaptane-functionalized MWCNTs have been prepared by treating hydroxyl-terminated MWCNTs with thiourea in the presence of hydrobromic acid and glacial acetic acid [79]. By using condensation reaction of an *N*-(4-hydroxyphenyl)glycine and formaldehyde, Bae et al. [80] prepared SWCNTs with azomethine ylide groups containing anchored phenol structures. Classic coordination complexes and organometallic compounds have been suggested by Kharisov and Kharissova [81] to increase the solubility of CNT and as a metal precursor for decoration and encapsulation of metals and oxides. Therefore, it is clear that although many chemical reactions have been explored to modify the surface of CNTs to improve their compatibility with polymers, there is plenty of room for further modifications.

5.3 Carbon Nanotube Functionalization for Improved Properties of Polymer Composites

CNT functionalization can be used for a variety of purposes, from improving dispersion, subsequent doping, and sensing biomolecules to improving interfacial adhesion with polymers by the promotion of the formation of covalent bonds. For polymer composite applications, the functional groups created on the surface of the nanotube have to match

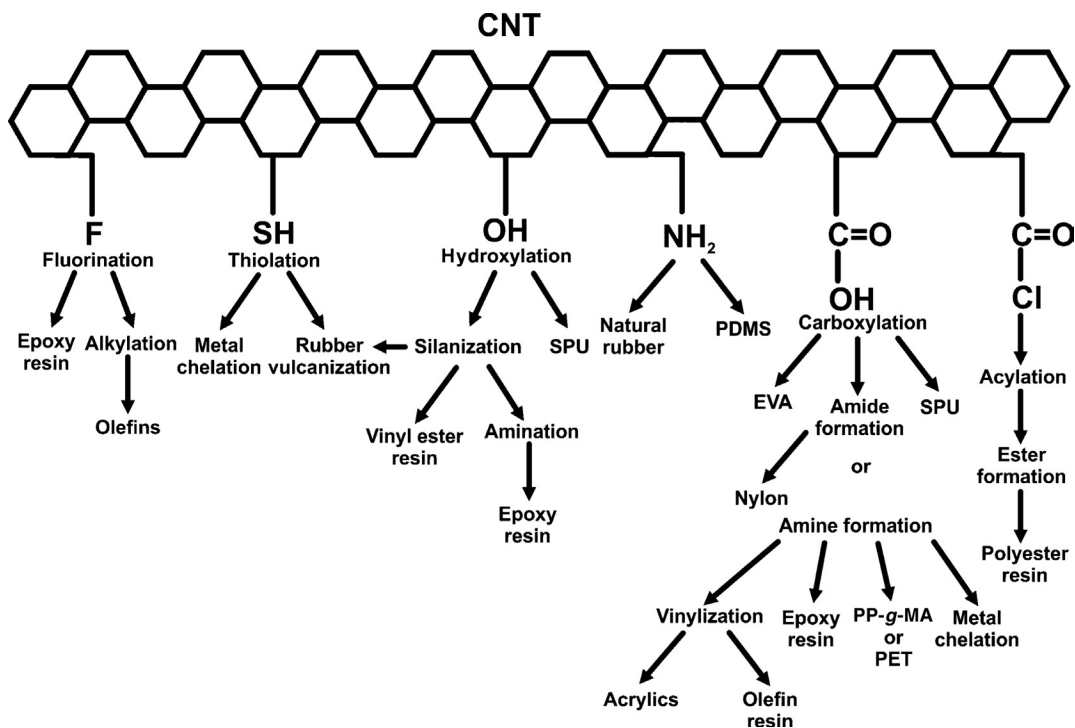


FIGURE 5.9 Routes for CNT functionalization depending on the chemical nature of the polymer matrix. *EVA*, Ethylene–vinyl acetate; *SPU*, segmented polyurethane; *PDMS*, polydimethylsiloxane; *PET*, polyethylene terephthalate; *PP-g-MA*, polypropylene grafted with maleic anhydride.

the active functional groups of the polymer of interest, which can be a challenging task. Fig. 5.9 suggests some functional groups that can interact better with common polymer matrices used for composite preparation. For example, CNT carboxylation can be used directly to fabricate functionalized ethylene–vinyl acetate (EVA) or segmented polyurethane (SPU) composites; however, after further chemical modifications forming amides or amines, they can be used for nylon, epoxy, olefin, or acrylic polymer composites.

