

---

# **Polymer Nanocomposites Containing Functionalised Multiwalled Carbon NanoTubes: a Particular Attention to Polyolefin Based Materials**

---

Emmanuel Beyou, Sohaib Akbar,  
Philippe Chaumont and Philippe Cassagnau

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/50710>

---

## **Introduction**

Incorporation of carbon nanotubes (CNTs) into a polymer matrix is a very attractive way to combine the mechanical and electrical properties of individual nanotubes with the advantages of plastics. Carbon nanotubes are the third allotropic form of carbon and were synthesized for the first time by Iijima in 1991 [1]. Their exceptional properties depend on the structural perfection and high aspect ratio (typically ca 100-300). Two types of CNTs are distinguished : single-walled CNTs (SWCNTs) consist of a single graphene sheet wrapped into cylindrical tubes with diameters ranging from 0.7 to 2nm and have lengths of micrometers while multi-walled CNTs (MWCNTs) consist of sets of concentric SWCNTs having larger diameters [2-5]. The unique properties of individual CNTs make them the ideal reinforcing agents in a number of applications [6-9] but the low compatibility of CNTs set a strong limitation to disperse them in a polymer matrix. Indeed, carbon nanotubes form clusters as very long bundles due to the high surface energy and the stabilization by numerous of  $\pi$ - $\pi$  electron interactions among the tubes. Non covalent methods for preparing polymer/CNTs nanocomposites have been explored to achieve good dispersion and load transfer [10-12]. The non-covalent approaches to prepare polymer/CNTs composites via processes such as solution mixing [13,14], melt mixing [14,15], surfactant modification [16], polymer wrapping [17], polymer absorption [18] and in situ polymerization [19, 20] are simple and convenient but interaction between the two components remains weak. Relatively uniform dispersion of CNTs can be achieved in polar polymers such as nylon, polycarbonate and polyimide because of the strong interaction between the polar moiety of the polymer chains and the sur-

face of the CNTs [21-24]. Moreover, it was found that MWNTs disperse well in PS and form a network-like structure due to  $\pi$ -stacking interactions with aromatic groups of the PS chains [25]. However, it is difficult to disperse CNTs within a non polar polymer matrix such as polyolefins. To gain the advantages of CNTs at its best, one needs: (i) high interfacial area between nanotubes and polymer; and, (ii) strong interfacial interaction. Unfortunately the solvent technique does not help much in achieving these targets and, as a result, a nanocomposite having properties much inferior to theoretical expectations are obtained. For example, the mechanical properties of polyethylene (PE) reinforced by carbon nanotubes do not improve significantly because the weak polymer-CNT interfacial adhesion prevents efficient stress transfer from the polymer matrix to CNT [26-28]. A strategy for enhancing the compatibility between nanotubes and polyolefins consists in functionalising the sidewalls of CNT to introduce reactive moieties and to disrupt the rope structure. Functional moieties are attached to open ends and sidewalls to improve the solubility of nanotubes [29-32] while the covalent polymer grafting approaches, including 'grafting to' [33-36] and 'grafting from' [37-39] that create chemical linkages between polymer and CNTs, can significantly improve dispersion and change their rheological behaviour. First, methods used for processing CNTs-based nanocomposites and for the functionalisation of carbon nanotubes (CNTs) with polymers will be described. This is followed by a review of the surface chemistry of carbon nanotubes in order to perform their dispersion in polyolefin matrix. Finally, general trends of the viscoelastic properties of CNTs/ polyolefin composites are discussed.

## 1. Methods to process polymer/carbon nanotubes composites

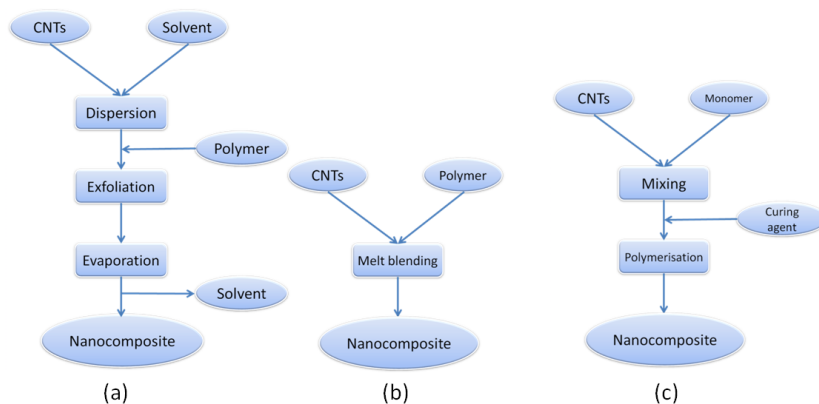
Similar to the case of carbon nanotube/solvent suspensions, pristine carbon nanotubes have not yet been shown to be soluble in polymers illustrating the extreme difficulty of overcoming the inherent thermodynamic drive of nanotubes to bundle [40]. Several processing methods available for fabricating CNT/polymer composites based on either thermoplastic or thermosetting matrices mainly include solution mixing, melt blending, and in situ polymerisation (figure 1) [41, 42].

### 1.1. Solution blending

The most common method for preparing polymer nanotube composites has been to mix the nanotubes and polymer in a suitable solvent before evaporating the solvent to form a composite film (Figure 1a). One of the benefits of this method is that agitation of the nanotubes powder in a solvent facilitates nanotubes' de-aggregation and dispersion. Almost all solution processing methods are based on a general theme which can be summarised as:

1. Dispersion of nanotubes in either a solvent or polymer solution by energetic agitation.
2. Mixing of nanotubes and polymer in solution by energetic agitation.
3. Controlled evaporation of solvent leaving a composite film.

In general, agitation is provided by magnetic stirring, shear mixing, reflux or ultrasonication. Sonication can be provided in two forms, mild sonication in a bath or high-power sonication using a tip or horn. An early example of solution based composite formation is described by Jin *et al* [43]. By this method, high loading levels of up to 50wt% and reasonably good dispersions were achieved. A number of papers have discussed dispersion of nanotubes in polymer solutions [44-46]. This can result in good dispersion even when the nanotubes cannot be dispersed in the neat solvent. Coleman *et al* [44] used sonication to disperse catalytic MWCNT in polyvinylalcohol/H<sub>2</sub>O solutions, resulting in a MWCNT dispersion that was stable indefinitely. Films could be easily formed by drop-casting with microscopy studies showing very good dispersion. Cadek *et al* [46] showed that this procedure could also be applied to arc discharge MWCNTs, double walled nanotubes (DWCNTs) and High-Pressure CO Conversion (HiPCO) SWCNTs. They also showed that this procedure could be used to purify arc-MWCNTs by selective sedimentation during composite production.



**Figure 1.** Schematic representation of different steps of polymer/CNTs composite processing: solution mixing (a); melt mixing (b); *in situ* polymerisation (c).

## 1.2. Melt mixing

While solution processing is a valuable technique for both nanotube dispersion and composite formation, it is completely unsuitable for the many polymer types that are insoluble. Melt processing is a common alternative method, which is particularly useful for dealing with thermoplastic polymers (Figure 1b). This range of techniques makes use of the fact that thermoplastic polymers soften when heated. Amorphous polymers can be processed above their glass transition temperature while semi-crystalline polymers need to be heated above their melt temperature to induce sufficient softening. Advantages of this technique are its speed and simplicity, not to mention its compatibility with standard industrial techniques [47, 48]. Any additives, such as carbon nanotubes can be mixed into the melt by shear mixing. However, Bulk samples can then be fabricated by techniques such as compression

moulding, injection moulding or extrusion. However it is important that processing conditions are optimised for the whole range of polymer–nanotube combinations. High temperature and shear forces in the polymer fluid are able to break the carbon nanotubes bundles and CNTs can additionally affect melt properties such as viscosity, resulting in unexpected polymer degradation [49]. Andrews and co-workers [50] showed that commercial polymers such as high impact polystyrene, polypropylene and acrylonitrile–butadiene–styrene (ABS) could be melt processed with CVD-MWCNT to form composites. The polymers were blended with nanotubes at high loading level in a high shear mixer to form master batches. An example of using combined techniques was demonstrated by Tang *et al* [51]. High density polyethylene pellets and nanotubes were melted in a beaker, then mixed and compressed. The resulting solid was broken up and added to a twin screw extruder at 170°C and extruded through a slit die. The resulting film was then compression moulded to form a thin film.

### 1.3. In Situ Polymerisation

This fabrication strategy starts by dispersing carbon nanotubes in vinyl monomers followed by polymerising the monomers (Figure 1c). This method produces polymer-grafted CNTs mixed with free polymer chains resulting in a homogeneous dispersion of CNTs. In situ radical polymerisation was applied for the synthesis of PMMA-based composites by Jia *et al* [52] using a radical initiator and the authors suggested that  $\pi$ -bonds of the CNT graphitic network were opened by the radical fragments of initiator and therefore the carbon nanostructures could participate in PMMA polymerisation by acting as efficient radical scavengers. Dubois *et al* [53] applied the in situ polymerization to olefin monomers by anchoring methylaluminoxane, a commonly used co-catalyst in metallocene-based olefin polymerization onto carbon nanotubes surface. Then, the metallocene catalyst was added to the surface-activated CNTs and the course of ethylene polymerization was found to be similar to the one without the presence of pristine MWCNTs. Epoxy nanocomposites comprise the majority of reports using in situ polymerisation methods [54, 55], where the nanotubes are first dispersed in the resin followed by curing the resin with the hardener. Zhu *et al* [56] prepared epoxy nanocomposites by this technique using end-cap carboxylated SWCNTs and an esterification reaction to produce a composite with improved tensile modulus ( $E$  is 30% higher with 1 wt % SWCNT).