This section revises the most common functionalizations that have been conducted to improve interfacial interactions with thermosetting, thermoplastic, and elastomeric polymer matrices, and discusses the effective properties of the resulting functionalized nanocomposites.

5.3.1 Thermosettings

The most common thermosetting resins used for polymer composites are epoxy, vinyl ester, unsaturated polyester, and phenolic resins. The family of epoxy resins is undoubtedly the most studied thermosetting matrix due to its relative high strength and stiffness, low curing shrinkage, and high dimensional and chemical stability; these properties make

epoxy resins suitable for high-end applications in diverse fields, such as automotive, aeronautics, and the electronic industry. As for other polymers, the addition of CNTs into epoxy resins may render multifunctional nanocomposites, which can increase its mechanical, electrical, and thermal properties. However, to improve the physicochemical interactions at the interface between CNTs and epoxy, and to improve CNT dispersion, specific chemical functionalizations have to be conducted. Many efforts have been conducted to promote this affinity due to the entangled nature of CNT bundles and the dissimilar polarity between CNTs and epoxies [82]. Regarding CNT dispersion, several techniques, such as ultrasonic dispersion [30], calendaring [83,84], ball-milling [85], stirring, and extrusion [86] have been attempted. An alternative that can tackle the issues of dispersion and interfacial adhesion is functionalization [4]. The most recommended CNT functionalization methods reported in the literature for epoxy polymers are those obtained by fluorination, amination, or silanization (Fig. 5.9). Acylation followed by ester formation is also an option for polyester resins (Fig. 5.9). Direct fluorination of CNTs and their subsequent derivatization provide a versatile tool for the preparation and manipulation of nanotubes with variable noncovalent functionalities [52,55]. Fluorinated CNTs can be integrated into epoxy composites through the formation of covalent bonds in the course of epoxy ring-opening esterification and curing chemical reactions [55]. However, for epoxy resins, CNT functionalization with amino groups or a proper silane (such as 3-glycidoxypropyltrimethoxysilane) have been more commonly reported [39,45,61]. Upon functionalization, the CNT hydrophobicity decreases due to the incorporation of amino or silane groups on the CNT that encourage more reactive sites to covalently bind with thermosetting polar groups [87]. The reaction mechanisms of amino-(left) or carboxylate (right)-functionalized CNTs in the preparation of nanocomposites based on an epoxy matrix are shown in Fig. 5.10.

The final composite is obtained by the reaction between the active functional groups of the epoxy resin and the terminal amine (or carboxyl) functional group of the functionalized CNT. The incorporation mechanism involves one of the epoxy terminal groups as an active or electron acceptor site, and a nucleophilic (amino) terminal group on the functionalized CNT. As a result, a covalent N–C bond is formed joining H atoms of the terminal amino group on the CNTs with the epoxy [88–90].

The preparation of amino CNTs by covalent modification is normally sequential. For example, Iannazzo et al. [91] report functionalization of MWCNTs by three sequential steps, carboxylation, acylation, and, finally, amine modification. Amine-functionalized CNT composites could thus render strong interfacial interactions due to covalent bonding between the amine-treated CNTs and the epoxide resin, improving the mechanical and thermal properties of these composites [61,92]. The interfacial strength is associated with the length, purity, structure, and CNT functionalization, and therefore has a great influence on the final properties of the resulting composites. It is also possible to achieve high thermal stability, as well as a significant increase in strength, using cyclic and aromatic amines. Thus obtaining a composite with high interfacial strength and minimal CNT agglomeration depends on the structure and type of the amine group.