### 1.4. Novel methods

Rather than avoid the high viscosities of nanotube/polymer composites, some researchers have decreased the temperature to increase viscosity to the point of processing in the solid state. Solid-state mechanochemical pulverisation processes (using pan milling [57] or twin-screw pulverisation [58]) have mixed MWCNTs with polymer matrices. Pulverisation methods can be used alone or followed by melt mixing. Nanocomposites prepared in this manner have the advantage of possibly grafting the polymer on the nanotubes, which account in part for the observed good dispersion, improved interfacial adhesion, and improved tensile modulus.

An innovative latex fabrication method for making nanotube/polymer composites has been used by first dispersing nanotubes in water (SWCNT require a surfactant, MWCNT do not) and then adding a suspension of latex nanoparticles [59,60]. For example, PEG-based amphiphilic molecule containing aromatic thiophene rings, namely, oligothiophene-terminated poly(ethylene glycol) (TN-PEG) was synthesized, and its ability to disperse and stabilize pristine carbon nanotubes in water was shown. This promising method can be applied to polymers that can be synthesised by emulsion polymerisation or formed into artificial latexes, e.g., by applying high-shear conditions [61].

Finally, to obtain nanotube/polymer composites with very high nanotube loadings, Vigolo et al [62] developed a “coagulation spinning” method to produce composite fibers comprising predominately nanotubes. This method disperses SWCNT using a surfactant solution, coagulates the nanotubes into a mesh by wet spinning it into an aqueous poly(vinyl alcohol) solution, and converts the mesh into a solid fiber by a slow draw process. In addition, Mamedov et al [63] developed a fabrication method based on sequential layering of chemically modified nanotubes and polyelectrolytes to reduce phase separation and prepared composites with SWCNT loading as high as 50 wt %.

## 2. Surface modifications of carbon nanotubes with polymers

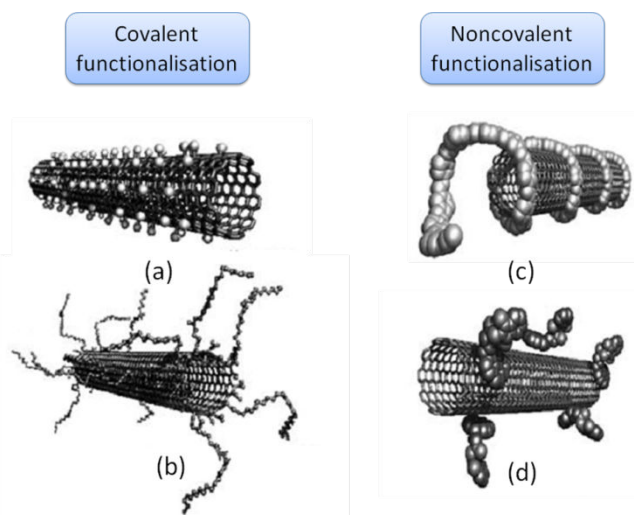
CNTs are considered ideal materials for reinforcing fibres due to their exceptional mechanical properties. Therefore, nanotube–polymer composites have potential applications in aerospace science, where lightweight robust materials are needed [64]. It is widely recognised that the fabrication of high performance nanotube–polymer composites depends on the efficient load transfer from the host matrix to the tubes. The load transfer requires homogeneous dispersion of the filler and strong interfacial bonding between the two components [65]. A dispersion of CNT bundles is called “macrodispersion” whereas a dispersion of individual nonbundled CNT is called a nanodispersion [66, 67]. To address these issues, several strategies for the synthesis of such composites have been developed. Currently, these strategies involve physical mixing in solution, *in situ* polymerisation of monomers in the presence of nanotubes, surfactant-assisted processing of composites, and chemical functionalisation of the incorporated tubes. As mentioned earlier, in many applications it is necessary to tailor the chemical nature of the nanotube’s walls in order to take advantage of their unique properties. For this purpose, two main approaches for the surface modification of CNTs are adopted i.e. covalent and noncovalent, depending on whether or not covalent bonding between the CNTs and the functional groups and/or modifier molecules is involved in the modification surface process. Figure 2 depicts a typical representation of such surface modifications.

### 2.1. Noncovalent attachment of polymers

The noncovalent attachment, controlled by thermodynamic criteria [68], which for some polymer chains is called wrapping, can alter the nature of the nanotube’s surface and make it

more compatible with the polymer matrix. Non-covalent surface modifications are based mainly on weak interactions, such as van der Waals,  $\pi$ - $\pi$  and hydrophobic interactions, between CNTs and modifier molecules. Non-covalent surface modifications are advantageous in that they conserve  $sp^2$ -conjugated structures and preserve the electronic performance of CNTs. The main potential disadvantage of noncovalent attachment is that the forces between the wrapping molecule and the nanotube might be weak, thus as a filler in a composite the efficiency of the load transfer might be low.

Non-covalent modification approaches typically use organic mediating molecules that range from low molecular weight molecules to supra- molecules to polymers.



**Figure 2.** Different routes for nanotubes' functionalisation: sidewall covalent functionalisation (a); defect-group covalent functionalisation (b); noncovalent polymer wrapping (c); noncovalent  $\pi$ -stacking (d).

### 2.1.1. Polymer wrapping

O'Connell et al. [68] reported that nanotubes could be reversibly solubilised in water by noncovalently associating them with a variety of linear polymers such as polyvinyl pyrrolidone (PVP) and polystyrene sulfonate (PSS). They demonstrated that the association between the polymer and the nanotubes is robust, not dependent upon the presence of excess polymer in solution, and is uniform along the sides of the tubes (Figure 1c). A general thermodynamic driving force for such wrapping in an aqueous environment has been identified [68].

Conjugated luminescent polymer poly- $\{(m\text{-phenylenevinylene})\text{-co-}[(1,5\text{-dioctyloxy-p-phenylene})\text{-vinylene}]\}$  (PmPV) and its derivatives [69-71] have been successfully used for the wrapping around nanotubes on account of stabilising noncovalent bonding interactions, presumably as a result of  $\pi$ - $\pi$  stacking (Figure 1d) and van der Waals interactions between PmPV

and the surfaces of the nanotubes. Star et al [72] also synthesised the Stilbenoid dendrimers, a hyperbranched variant of the PmPV polymer, which exhibits an appropriate degree of branching, and it was found to be more efficient at breaking up nanotube bundles, provided it is employed at higher polymer-to-nanotube ratios than was the “parent” PmPV polymer.

In addition, the behavior of single walled and multi walled carbon nanotubes in aqueous solutions of Gum Arabic, a natural polysaccharide, has been described by Nativ-Roth et al [73]. They observed that while the as-prepared nanotube powders contain highly entangled ropes and bundles, the dispersions are mainly composed of individual tubes suggesting that the ability of Gum Arabic to exfoliate the bundles, and stabilize individual tubes in aqueous dispersions, can be utilized in the preparation of carbon nanotube-polymer composites. In the latter case, the dispersing polymer acts as a compatibilizer and as an adhesion promoter leading to strengthening of the matrix-nanotube interface.

It is clear from these accounts that noncovalent functionalisation of carbon nanotubes can be achieved without disrupting the primary structure of the nanotubes themselves.

### *2.1.2. Polymer absorption*

Xia et al [74] has described a method to prepare polymer-encapsulated MWCNTs : it has been successfully prepared through ultrasonically initiated in situ emulsion polymerisations of n-butyl acrylate (BA) and methyl methacrylate (MMA) in presence of MWCNT. By employing the multiple effects of ultrasound, i.e., dispersion, pulverizing, activation, and initiation, the aggregation and entanglement of carbon nanotubes in aqueous solution can be broken down, while in situ polymerization of monomer BA or MMA on the surface of MWCNTs proceeds and the MWCNTs are coated by the formed polymer.

The hydrophilic regions of surfactants interact with polar solvent molecules, and the hydrophobic regions can adsorb onto nanotube surfaces [75]. Thus, the process of dispersing CNTs from aggregates, bundles, or ropes into separated individual CNTs depends strongly on the length of the hydrophobic regions and the types of hydrophilic groups of the surfactant. A topological, noncovalent solution to improving the dispersion of SWNTs by encasing them in cross-linkable surfactant micelles was demonstrated by Kang and Taton [16]. SWCNTs were dispersed in the dimethylformamide (DMF) solutions of amphiphilic poly(styrene)-block-poly(acrylic acid) copolymer. Water was added to the solutions and the poly(styrene)-block-poly(acrylic acid) copolymer wrapped the SWCNTs and formed micelle. Then the PAA blocks of the micellar shells were permanently crosslinked by addition of a water-soluble diamine linker and a carbodiimide activator. This encapsulation significantly enhances the dispersion of SWCNTs in a wide variety of polar and nonpolar solvents and polymer matrices [76]. Encapsulated SWNTs can be used as an alternative starting material to pure SWNTs for the production and investigation of nanotube composite materials.

## **2.2. Covalent attachment of polymers**

Functionalisation of carbon nanotubes with polymers is a key issue to improve the interfacial interaction between CNTs and the polymer matrix when processing polymer/CNT



nanocomposites. The covalent reaction of CNT with polymers is important because the long polymer chains help to dissolve the tubes into a wide range of solvents even at a low degree of functionalisation. There are two main methodologies for the covalent attachment of polymeric substances to the surface of nanotubes, which are defined as “grafting to” and ‘grafting from’ methods [76, 77]. The former relies on the synthesis of a polymer with a specific molecular weight followed by end group transformation. Subsequently, this polymer chain is attached to the graphitic surface of CNT. A disadvantage of this method is that the grafted polymer contents are limited because of high steric hindrance of macromolecules. The ‘grafting from’ method involved the immobilisation of initiators onto the substrate followed in situ surface polymerization to generate grafted polymer chains. Because the covalent attachment of the surface modifiers involves the partial disruption of the sidewall  $sp^2$  hybridization system, covalently modified CNTs inevitably lose some degree of their electrical and/or electronic performance properties [78].

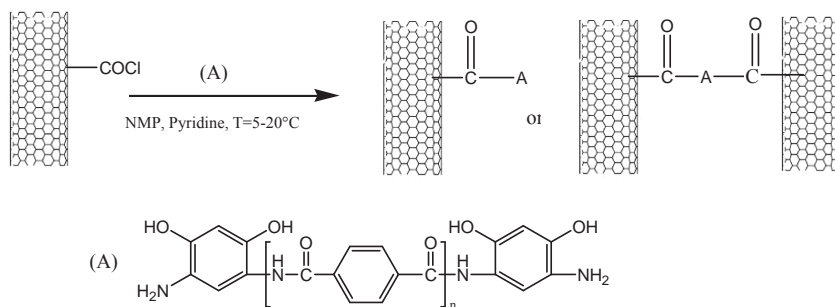
### 2.2.1. ‘Grafting to’ method

Since the curvature of the carbon nanostructures imparts a significant strain upon the  $sp^2$  hybridised carbon atoms that make up their framework, the energy barrier required to convert these atoms to  $sp^3$  hybridisation is lower than that of the flat graphene sheets, making them susceptible to various addition reactions. Therefore, to exploit this chemistry, it is only necessary to produce a polymer-centred transient in the presence of CNT material. Alternatively, defect sites on the surface of oxidized CNTs, as open-ended nanostructures with terminal carboxylic acid groups, allow covalent linkages of oligomer or polymer chains. So, the ‘grafting to’ method involves the chemical reaction between as-prepared or commercially available polymers with reactive end groups and nanotubes’ surface functional groups or the termination of growing polymer radical, cation and anion formed during the polymerization of various monomers in the presence of CNTs or the deactivation of living polymer chain ends with the CNT surface.

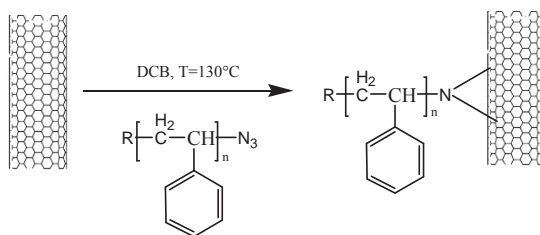
For example, oxidized SWCNTs were grafted with amino-terminated poly (N-isopropylacrylamide) (PNIPAAm) by carbodiimide-activated reaction, which yielded a 8wt% polymer content [77]. In a different approach, oxidized MWCNTs were attached onto polyacrylonitrile (PAN) nanoparticles through the reaction of the reduced cyano-groups of the polymer and the carboxylic moieties of CNT surface [79]. In addition, the amidation reaction was used for grafting of oligo-hydroxyamides to MWCNTs as described in figure 3 [80].

Ester-based linkages have been used by Baskaran et al. [81] by performing the reaction of hydroxy-terminated PS with thionyl chloridetreated MWCNTs, resulting in a hybrid containing 86wt% of CNTs. The esterification reaction was also used for grafting polyethylene glycol (PEG) chains to acylchloride-activated SWCNTs [82]. Silicone-functionalised CNT derivatives were prepared by opening terminal epoxy groups of functionalised polydimethylsiloxanes (PDMS) by the carboxylic groups of acid-treated MWCNTs [83]. Another example of the “grafting to” approach has been reported by Qin et al. [84] through the grafting of polystyrene with azide end group onto SWCNTs (Figure 4).





**Figure 3.** Synthesis of oligo-hydroxyamide-grafted MWNT. Reproduced from [80] with permission of Elsevier.



**Figure 4.** reaction of azide-terminated polystyrene onto CNTs surface. Reproduced from [80] with permission of ACS publications.

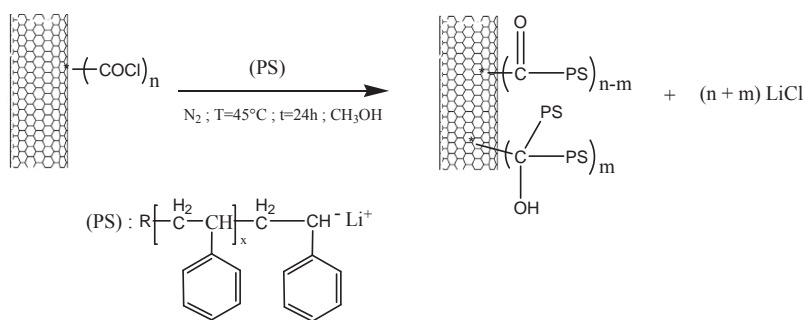
In an analogous approach, alkyne-decorated SWCNTs and PS-N<sub>3</sub> were coupled via [3+1] Huisgen cycloaddition between the alkyne and azide end groups [85]. A new method was developed by Hung et al. [86] for preparing polystyrene-functionalized multiple-walled carbon nanotubes (MWNTs) through the termination of anionically synthesized living polystyryllithium with the acyl chloride functionalities on the MWNTs. The acyl chloride functionalities on the MWNTs were in turn obtained by the formation of carboxyls via chemical oxidation and their conversion into acyl chlorides (Figure 5).

Lou et al. [87] reported the radical grafting of polyvinylpyridine chains onto the surface of nanotubes through the thermolysis of poly(2-vinylpyridine) terminated with a radical-stabilizing nitroxide (Figure 6), resulting in grafting densities up to 12 wt.-%.

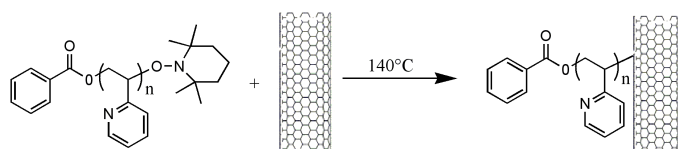
### 2.2.2. 'Grafting from' technique

Mostly, it involves the polymerisation of monomers from surface-derived initiators on either MWCNTs or SWCNTs. These initiators are covalently attached using the various functionalisation reactions developed for small molecules [77]. Then, the polymer is bound via in situ radical, cationic, anionic, ring opening and condensation polymerizations. The advantage of

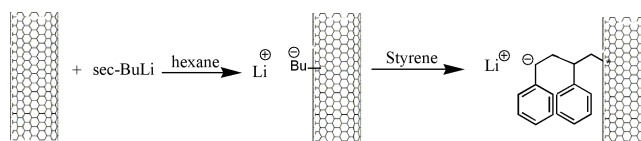
'grafting from' approach is that the polymer growth is not limited by steric hindrance, allowing high molecular weight polymers to be efficiently grafted as well as quite high grafting density [9].



**Figure 5.** substitution reaction of living polystyryllithium anions with acyl chloride-modified CNTs. Reproduced from [86] with permission of John Wiley and Sons.



**Figure 6.** Radical grafting of TEMPO-end capped PVP to MWCNTs. Reproduced from [87] with permission of Elsevier.



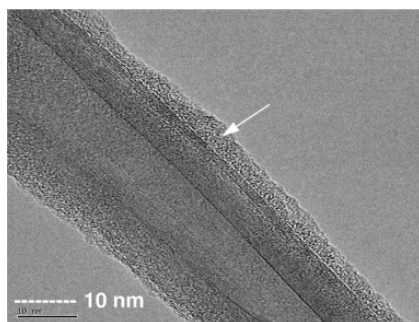
**Figure 7.** Anionic polymerisation of styrene onto carbon nanotubes

For example, Viswanathan et al [88], have developed a procedure based on the SWCNT surface treatment with butyllithium providing initiating sites for the anionic polymerization of styrene (Figure 6).

The latter procedure eliminates the need for nanotube pretreatment prior to functionalization and allows attachment of polymer molecules to pristine tubes without altering their original structure.

In addition, polyethylenimine has been grafted onto the surface of MWNTs by performing a cationic polymerization of aziridine in the presence of amine-functionalized MWNTs (NH<sub>2</sub>-MWNTs [89]). The grafting of PEI was realized through two mechanisms, the activated monomer mechanism (AMM) or the activated chain mechanism (ACM), by which protonated aziridine monomers or the terminal iminium ion groups of propagation chains, respectively, are transferred to amines on the surface of MWNTs [89].

Bonduel et al. [90] reported the homogeneous surface coating of long carbon nanotubes by in situ polymerization of ethylene as catalyzed directly from the nanotube surface-treated by a highly active metallocene-based complex. It allowed for the break-up of the native nanotube bundles leading, upon further melt blending with HDPE, to high-performance polyolefinic nanocomposites [90]. In another attempt, an easy method for preparing polystyrene-grafted multi-walled carbon nanotubes (MWCNTs) with high graft yields was developed by using free radical graft polymerisation from photoinduced surface initiating groups on MWCNTs [91]. Conventional microscopy, including optical, atomic force, scanning electronic microscopy (SEM), and transmission electronic microscopy (TEM), reveal the dispersion state or quality of CNTs within a very limited area of a given nanofiller composite [67]. High resolution-TEM image of the MWCNTs-PS (Figure 8) shows that the surface of the MWCNTs-PS is covered with 4–5nm thick amorphous PS layers while the wall surface of purified MWCNTs was smooth, without any detectable polymer Layer [91].