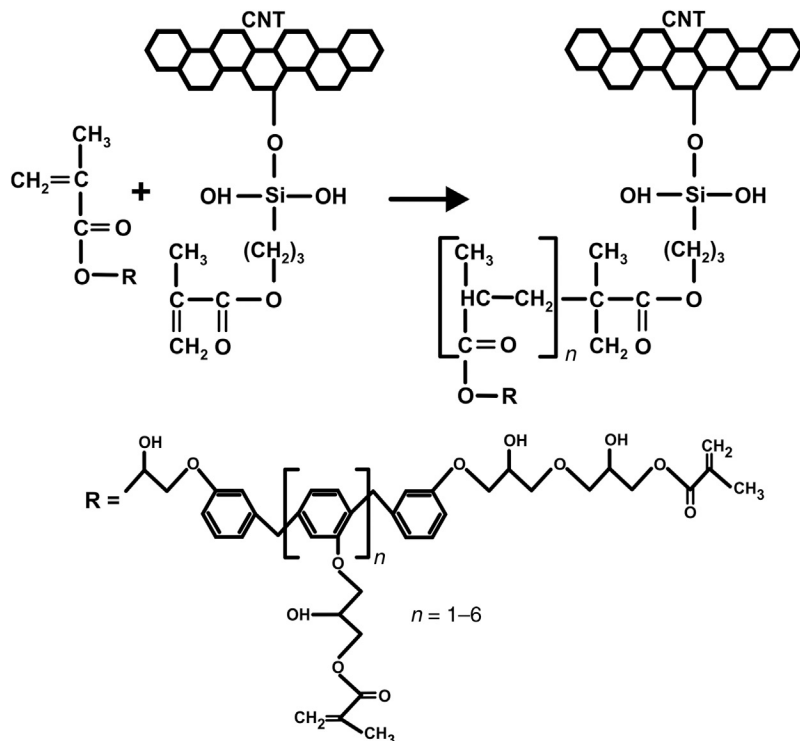


FIGURE 5.11 Reaction mechanism between an MPS-silicized CNT and a vinyl ester resin.

as 3-glycidoxypropyltrimethoxy or 3-aminopropyltriethoxy) are commonly used [39,45]. For vinyl ester and polyester resins, acrylate or vinyl olefin silanes are normally preferred [6]. As an example, Fig. 5.11 shows the interaction mechanism between an MPS-silicized CNT (Fig. 5.5) and a vinyl ester resin. This silane has a methacrylate organoreactive group and trimethoxy hydrolyzable groups, which match the organofunctional groups of the vinyl ester resin employed [43].

The vast majority of published works on mechanical and thermal reinforcement of polymer matrix nanocomposites that use functionalized CNTs are thermosetting matrices. This is probably because of the superior mechanical and thermal performance of thermosettings, as compared to thermoplastics and elastomers. Although both types of CNTs (SWCNTs and MWCNTs) have been extensively addressed, the majority of the reported work focuses on MWCNTs, probably because of their higher availability in large amounts, which is needed to fabricate polymer nanocomposites. It is generally accepted that the mechanical and thermal properties of thermosetting polymer composites increase when CNT weight concentration is increased, but such an increase is nonmonotonic. It has been suggested that the upper bound in CNT concentration to reach mechanical reinforcement is the percolation concentration, which may be easily estimated by electrical conductivity measurements [94]. This is because above certain critical CNT concentration, CNT

agglomeration and a large increase in resin viscosity occur, which greatly hinder the mechanical and thermal properties of nanocomposites. Such a critical CNT concentration depends on the CNT type, aspect ratio, functional groups on its surface, resin chemistry, resin viscosity, and dispersion method, among other factors [95–98]. This drawback is particularly relevant for tensile properties, as besides stress concentrations caused by CNT agglomeration, the increased viscosity of the solution may generate trapped bubbles, causing crack tip opening and rapid crack propagation upon tensile loading, greatly hindering their mechanical properties [39,99]. Therefore, if these factors are not carefully controlled, it is not unusual to obtain even lower mechanical/thermal properties with the inclusion of CNTs [95,96,99]. Aside from the large efforts of the scientific/industrial community to improve the CNT dispersion within the polymer, two of the most practical ways to better control this issue is through keeping the CNT concentration significantly low (just above the percolation threshold) and using CNT functionalization to improve the dispersion and mechanical bonding with the host polymer. Both strategies are reflected in Table 5.1, where a few examples of mechanical and thermal properties of CNT/thermosetting polymer nanocomposites using functionalized CNTs have been collected. In this table, the CNT weight concentration is indicated in parenthesis underneath the CNT type (MWCNT or SWCNT) and the increase (+ Δ) or decrease (– Δ) in three mechanical and two thermal properties have been collected from the literature. The subscript “0” refers to the neat matrix, and the properties addressed are the elastic modulus (E), the ultimate stress (strength, σ^u), the ultimate strain (ϵ^u), the glass transition temperature (T_g , determined by either differential scanning calorimetry or dynamic mechanical analysis), and the thermal degradation temperature (T_d , determined by TGA).