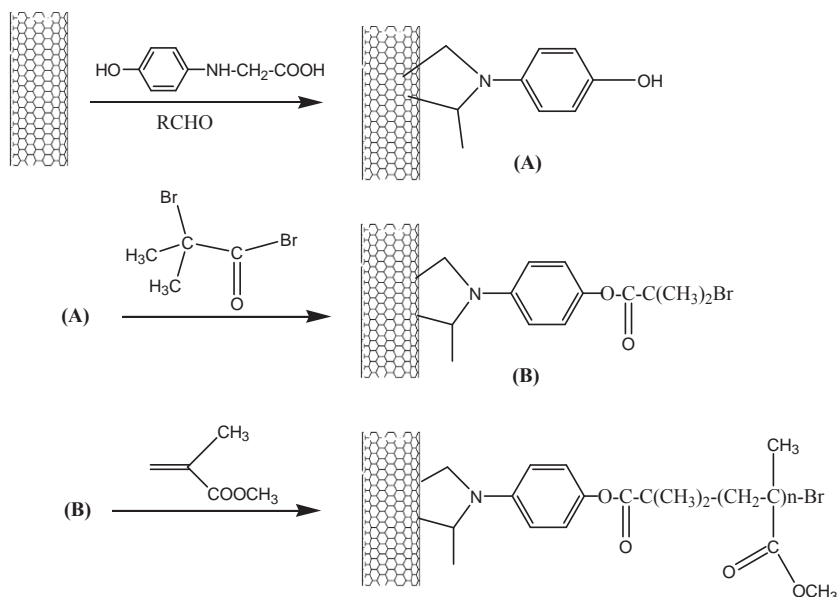


**Figure 8.** HR-TEM image of PS-g-MWCNT. Reprinted from [91] with permission of Elsevier.

Controlled radical polymerisation techniques such as nitroxide mediated polymerisation (NMP), atom transfer radical polymerisation (ATRP) and radical addition fragmentation transfer (RAFT) have been also used to graft polymer chains from the CNT surface [92-103] (see figure 9 as example).

### 3. Carbon nanotubes nanocomposites based on Polyolefins

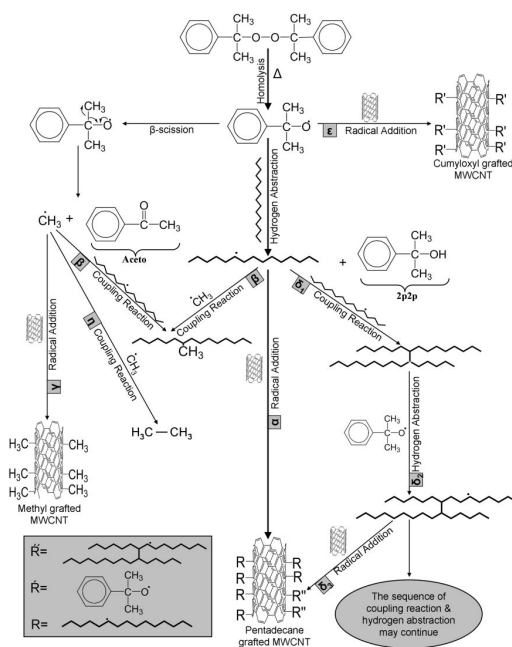
Polyethylene (PE) is one of the most widely used commercial polymer due to the excellent combination of low coefficient of friction, chemical stability and excellent moisture barrier properties [104]. The combination of a soft polymer matrix such as PE with nanosized rigid filler particles may provide new nanocomposite materials with largely improved modulus and strength. To improve the stiffness and rigidity of PE, CNTs can be used to make CNT/PE composites [104-107]. The mechanical properties of polyethylene (PE) reinforced by carbon nanotubes do not improve significantly because the weak polymer-CNT interfacial adhesion prevents efficient stress transfer from the polymer matrix to CNT [108-110]. The lack of functional groups and polarity of PE backbone results in incompatibility between PE and other materials such as glass fibres, clays, metals, pigments, fillers, and most polymers. A strategy for enhancing the compatibility between nanotubes and polyolefins consists in functionalising the sidewalls of CNT with polymers either by a 'grafting to' or a 'grafting from' approach. As discussed before, the "grafting from" approach involves the growth of polymers from CNT surfaces via in situ polymerisation of olefins initiated from chemical species immobilised on the CNT. As an example, Ziegler-Natta or metallocene catalysts for ethylene polymerisation can be immobilised on nanotubes to grow PE chains from their surface. However, covalent linkages or strong interactions between PE chains and nanotubes cannot be created during polymerisation [90, 111-113]. The "grafting to" technique involves the use of addition reactions between the polymer with reactive groups and the CNT surface. However, the synthesis of end-functionalized polyethylene (PE), which is necessary in the "grafting to" approach, is difficult [114]. Another promising route for a chemical modification of MWCNTs by PE is to use free radical initiators such as peroxides. The general mechanism of free radical grafting of vinyl compound from hydrocarbon chains detailed by Russell [115], Chung [116] and Moad [117] seems to express a widespread view. The grafting reaction starts with hydrogen abstraction by alkoxy radicals generated from thermal decomposition of the peroxide. Then, the active species generated onto the hydrocarbon backbone react with unsaturated bonds located on the MWCNTs surface. This chemical modification is thus conceivable during reactive extrusion because the radicals' lifetimes (in the range of few milliseconds) are compatible with typical residence time in an extruder (around one minute).



**Figure 9.** ATRP 'grafting from' modification approach. Reproduced from [92] with permission of ACS publications.

### 3.1. Radical grafting of polyethylene onto MWCNTs

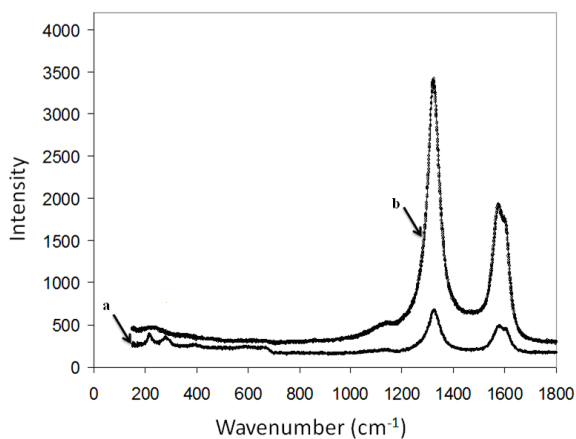
The main drawback of the free radical grafting is the low selectivity of the radical center, specially at high temperatures (in the range of 150-200°C, required for extrusion of polyethylene), leading to side reactions such as coupling and chain scission [115, 118]. Moreover, performing this chemical modification by reactive processing brings in many constraints inherent to the processing (e.g. short reaction time, viscous dissipation and high temperature). For instance, the difference of viscosity between the monomer and the molten polymer could enhance these side reactions. So, to separate these physical influences from the chemical modification, the grafting reaction can be predicted with a model compound approach based on a radical grafting reaction between peroxide-derived alkoxy radicals, and a low molar mass alkane representing characteristics moieties of PE.



**Figure 10.** General reactive pathways of free radical grafting of pentadecane onto MWCNTs ; Reproduced from [119] with permission of Elsevier.

### 3.1.1. A model compound approach through the use of pentadecane

Covalent functionalization of pentadecane-decorated multiwalled carbon nanotubes (MWCNTs) has been studied as a model compound approach for the grafting of poly (ethylene-co-1-octene) onto MWCNTs by reactive extrusion [119]. It was accomplished through radical addition onto unsaturated bonds located on the MWCNTs' surface using dicumyl peroxide as hydrogen abstractor. Pentadecane ( $C_{15}H_{32}$ ) has been resorted as model for polyethylene because high boiling points of long chain alkanes permit study under high temperature conditions, typically over  $150^{\circ}C$ . It also gives clues about low viscosity at  $150^{\circ}C$ , on top of that the formed products in the grafting experiment can hence be analysed more easily than in the polymer melt. Figure 10 sums up main reactive pathways of free radical grafting of pentadecane onto MWCNTs with dicumyl peroxide as initiator. The hydrogen abstraction reactions from alkyl hydrocarbon bonds was studied starting from the reaction of DCP-derived radicals with pentadecane.