As seen from this table, among the thermosetting polymers the most reported one is undoubtedly the family of epoxies, likely because of their better mechanical and thermal

Table 5.1 Variation in the Mechanical and Thermal Properties of CNT-Functionalized Thermosetting Polymer Nanocomposites, With Respect to the Neat Matrix

Thermosetting Matrix	CNT Types (wt.%)	CNT Functionalization	$\Delta E/E_0$	$\Delta\sigma^u/\sigma_0^u$	$\Delta\epsilon^u/\epsilon_0^u$	ΔT_g (°C)	ΔT_d (°C)	Reference
Epoxy	MWCNT (0.80)	Amino groups	—	—	—	+18	—	[61]
Epoxy	SWCNT (1.0)	Amino groups	+31% (T)	+25%	+31%	—	—	[100]
Epoxy (rubbery)	MWCNT (1.0)	Acid oxidized	+28% (T)	+104%	+60%	—	—	[95]
Epoxy (glassy)	MWCNT (1.0)	Acid oxidized	+4% (T)	–1%	+8%	—	—	
Epoxy	MWCNT (0.25)	Amino groups	+19% (F)	+26%	—	–10	+30	[101]
Epoxy	MWCNT (0.20)	3-Aminopropyl-triethoxysilane	+22% (F)	+23%	—	+11	—	[39]
Polyester	MWCNT (0.5)	Amino groups	—	+15% (T)	—	—	—	[102]
Vinyl ester/ polyester	MWCNT (0.30)	Amino groups	+31% (T)	+20%	—	—	—	[103]
Vinyl ester	MWCNT (0.2)	MPS	+7% (C)	+5%	+5%	—	—	[6]

C, Compressive; F, flexural; T, tensile.

properties compared to vinyl esters and unsaturated polyesters, as well as their lower curing shrinkage. However, given their lower costs and versatility, vinyl ester and even polyester resins are currently utilized in a large variety of industrial applications, such as automotive, shipbuilding, wind-turbine blade manufacturing, and piping industry, among many others [102,104]. Another distinctive feature observed in Table 5.1 is the very low CNT concentrations used, which are typically around 0.2–0.3 wt.%, that is, just above the electrical percolation threshold [105]. CNT weight concentrations above 0.5 wt.% are deemed high for CNT/thermosetting polymer nanocomposites, and such high concentrations may hinder their mechanical properties. This is significantly different for thermoplastic and elastomeric matrices, where higher CNT concentrations are typically needed, as will be further discussed.

As seen in Table 5.1, amino functional groups are undoubtedly the ones used to functionalize both types of CNTs to improve the mechanical and thermal properties of epoxy nanocomposites [61,89,100,101]; functionalizing CNTs with amines has also been attempted for vinyl ester and unsaturated polyester resins [102,103]. Care needs to be taken, as amine functionalization is expected to modify the kinetics of the epoxy curing reaction, which under certain circumstances, could yield a reduction of the glass transition temperature of the nanocomposite [101]. Depending on the epoxy matrix, carboxylated MWCNTs may also improve the mechanical properties of epoxy composites [95], but is more common that a second, more specific, chemical functionalization is conducted after CNT oxidation. An alternative for a more specific functionalization is the use of an adequate silane, which is frequently used as a sequential treatment after CNT oxidation [6,39]. In this regard, Avilés et al. [6] have pointed out that the concentration of silane in solution, used to functionalize the CNT, plays a paramount role in the resulting mechanical properties of the nanocomposite. As discussed in connection to Fig. 5.6, overly high concentrations of silane may form an excess of polysiloxanes at the interface, decrementing the mechanical (and thermal) properties of polymer composites.

5.3.2 Thermoplastics

Thermoplastic polymers are of great commercial interest because of their ease of processing and variety of applications. Thermoplastic polymers, such as polyethylenes and polypropylenes (commodities), constitute the largest polymer production. The preparation of nanocomposites based on thermoplastic polymers is generally performed by incorporation of reinforcements/fillers using melt-mixing process. Different strategies have been used to facilitate the homogeneous dispersion of nanofillers, such as CNTs in thermoplastic polymers. These strategies include the high-shear melt processing of the thermoplastic polymer to promote the breakdown and dispersion of the nanotubes, or the use of so called “compatibilizers,” among other methods [106]. Compatibilizers are materials that are added to a mixture of incompatible polymers or polymer/fillers to suppress their phase separation by promoting the interaction between the components of the mixture [107]. Nonpolar polymers grafted with polar molecules, such as polyolefins grafted with maleic

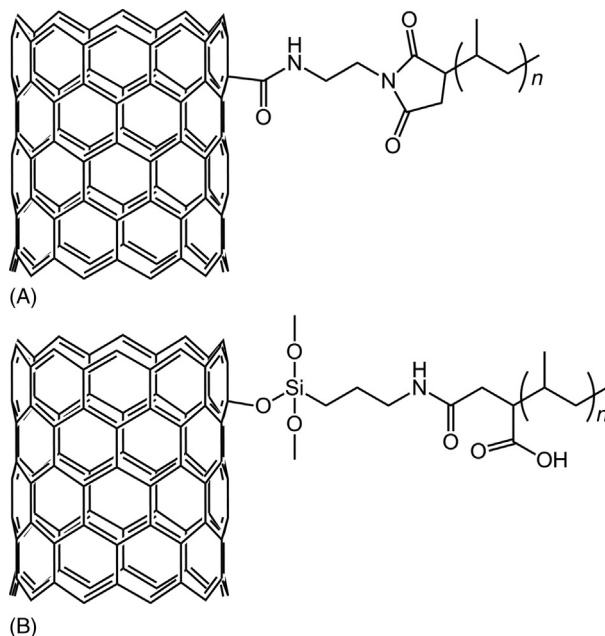


FIGURE 5.12 CNTs grafted with PP obtained from the reaction of functionalized CNTs and PP-g-MA. (A) Amine-functionalized CNTs and (B) CNTs functionalized with 3-aminopropyltriethoxysilane.

anhydride, are among the most used compatibilizers. For instance, Lee et al. [108] reported the use of two types of compatibilizers, polypropylene (PP)-grafted maleic anhydride (PP-g-MA) and styrene-ethylene-butylene-styrene-grafted maleic anhydride (SEBS-g-MA), for the preparation of MWCNT/PP composites. MWCNTs were chemically functionalized through acid, amine, and heat treatments. The authors found that the electrical conductivity of the composite was dramatically increased when the heat-treated MWCNTs were added and was further increased with the addition of SEBS-g-MA. The preparation of PP-grafted MWCNTs by melt mixing of PP-g-MA with amine-functionalized MWCNTs (Fig. 5.12A) is also a successful functionalization method that improves the CNT dispersion and mechanical properties of the resulting composite [109]. An alternative is to use an adequate silane, such as 3-aminopropyltriethoxysilane, which results in PP composites with increased flame retardancy and thermal stability [110]; it has been reported that the maleic anhydride moiety reacts with the amine groups of functionalized MWCNTs, yielding amide linkage between MWCNTs and PP-g-MA, Fig. 5.12B.

The grafting method is not only applicable to PP, but also to other polymers such as polyethylene [111], EVA copolymers [112], and polystyrene [113], among many others.

Inclusion of functionalized CNTs in many other thermoplastic polymers, such as those obtained by polycondensation (e.g., polyesters and polyamides), has also been reported. For example, for polyethylene terephthalate, 4-alkoxybenzoic acids [114],

Table 5.2 Variation in the Mechanical Properties of CNT-Functionalized Thermoplastic Polymer Nanocomposites, With Respect to the Neat Matrix

Thermoplastic Matrix	CNT Type (wt.%)	CNT Functionalization	Processing Method	$\Delta E/E_0$	$\Delta\sigma^u/\sigma_0^u$	Reference
PP	MWCNT (0.10)	Acid oxidized	Melt mixing	+20%	+3%	[119]
	MWCNT (1.0)			+78%	+6%	
PP	MWCNT (1.0)	Acid oxidized	Melt mixing	+31%	+10%	[120]
		Acid oxidized + IA		+40%	+10%	
PP	MWCNT (1.5)	Amino groups	Melt mixing	+1.1	+1.4	[109]
PET	MWCNT (0.5)	Acid oxidized	In situ polymerization	+1.0	+2.0	[115]
		Diamine		+1.09	+2.4	
PET	MWCNT (0.5)	Acid oxidized	Melt mixing	+2.6%	+47%	[116]
PEN	MWCNT (0.5)	Acid oxidized	Melt mixing	+18%	+32%	[121]
Nylon-6	MWCNT (1.0)	Acid oxidized	Melt mixing	+1.15	+1.24	[122]

PEN, Polyethylene naphthalate; IA, itaconic acid.