**Figure 11.** Raman spectra of: p-MWCNTs (a) and penta-g-MWCNTs (b).

However, the alkoxy radicals can undergo additional reactions including  $\beta$ -scission leading to the formation of methyl radicals [117]. These latter preferentially induce coupling reaction (Fig. 10, route b and h) or attack onto the  $sp^2$  carbon of the MWCNTs (Fig. 10, route g) whereas cumyloxy radicals are more prone to hydrogen abstraction from pentadecane [120]. The formed pentadecyl radicals through hydrogen abstraction are able to react with MWCNTs by radical addition onto  $sp^2$  carbon of the MWCNTs (Fig.10, main route a) and with other radical species via the common radical coupling reactions (Fig. 10, routes d1 and b). According to the results of Johnston [121,122], based on a study of the crosslinking reaction of poly (ethylene-co-1-octene) in the presence of DCP at 160 °C, coupling reactions are four times more prone to happen than scission reactions so the authors assumed that pentadecyl radicals do not undergo scission reactions [119]. Direct evidence for covalent sidewall functionalization has been found by Raman spectroscopy [123-124]. G band is a characteristic feature of the graphitic layers and corresponds to the tangential vibration of the carbon atoms. The second characteristic mode is a typical sign for defective graphitic structures (D band). The  $A_D/A_G$  ratio, which was defined as the intensity ratio of the D-band to G-band of CNTs, directly indicates the structural changes in nanotubes. Some authors used D to G area ratios ( $A_D/A_G$ ) rather than intensity [125] which is a better indicator. The relatively high area ratio of the G band relative to D band for penta-g-MWCNT ( $A_D/A_G = 1.51$ ) in comparison with that of p-MWCNT (i.e. ( $A_D/A_G = 1.20$ )) could be designated as an indicator of grafting species. The ratio between the G band and D band is a good indicator of the changes in chemistry of CNTs. Interestingly, Raman spectra of p-MWCNTs and penta-g-MWCNTs (Figure 11a and 11b, respectively) showed two main peaks around 1350 $cm^{-1}$  (D band) and 1586 $cm^{-1}$  (G band). The relatively high intensity of the G band relative to D band ( $I_G/I_D = 1.25$ ) for penta-g-MWCNT sample in comparison with that of p-MWCNT (i.e.  $I_G/I_D = 0.95$ ) was designated as an indicator of grafting species [119].

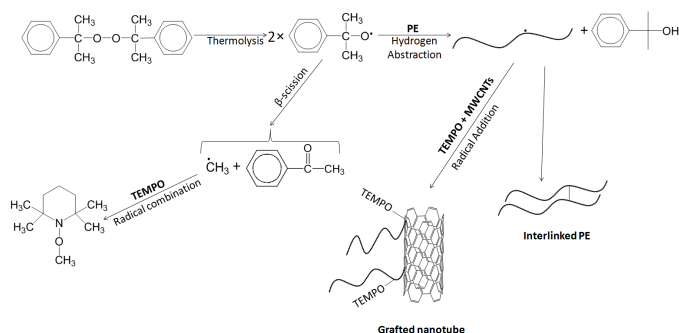


It is important to determine whether the results of a CNT surface modification process agree qualitatively with expectations, and equally important is the need for a quantitative assessment of the extent and nature of surface modifications. The course of the generated radical species and the extent of the grafting reaction in regards to the DCP concentration and temperature can be studied through gas chromatography and thermogravimetric analysis (TGA) [119, 126]. TGA permits measurement of the total weight fraction of surface modifiers introduced onto the surfaces of CNTs if the surface-modified CNTs are free of impurities. Indeed, it is well known that heating functionalized nanotubes in an inert atmosphere removes the organic moieties and restores the pristine nanotubes structure. TGA can indicate the degree of surface modification because the type and quantity of surface modifier is identified. It was found that the higher grafting density, as high as 1.46 mmol/g, was obtained at 150°C. At higher temperatures, the grafting density decreases because the  $\beta$ -scission reaction of cumyloxy radical accelerates as the temperature increases, leading to the formation of methyl radicals. These latter preferentially react by combination whereas cumyloxy radicals are more prone to hydrogen abstraction from pentadecane. At 150°C, for initiator concentration higher than 3wt%, the grafting density decreases from 1.464mmol/g to 0.371mmol/g upon increasing DCP concentration up to 5%. Thus, to get high grafting efficiency, one should opt for optimal initiator concentration, i.e. 3wt%, and choose the most favourable reaction temperature, i.e. 150°C. Incorporation of TEMPO as radical scavenger in the grafting reaction of pentadecane onto MWCNTs serves two purposes: firstly, it actively suppresses radical combination reactions and hence promotes pentadecyl radicals' addition to nanotubes (~16% increase in grafting density); and secondly, it effectively changes the polarity balance of the grafted species, making pentadecane and TEMPO functionalised nanotubes soluble in solvents such as THF and chloroform [126].

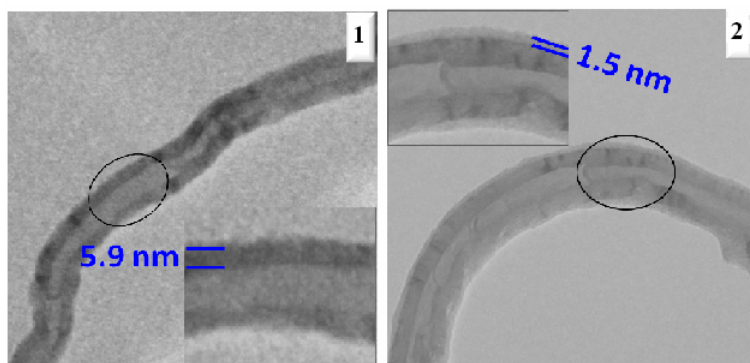
### 3.1.2. Synthesis of PE grafted carbon nanotubes via peroxide

To make full use of the strength of carbon nanotubes in a composite, it is important to have a high-stress transfer at the matrix-nanotube interface via strong chemical bonding, as discussed by Mylvaganam et al [127]. They have investigated the possible polyethylene-nanotube bonding with the aid of a quantum mechanics analysis with the polyethylene chains represented by alkyl segments, and the nanotubes modeled by nanotube segments with H atoms added to the dangling bonds of the perimeter carbons. Their study has predicted (i) covalent bond formation between alkyl radicals and carbon nanotubes is energetically favourable; and, (ii) this reaction may take place at multiple sites of nanotubes [126]. Hence one way to improve the load transfer of carbon nanotubes/PE composite via chemical bonds at the interface is to use free-radical generators such as peroxide or incorporate nanotubes by means of in situ polymerisation.

Figure 12 sums up main reactive pathways of free radical grafting of PE onto MWCNTs with dicumyl peroxide as initiator and TEMPO as radical scavenger.



**Figure 12.** Reaction scheme for PE grafting onto MWCNTs with TEMPO as a radical scavenger. Reproduced from [128] with permission of John Wiley and Sons.



**Figure 13.** TEM images of p-MWCNTs (1) and PE-g-MWCNTs (2). Reproduced from [128] with permission of John Wiley and Sons.

The formed PE-based radicals are able to react with MWCNTs by radical addition onto  $sp^2$  carbon of the MWCNTs (Figure 12) and with other radical species via the common radical coupling reactions. As discussed using a model compound approach (section 2.1.1), the presence of TEMPO radicals creates competitive combinations reactions (that are actually reversible reactions) which may favour the addition of PE-based radicals to MWCNTs (Figure 12). Before carrying out thermogravimetric analysis to gain a quantitative picture of the extent of nanotubes' functionalisation, the adsorbed (non-covalently attached) PE chains were removed from the grafted ones (covalently attached) by extensive washings with dichlorobenzene (DCB). PE-grafted onto MWCNTs are well known to degrade at 300-540°C, which are nearly the same temperatures as pure PE reactants and the weight of grafted PE is estimated to be in the range 20-24% depending on the experimental procedure [128]. The corresponding grafting densities, calculated using a specific surface area (SSA) of 225m<sup>2</sup>/g for MWCNTs [115, 129] are varying from 1.1mg.m<sup>-2</sup> to 1.4mg.m<sup>-2</sup>. LDPE grafting density on

nanotubes is  $1.1\text{mg.m}^{-2}$  while incorporation of TEMPO raises the grafting density to  $1.4\text{mg.m}^{-2}$  [128]. Then, it is usual to examine the morphological structures of p-MWCNTs and PE-grafted MWCNTs by transmission electron microscopy (TEM). In these experiments, a few drops of dilute solutions of PE-grafted nanotubes in hot DCB are initially deposited onto a carbon-coated copper grid and further observed in a dried state after evaporation of the solvent (Figure 13).

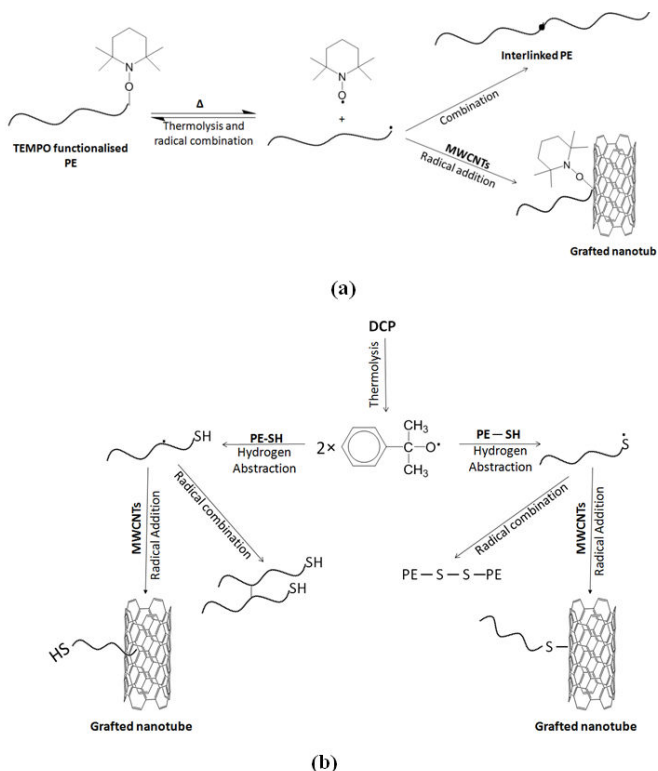
A “grafting to” approach based on a radical process can also involve a polymer with reactive end groups.

### 3.1.3. Synthesis of PE grafted carbon nanotubes via end functionalised PE

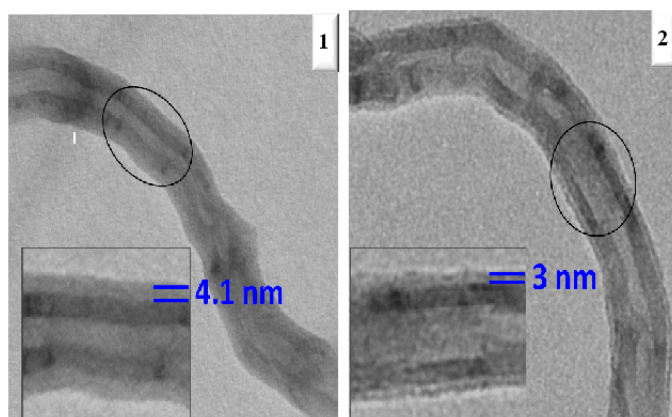
Recently, D’Agosto and Boisson [130-134] developed new strategies that rely on a one step *in situ* functionalisation reaction within an ethylene polymerisation reactor to introduce a variety of functional groups including alkoxyamine [130-132] and thiol [132,134] functions at the end of polyethylene chains. Di-polyethylenyl magnesium compound ( $\text{MgPE}_2$ ) were prepared using a neodymium metallocene complex which catalysed polyethylene chain growth on magnesium compounds.  $\text{MgPE}_2$  was *in situ* reacted with 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) radical or elemental sulphur to provide a macroalkoxyamine (PE-TEMPO) and polysulphur based product (PE- $\text{S}_n$ -PE) respectively. PE-SH was obtained by simple reduction of PE- $\text{S}_n$ -PE. According to these results, a strategy based on the use of those polyethylenes was investigated to generate radical-terminated chains formed either by thermal loss of a nitroxide (PE-TEMPO) or H-abstraction onto a thiol (PE-SH) and graft them onto CNTs (Figure 14) [128].

Indeed, Lou [87] showed an efficient attachment of poly(2-vinylpyridine) (P2VP) end-capped by TEMPO to CNT sidewalls by heating of TEMPO-terminated P2VP. Using the same strategy Liu [137] functionalized shortened CNTs with PS and poly[(*tert*-butyl acrylate)-*b*-styrene] and Wang [138] grafted poly(4-vinylpyridine-*b*-styrene) onto CNTs. In figure 14a, the homolytic cleavage of TEMPO-terminated PE leads to the formation of stable nitroxyl radicals and PE radicals. The reversible termination of the polyethylene chain is the key step for reducing the overall concentration of the radical chain end. The extremely low concentration of reactive chain ends is expected to minimize irreversible termination reactions, such as combination or disproportionation [135] (Figure 14a). Thiol-terminated polyethylene has been also grafted onto CNTs using a similar procedure. The thiol based compounds are widely used for controlling molar mass in free radical polymerizations via a chain transfer process. The chain transfer process displays two contiguous steps: transfer of the thiyl hydrogen to the growing polymer chain followed by re-initiation, whereby a thiyl radical adds to a monomeric double bond. In the presence of DCP-derived radicals and MWCNTs, thiyl radicals are formed and are expected to react by radical addition onto  $\text{sp}^2$  carbon of the MWCNTs. For both samples PE-TEMPO and PE-SH, the weight loss observed by thermogravimetric analysis (TGA) has been increased to 36% and 34%, respectively despite their low molar masses (e.g.  $1400\text{g/mol}$  and  $980\text{g/mol}$ ) in comparison with that of LDPE (weight loss = 20-24% ;  $M_w = 90000\text{g/mol}$  ; see section 2.1.2.). These results indicated that the use of short end-functionalized PE chains has permitted a significant increase of the grafting density

(e.g. 1.78 and 2.80  $\mu\text{mol.m}^{-2}$ , respectively). These values are approximately increased by two orders of magnitude in comparison with the LDPE grafting density (e.g. 0.012  $\mu\text{mol.m}^{-2}$ ) suggesting that longer polymer chains cover a larger surface decreasing the grafting density, as previously described by Jerome et al [87,136] for the attachment of poly(2-vinylpyridine) (P2VP) and polystyrene (PS) onto MWCNTs. Indeed, they observed that PS grafting density decreases from 0.045  $\mu\text{mol.m}^{-2}$  to 0.01  $\mu\text{mol.m}^{-2}$  by increasing the molecular weight of PS-TEMPO from 3000g/mol to 30000g/mol [138]. The TEM observations (Figure 15) were consistent with the TGA results : the grafted polymer contents can be highered by using end-functionalized PE [129].



**Figure 14.** Reaction scheme for end functionalised PE grafting onto MWCNTs: (a) via PE-TEMPO; (b) via PE-SH. Reproduced from [128] with permission of John Wiley and Sons.



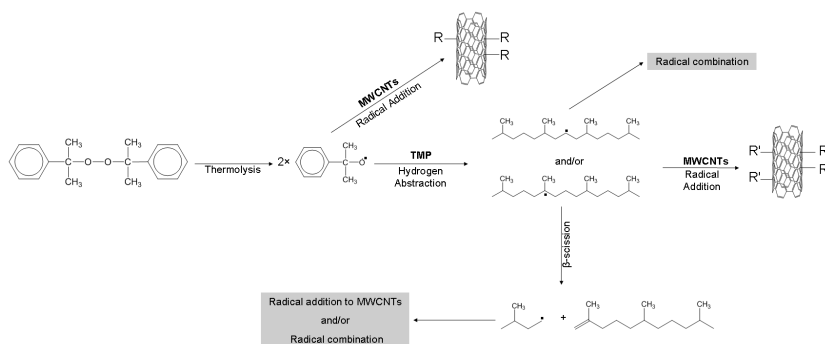
**Figure 15.** TEM images of PE<sub>f-TEMPO</sub>-g-MWCNTs (1) and PE<sub>f-SH</sub>-g-MWCNTs (2). Reproduced from [128] with permission of John Wiley and Sons.

### 3.2. Radical grafting of polypropylene on carbon nanotubes

Polypropylene (PP) is a widely used commercial polymer due to the excellent combination of mechanical resistance, chemical stability and excellent moisture barrier properties [104]. Although physical blending with CNTs is an economic way to modify polypropylene performance, compatibilizing agents are necessary for creating strong interface between filler particles and the polymer phase. Maleic anhydride grafted polypropylene (MA-g-PP) is often used as a compatibilizer which can improve the PP/CNTs composite properties by strong hydrogen bonding between hydroxyl groups located on the acidic-treated CNTs surface and anhydride groups of MA-g-PP [139, 140]. Recently, an original and simple method for promoting mobility sensitivity of carbon nanotubes (CNTs) to an external stress field in polypropylene (PP) matrix was developed [141]. In particular, an interfacial melt reaction initiated by free radicals were used as a tool to prepare PP/CNTs nanocomposites. The presence of tetrakis(phenylmethyl)thioperoxydi(carbothioamide) (TBzTD) increased the interfacial reaction between the PP chains and the CNTs. In addition, the grafted TBzTD to PP backbone could form a physical interaction with CNTs *via* a  $\pi$ - $\pi$  interaction [141]. According to their previous results [119, 126] based on a study of the radical grafting of polyethylene derivatives onto MWCNTs, Farzi et al. investigated MWCNTs' sidewall functionalization by tetramethylpentadecane and PP in the presence of 1wt% DCP at 160°C.

#### 3.2.2. A model compound approach through the use of 2,6,10,14-tetramethylpentadecane

Similarly to the pentadecane grafting procedure (see section 2.1.1.), 2,6,10,14-tetramethylpentadecane (TMP, C<sub>19</sub>H<sub>40</sub>) has been used as model for the grafting reaction of PP onto MWCNTs [129]. Thermolysis of dicumyl peroxide initiator performed in TMP and in presence of MWCNTs is depicted in Figure 16.



**Figure 16.** Reaction scheme for the addition of TMP onto CNT in the presence of DCP. Reproduced from [129] with permission of Elsevier.

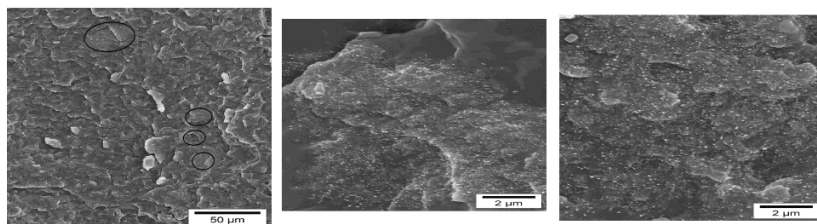
As shown in Figure 16, the formed peroxide radicals are prone to hydrogen abstraction from hydrocarbon substrates and it is expected that the active species generated onto the hydrocarbon backbone react with unsaturated bonds located on the MWCNTs surface keeping in mind that side reactions such as chain scission for PP derivatives may occur at high temperatures (Figure16) [115, 118]. For experiments conducted in dichlorobenzene (DCB) as solvent at 160°C with 1.5wt% DCP, TMP grafting density was as high as 0.92 mg/m<sup>2</sup>.