diamines [115], acid oxidation, and itaconic acid [116] have been used to functionalize MWCNTs. For polyamides, acid treatments [117] and the use of compatibilizers based on styrene–maleic anhydride copolymer [118] have also been addressed. The final aim of this functionalization and/or use of processing aids or compatibilizers is to improve the effective properties of polymer nanocomposite. Table 5.2 presents a brief literature collection listing improved mechanical properties due to the use of functionalized MWCNTs in thermoplastic polymers matrices (numbers are with respect to the neat polymer matrix). As seen from this table, melt mixing is undoubtedly the most used processing method, likely because of ease of use and scalability. However, this process demands a relative large amount of material and this is likely the reason why the use of MWCNTs has been preferred over SWCNTs for thermoplastic melt mixing processing. Larger improvements in mechanical properties can be achieved by using in situ polymerization [115], although this technique may be difficult to scale up. It can also be seen from the Table 5.2 that acid oxidation (commonly by means of nitric and/or sulfuric acids) and amination are common routes for CNT functionalization that result in composites with improved mechanical properties and that grafting organic or inorganic molecules is also of assistance. A common feature (not indicated in the Table 5.2) is that the increments in stiffness (E) and strength (σ^u) in CNT/thermoplastic nanocomposites are concomitant with a significant reduction in ultimate strain (elongation at break) with respect to its neat polymer. This is because CNTs act as physical (or chemical) crosslinking sites that restrict polymer chain motion [115,119,120]. A way to mitigate this effect may be through grafting polymer molecules on the CNTs prior to composite processing [109]. Thermal properties, such as T_g , T_d , and melting/crystallization temperatures of thermoplastic composites, have also been reported to increase by using functionalized CNTs [3,119–121]. It is generally

accepted that functionalized CNTs act as nucleating agents that elevate the crystallization temperature of thermoplastics [109].

5.3.3 Elastomers

Elastomers present a broad range of elasticity as their segment links are free enough to assume different conformations of equal energy. This is the result of having a glass transition temperature below room temperature. Also, elastomers may return to their initial shape after being deformed as they have high molecular weights and are crosslinked. The family of elastomers include several types of rubbers, such as natural rubber, butyl rubber, nitrile rubber, polyisoprene, polychloroprene, styrene-butadiene rubber, silicon rubbers, fluoroelastomers, polysulfide rubber, EVA, ethylene propylene diene monomer (EPDM), as well as thermoplastic elastomers, such as SPUs. These polymers, copolymers, or even physical blends have been filled with unmodified and modified CNTs, but several challenges still prevail to improve their processing conditions, and to apply appropriate CNT functionalizations that lead to improved CNT dispersion, mechanical, electrical, thermal, and actuating properties, among others [123–126]

CNTs can be either physically or chemically modified to improve dispersion and compatibility with an elastomeric matrix. For example, regarding physical interactions, MWCNTs can be modified with ionic liquids, such as 1-ethyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl), that promote cation $\pi/\pi-\pi$ interactions to significantly improve the mechanical properties of styrene-butadiene rubber composites [127]. In a similar manner, MWCNTs have been modified with ionic liquids, such as 1-butyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide, to provide high electrical conductivity, improved tensile modulus, and thermal stability to polychloroprene rubber [128]. These improvements strongly depend on the physicochemical features of the CNTs used. The most common groups attached to the CNTs for covalent rubber modification are hydroxyl, carboxyl, amines, and silane coupling agents (after oxidation). Although some improvements have been reported, in some cases the limited amount of functional groups introduced does not guarantee the creation of a proper interface and therefore, marginal improvements in mechanical properties are frequently reported.

Elastomers based on SPUs have been modified with acid-oxidized MWCNTs and SWCNTs, improving CNT dispersion, stiffness, and the strength of the resulting composites [129,130]. For these composites, improvements in stiffness and strength heavily depend on the use of low CNT concentrations (close to the percolation threshold), and these improvements are normally concomitant with significant reductions of elongation at break [129,130]. In the case of segment polyurethanes, it has been observed that the resulting properties of the CNT composite are more influenced by the rigid segment content than by the CNT content [131]. Similarly, highly crystalline (40% rigid segments) thermoplastic polyurethanes based on hexamethylene diisocyanate, butanediol, polycaprolactone, and polycarbonate diol have been mixed with acid-oxidized MWCNTs [132], showing improved mechanical properties. To improve further the interactions between the CNTs and

thermoplastic polyurethanes, some attempts have been made to graft the polyol used for the polyurethane synthesis on the CNTs. Jing et al. [133] grafted polycaprolactone onto MWCNTs to improve the dispersion and mechanical properties of the resulting composite. Other routes to functionalize CNTs for polyurethane matrices include the use of toluene diisocyanate, polyethylene glycol, and 3-amino-1,2,4-triazole [134,135].

In the case of polyolefin elastomers, the addition of MWCNTs substantially increases their melt viscosity. Therefore, different works have focused on the addition of thermoplastic polymers to facilitate processing of these elastomeric polyolefins in the presence of MWCNTs [136]. It has been reported that in PP/EPDM blends, SWCNTs act as nucleation centers, which affect the physical and mechanical properties of the composites [137]. In situ incorporation of oxidized MWCNTs during the preparation of a thermoplastic elastomer has resulted in improved MWCNT dispersion in the polymer matrix, as revealed by small-angle X-ray analysis [138]. Likewise, thermoplastic polymers grafted with polar molecules have been used as compatibilizers to favor the dispersion of CNTs in the nanocomposite matrix. This method of preparation has led to a significant increase of the elastic modulus of nanocomposites. For instance, Hemmati et al. [139] reported that nanocomposites based on PP/EPDM (80/20) blends containing 0.5 wt.% SWCNTs and 1 wt.% PP grafted with maleic anhydride as compatibilizer resulted in an increase of tensile modulus of about 60%. The use of compatibilizer prevented the decrease of elongation at break that normally occurs with the addition of CNTs. Another relevant study focused on the functionalization of MWCNTs by acid treatment and the grafting of PP on the MWCNTs [140]. The use of PP-grafted MWCNTs improved the mechanical properties of a PP/EPDM thermoplastic elastomer, achieving a 40% increase of the tensile modulus without decreasing its elongation at break.

Acid oxidation using nitric and/or sulfuric acids are among the preferred CNT functionalization methods used for elastomers. By using 2.8 M nitric acid for 38 h, Bhattacharyya et al. [141] prepared carboxylated MWCNTs and dispersed them in natural rubber assisted by sodium dodecyl sulfate. The resulting composite showed improvements in elastic modulus (10-fold), tensile strength (2-fold), and storage modulus (60-fold) with a concomitant reduction in elongation at break, attaining a low electrical percolation threshold (~ 1 wt.%). A polydimethylsiloxane matrix was reinforced with alkylamine-modified MWCNTs to obtain dielectric elastomers for capacitive force sensors [142]. For this, a 1:3 v/v ratio of nitric:sulfuric acids was used to oxidize MWCNTs, and subsequently treated with various alkylamines (such as hexylamine, octadecylamine, and dodecylamine) for amide formation. Similarly, when a polyester-modified polydimethylsiloxane solution was used on nitric acid-oxidized MWCNTs, the dispersion, the mechanical and thermal properties of silicone rubber composites were improved [143].

The use of silanes has also been pursued to improve CNT dispersion and the effective properties of elastomeric composites. CNTs with different aspect ratios were modified by a silane-coupling agent and embedded into a silicone elastomer matrix to obtain composites with improved CNT dispersion and enhanced dielectric loss and permittivity [144]. Shanmugaraj et al. [145] oxidized MWCNTs with 10 N sulfuric acid in the

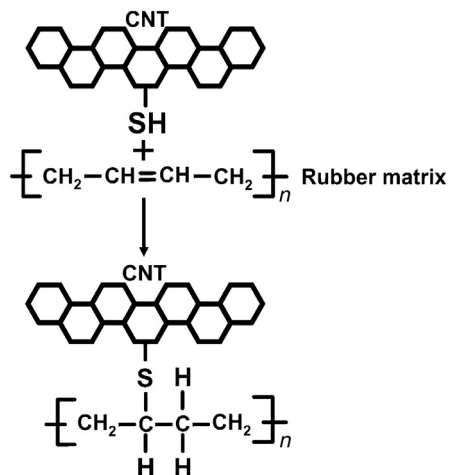


FIGURE 5.13 Thiol crosslinking mechanism for unsaturated rubbery matrices.

presence of potassium dichromate and then conducted a silanization with 3-aminopropyltriethoxysilane, improving the elastic modulus and tensile strength of natural rubber composites. As customary for elastomeric systems, the large final strain of natural rubber was compromised with the introduction of CNTs, but the authors showed that the use of an adequate silane may lessen this negative effect. It has been reported that the use of MWCNTs functionalized with 7-octenyltrichlorosilane favors a significant increase in the elastic modulus of a commercial crosslinked polydimethylsiloxane (Sylgard 184). This was attributed to the fact that 7-octenyl trichlorosilane molecules are able to participate in the crosslinking reaction of polydimethylsiloxane [146]. By further functionalizing oxidized MWCNTs with bis(triethoxysilylpropyl)tetrasulfide, it has also been suggested that in situ silanization (where silane was directly added into the mixing process) may be of higher benefit for the generation of chemical linkages (and consequently, resulting effective properties) of natural rubber composites [147].