### 3.2.2. Synthesis of PP grafted carbon nanotubes via peroxide

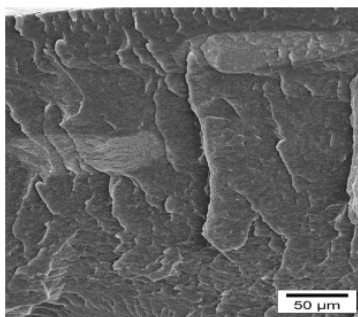
Farzi et al. [129] have successfully grafted PP onto MWCNTs through a radical grafting reaction, carried out under similar experimental conditions to PE [128] and TMP [129] (1.5wt% DCP, 160°C) and using 1,2-dichlorobenzene (DCB) as solvent able to solubilize PP partially at elevated temperature. The corresponding PP-grafted nanotubes were analysed by TGA after a purification by soxhlet extraction in DCB. However, the authors were not able to obtain reproducible results with weight losses varying from 50% to 80% for the above-mentioned experiment. This behaviour was attributed to the purification procedure which did not permit to remove all the free PP chains. The authors have also speculated on the degradation behaviour of PP through the well-known  $\beta$ -scission reaction occurring in the presence of radical species therefore the authors were not able to give a PP grafting density. Then, the aforementioned PP coated MWCNTs have been dispersed within a commercially available PP matrix using a contra-rotating Haake Rheomixer and the amount of nanofiller in the final composites has been fixed to 3wt%. The evaluation of MWCNTs dispersion has been examined by using scanning electron microscopy (SEM) (Figure 17).

SEM images of the PP/PP-g-MWCNTs composites MWCNTs containing of 3wt% (Figure 17) demonstrated that there were still some areas where PP-g-MWCNTs were not found which was obviously connected with improper filler distribution. For a simple melt blend of PP with untreated MWCNTs, SEM images of the resulting material only showed clusters of a few tens micrometers of diameter evidencing a poor interfacial adhesion in the material

(Figure 18), as reported by Lee [140] for untreated MWCNT/PP composites MWCNTs containing of 2wt%.



**Figure 17.** SEM micrographs of PP/PP-g-MWCNT composites with MWCNTs loading of 3wt%. Reproduced from [129] with permission of Elsevier.



**Figure 18.** SEM micrographs of PP/MWCNTs composites with MWCNTs loading of 3wt%. Reproduced from [129] with permission of Elsevier.

It was concluded from these results that the grafting of PP onto MWCNTs provided a low steric barrier against the strong intermolecular Van der Waals interactions among nanotubes within the PP matrix.

In a similar approach, isotactic polypropylene (iPP) was successfully grafted onto multiwalled carbon nanotubes (MWCNTs) by direct macroradical addition by sonication in hot xylene with BPO as an initiator [142]. It was found that both iPP macromolecular radicals and small-molecular benzoic acid free radicals were grafted onto MWNTs. iPP-g-MWNTs dispersed more uniformly in iPP than pristine MWNTs.

### 3.3. Rheological behaviour of polyolefin based carbon nanotubes nanocomposites

It has been well known for a century that the addition of fillers, mostly carbon black, to rubber compounds has a strong impact on the viscoelastic properties of materials. In recent years, polymer nanocomposites have been developed as a new class of composites [143]. Ac-



tually from a rheological point of view, a direct consequence of incorporation of fillers in molten polymers is the significant change in the steady shear viscosity behavior and the viscoelastic properties. The level of filler dispersion is expected to play a major role in determining the filler effects on non linear responses of nanocomposites. Generally speaking, thermoplastic polymers filled with nano-particles show a solid-like behavior response which includes a non-terminal zone of relaxation, apparent yield stress and a shear-thinning dependence of viscosity on particle concentration, aspect ratio and dispersion.

Since the melt rheological properties of filled polymers are sensitive to the structure, concentration, particle size, shape and surface characteristics of the fillers, rheology offers original means to assess the state of the dispersion in nanocomposites and to investigate the influence of flow conditions upon nano-filler dispersion itself [144]. As discussed previously, one of the most important challenges in filled polymer developments and applications is to obtain a homogeneous dispersion of CNT in polymer matrix by overcoming the van der Waals interaction between elementary tubes. As a result, it can be expected that the rheological percolation, and subsequently the non-linearity effect, depend on nanotube dispersion and aspect ratio. As matter of fact, a great level of activity in the domain of the rheology of polymers filled with CNT is reported in the more recent scientific literature. The rheological behavior of melt thermoplastic polymer filled with NTC was reported to depend on nanotube dispersion, aspect ratio and alignment under flow. However, among the different studies on liquid systems filled with carbon nanotubes two types of relaxation mechanisms of CNT must be differentiated according to the matrix viscosity: Do the carbon nanotubes behave as Brownian particles? The Doi-Edwards theory for dilute regime (the nanotubes are free to rotate without any contacts) allows the rotary diffusivity  $D_{r0}$  of a rod (Length:  $L$  and diameter:  $d$ ) in an isotropic suspension to be calculated by equation (1), in which  $k_B$  is the Boltzmann constant and  $\eta_m$  is the viscosity of the suspending medium

$$D_{r0} = \frac{3k_B T (\ln(L/d) - 0.8)}{\pi \eta_m L^3} \quad (1)$$

In semi-dilute regime, the rotary diffusivity  $D_r$  can be written as equation (2), where  $A$  is a dimensionless constant whose value is generally large ( $A \sim 1000$ ).

$$D_r = A D_{r0} (\nu L^3)^{-2} \quad (2)$$

Consequently, the rotary diffusion of CNT varies according to matrix viscosity:

$$D_r \propto 1/\eta_m \quad (3)$$

Actually, the rheological behavior of CNT suspension is observed close to the Doi-Edwards theory on the Brownian dynamics of rigid rods. However, it was observed that low shear deformations induced an aggregation mechanism, but these aggregates broke down at high

shear, forming small aggregates with less entanglements [145]. The shear rheology of such carbon nanotube suspensions was reviewed by Hobbie [146] from the perspective of colloid and polymer science.

According to the Doi-Edwards theory, Marceau et al [147] have shown that the suspensions of CNT, at low concentration ( $\phi=0.2\%$ ) and in low fluid matrix ( $\eta_m=5$  Pa.s), behave as Brownian entities ( $D_i=5.0 \times 10^{-5} \text{ s}^{-1}$ ). The diffusion time of these CNTs is then  $\tau_r=1/2D_i \approx 10^4 \text{ s}$ . If we imagine that these same CNT are dispersed in high viscous polymer matrix such as molten PP ( $\eta_m \sim 1 \times 10^3$  Pa.s), their relaxation time will be then:  $\tau_r \approx 2 \times 10^6 \text{ s}$ . The order magnitude of the relaxation time is then one month! Consequently, the carbon nanotubes cannot be considered anymore as Brownian entities in most of the papers that have been addressed to the viscoelastic behavior of carbon nanotubes dispersed in high viscous molten polymers. The main challenge in such nanocomposite systems is to control the dispersion of the nanotubes in high viscous fluid in order to have the lowest percolation threshold regarding the electrical properties. For example, by improving the CNT dispersion using functionalized single wall nanotubes, Mitchell et al [148] observed that the percolation threshold dropped from 3wt% to 1.5% in PS nanocomposites.

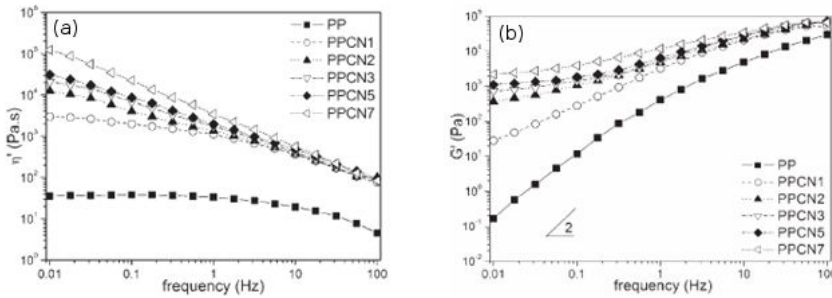
Actually, the dispersion of CNT in polymer matrix is strongly difficult mainly due to the nanotube-nanotube interactions higher than the nanotube-polymer interaction. However, optimal dispersion of CNTs can be achieved in polar polymers such as polyamides, polyesters or polycarbonate. This optimal dispersion is generally measured, at least from a qualitative point of view, from the electrical and/or rheological percolation threshold. Nevertheless, the dispersion of CNT in polyolefin (PP, PE or copolymer of ethylene) is most of the time a real challenge due to unfavorable and low nanotube-polymer interactions. On the other hand, the fact that CNT have a high aspect ratio and are not Brownian in polymer matrix leads to the conclusion that the different works of the literature are difficult to compare. The samples, studied in rheology or electric conductivity, have generally undergone different processing conditions. As a result, CNT nanocomposites are totally out of isotropic dispersion and the isotropic equilibrium of CNTs can never be achieved. However, general trends in CNT nanocomposite can be described from the open literature.

From a sample preparation point of view, dispersion of CNTs in polyolefins were generally prepared via conventional melt processing, i.e melt blending in batch mixer or in twin screw extruder). Marginal methods may also be used as for example solid-state shear pulverization [149] or in situ lubrication methods [150]. Numerous studies [151-156] have been devoted to the linear viscoelasticity of PP nanocomposites based on CNT dispersion.

All of these papers reported an increase in shear viscosity and storage and loss moduli of the nanocomposites with increasing the CNT concentration as shown in Figure 19.