Organosulfur compounds can also be used to improve the CNT adhesion to elastomeric matrices. In that respect, Fig. 5.13 shows a possible mechanism for thiol crosslinking of an unsaturated rubbery matrix (polybutadiene) using a thiol-modified CNT.

Other functionalization routes that report improved effective properties of elastomeric composites include reversible addition-fragmentation chain transfer grafting of acrylonitrile and diurethane monoacrylate on MWCNTs for polyurethane composites with actuating properties [148], functionalization with polymers of low glass transition temperature, such as polybutyl acrylate homopolymer for triblock copolymer thermoplastic elastomers [149], and $KMnO_4$ oxidation followed by chemical reduction with diisobutyl aluminum hydride for EVA composites [150].

An important phenomenon that needs to be taken into account when analyzing the elastic behavior of filled rubbers (either functionalized or not) is the Payne effect [151].

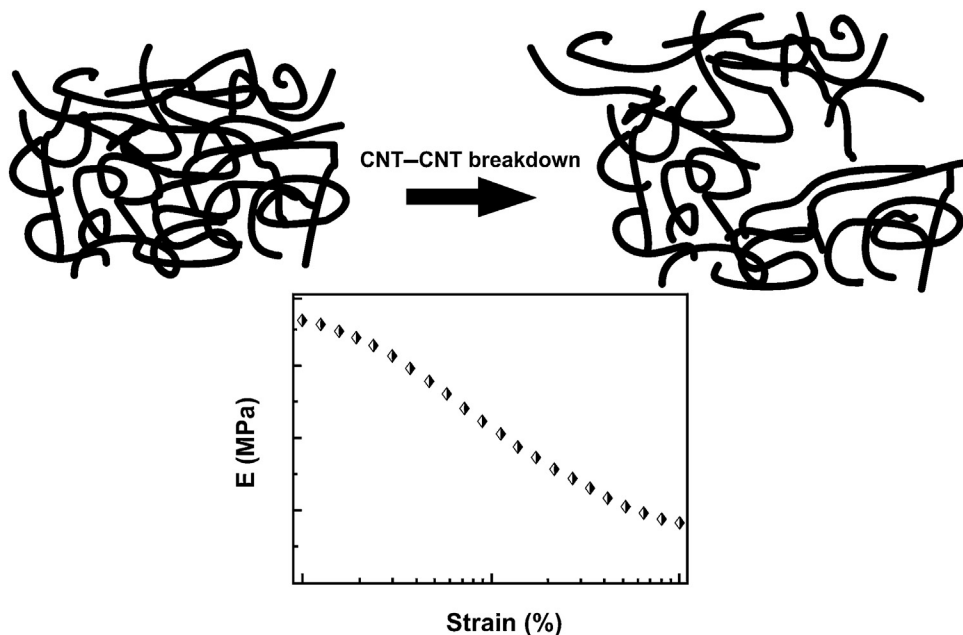


FIGURE 5.14 The strain softening (Payne) effect caused by the loss of CNT-to-CNT interactions with applied strain.

The Payne effect describes an experimentally observed “strain softening” behavior of many filled elastomeric polymers (including those filled with CNTs), where the dynamic elastic modulus decreases with increased applied strain. This effect is strongly related to the material microstructure and occurs for filled rubbery polymers, being minor or inexistent for unfilled rubbers. For the case of CNT-filled rubbers, the Payne effect is attributed to the loss of interactions among CNTs or weakening of the filler–filler interactions as a result of increased strain [141,152,153], as schematically represented in Fig. 5.14. It has been pointed out that the Payne effect is more severe for rubbers filled with MWCNTs than for those filled with carbon black [152]. This behavior has also been observed for nanocomposites based on synthetic rubbers, such as styrene butadiene filled with CNTs [154]. As the Payne effect heavily depends on the filler–filler and filler–matrix interactions [141], it is expected that adequate CNT functionalizations may be able to decrease this nonlinear effect.

Acknowledgments

Economic support from CONACYT (Mexico) through CIAM project No. 188089 and CONICYT (Chile) through project No. 120003 is acknowledged. Dr. MYP also acknowledges support from CONICYT through project FONDECYT 1131139. The authors wish to thank Omar Rodriguez (CICY) for his artistic assistance with the figures.

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