Furthermore, a general rheological trend for nanocomposites studied in most of these papers is the appearance of a transition from a liquid-like behaviour to a solid-like behaviour, i.e. the apparition of a plateau (second plateau modulus,  $G_o = \lim_{\omega \rightarrow 0} G'(\omega)$ ) of the storage modulus at low frequency which is obviously higher than the loss modulus. Obviously, it is ad-

mitted that the increase of the CNT concentration is driving this transition. Above this critical transition, generally associated with the percolation threshold, these nanocomposites show a solid-like behavior response, which includes a non-terminal zone of relaxation leading to apparent yield stress and a shear-thinning dependence on viscosity  $|\eta^*(\omega)| \propto \omega^{-1}$ .



**Figure 19.** Variation versus frequency of the storage shear modulus  $G'(\omega)$  and absolute complex viscosity  $\eta^*(\omega)$  at different concentrations of CNT (1 to 7%). Reproduced from [151] with permission of John Wiley and Sons.

This non-terminal frequency behavior is generally attributed to the formation of an interconnected nanotube network in the polymer matrix. Therefore, the solid-like behavior is associated nanotube–nanotube interactions which increase with the CNT content. Eventually, these interactions lead to percolation and the formation of an interconnected structure of nanotubes in the matrix. Due to the high aspect ratio of CNT (generally,  $L/d > 150$ ), the existence of this percolation threshold is expected at low concentration. For example, from Fig 19, the percolation threshold can be estimated to be less than 2% of CNT. This percolation threshold is generally observed in the range 0.5%-5% depending on CNT nature (aspect ratio, surface chemical modification) and on the processing methods for nanocomposite preparation.

If a lot of works have been devoted to the linear viscoelasticity of CNT nanocomposites whereas a few works have been reported on non-linear properties such as for example the melt flow instabilities. Interestingly, Palza et al [157] showed that carbon nanotubes modify the main characteristics of the spurt instability developed by the linear polyethylene. Furthermore, the sharkskin instability, developed in short chain branched polyethylene, is reduced at low amounts of MWCNT. Furthermore, the critical shear rate for the on-set of the spurt and the sharkskin instabilities decreases in the nanocomposites probably due to the physical interactions between the polymer and the nanofiller. Finally, at high shear rates, the gross melt fracture instability is completely erased in the nanocomposites based on the linear polymer whereas in short chain branched polyethylene the amplitude of this bulk distortion is rather moderated. Clearly, the carbon nanotubes have a drastic effect on the main flow instabilities observed in polyethylene. Consequently, the processing of CNT nanocomposites, i.e under non-linear deformation, is an open investigation domain.

## 4. Conclusion

The most frequent method for preparing polymer nanotubes composites has been mixing nanotubes and polymer in a suitable solvent and to evaporate the solvent to form composite film. But to increase the advantages at its best, one needs: (i) high interfacial area between nanotubes and polymer; and, (ii) strong interfacial interaction. Unfortunately this solvent technique does not help much in achieving these targets; and as a result a nanocomposite having properties much inferior to theoretical expectations are obtained. In order to obtain higher contact area between nanotubes and polymer, the issue of dispersion needs to be addressed. Uniform dispersion of these nanotubes produces immense internal interfacial area, which is the key to enhancement of properties of interest. On the other hand, modification of nanotubes surface through functionalisation is required for creating an effective interaction with the host matrix and to make nanotubes soluble and dispersible.

The idea of grafting PE or PP with the help of peroxide during extrusion is exciting. It was shown that cumyloxy radical generated by thermolysis of DCP can abstract hydrogen from polyolefin chains, thus creating polyolefin macroradicals. Then, these macroradicals add to the unsaturated carbon bonds on the surface of the nanotubes. The upside of this strategy is that radicals have short lifetimes which make the procedure possible in an extruder where the residence time is generally low. On the contrary, the downside is the low selectivity of radicals leading to a competition between radical combination reactions and radical addition reactions. Alkanes can be used as model for PE to perform the grafting of PE onto nanotubes. The results were interesting however the degree of PE grafting remained lower than the model (weight loss by TGA = 22% as compared to a weight loss of 30% in case of pentadecane). LDPE grafting density on nanotubes was  $1.1\text{mg}\cdot\text{m}^{-2}$  while incorporation of TEMPO raised the grafting density to  $1.4\text{mg}\cdot\text{m}^{-2}$ . End functionalised PE can also be used for PE grafting onto nanotubes with dichlorobenzene as solvent. As emphasized by TEM images, a layer of considerable thickness has been grafted around the periphery of the nanotubes.

In order to follow the same strategy for nanotubes functionalisation with PP, tetramethylpentadecane has been selected as a model compound for PP. It was successfully grafted onto carbon nanotubes with a grafting density of  $0.92\text{ mg}/\text{m}^2$ . However, the grafting of PP onto nanotubes did not permit to obtain reproducible results. SEM images of the PP-g-MWCNTs nanocomposites with filler loadings of 3wt% in PP matrix did not show a significant improvement in MWCNTs dispersion within the PP matrix although sizes of the aggregates were slightly reduced.

In addition, it can be expected that the rheological percolation, and subsequently the non-linearity effect, depend on nanotube dispersion and aspect ratio. Low shear deformations induced an aggregation mechanism, but these aggregates broke down at high shear, forming small aggregates with less entanglements. In a high viscous polymer media, it was shown that carbon nanotubes could not be considered anymore as Brownian entities. A general rheological trend for CNTs-based nanocomposites is the appearance of a transition from a liquid-like behaviour to a solid-like behaviour increasing with the CNT content because it is

associated to nanotube–nanotube interactions. Due to the high aspect ratio of CNT the percolation threshold can be expected to be less than 2% of CNT.

## Author details

Emmanuel Beyou, Sohaib Akbar, Philippe Chaumont and Philippe Cassagnau

Université de Lyon, Université Lyon 1, CNRS UMR5223, Ingénierie des Matériaux Polymères: IMP@UCBL, 15 boulevard Latarget, F-69622 Villeurbanne, France

## References

- [1] Iijima, S. (1991). Helical microtubules of graphitic carbon. *Nature*, 354, 56-58.
- [2] Baughman, R. H., Zakhidov, A.A., & de Heer, W. A. (2002). Carbon Nanotubes--the Route Toward Applications. *Science*, 297(5582), 787-792.
- [3] Moniruzzaman, M., & Winey, K. I. (2006). Polymer Nanocomposites Containing Carbon Nanotubes. *Macromolecules*, 39(16), 5194-5205.
- [4] Grossiord, N., Loos, J., Regev, O., & Koning, C. E. (2006). Toolbox for dispersing carbon nanotubes into polymers to get conductive nanocomposites. *Chemistry of Materials*.
- [5] Ciardelli, F., Coiai, S., Passaglia, E., Pucci, A., & Ruggeri, G. (2008). Nanocomposites based on polyolefins and functional thermoplastic materials. *Polymer International*, 57(6), 805-836.
- [6] Judeinstein, P., & Sanchez, C. (1996). Hybrid organic-inorganic materials: A land of multi-disciplinarity *Journal of Materials Chemistry*, 6(4), 511-525.
- [7] Connell, M.O. Carbon Nanotubes. *Properties and Applications; CRC Press, 2006.*, 360, 9780849327483.
- [8] Gogotsi, Y. *Carbon Nanomaterials* CRC Press, 2006., 344, 9780849393860.
- [9] Spitalsky, Z., Tasis, D., Papagelis, K., & Galiotis, C. (2010). Carbon nanotube-polymer composites: Chemistry, processing, mechanical and electrical properties. *Progress in Polymer Science*, 35(3), 357-401.
- [10] Osswald, S., Flahaut, E., & Gogotsi, Y. (2006). In situ Raman spectroscopy study of oxidation of double- and single-wall carbon nanotubes. *Chemistry of Materials*, 18(6), 1525-1533.
- [11] Yang, Q., Wang, L., Xiang, W., Zhu, J., & Li, J. (2007). Grafting polymers onto carbon black surface by trapping polymer radicals. *Polymer*, 48(10), 2866-2873.

- [12] Deng, X., Jia, G., Wang, H., Sun, H., Wang, X., Yang, S., Wang, T., & Liu, Y. (2007). Translocation and fate of multi-walled carbon nanotubes in vivo. *Carbon*, 45(7), 1419-1424.
- [13] Shaffer, M. S. P., & Windle, A. H. (1999). Fabrication and Characterization of Carbon Nanotube/Poly(vinyl alcohol) Composites. *Advanced Materials*, 11(11), 937-941.
- [14] Baskaran, D., Mays, J. W., & Bratcher, M.S. (2005). Noncovalent and nonspecific molecular interactions of polymers with multiwalled carbon nanotubes. *Chemistry of Materials*, 17(13), 3389-3397.
- [15] Haggemuller, R., Gommans, H. H., Rinzler, A. G., Fischer, J. E., & Winey, K. I. (2000). Aligned single-wall carbon nanotubes in composites by melt processing methods. *Chemical Physics Letters*.
- [16] Kang, Y. J., & Taton, T. A. (2003). Micelle-encapsulated carbon nanotubes: A route to nanotube composites. *Journal of the American Chemical Society*, 125(19), 5650-5651.
- [17] Star, A., & Stoddart, J. F. (2002). Dispersion and solubilization of single-walled carbon nanotubes with a hyperbranched polymer. *Macromolecules*, 35(19), 7516-7520.
- [18] Barraza, H. J., Pompeo, F., O'Rear, E. A., & Resasco, D. E. (2002). SWNT-filled thermoplastic and elastomeric composites prepared by miniemulsion polymerization. *Nano Letters*, 2(8), 797-802.
- [19] Bonduel, D., Mainil, M., Alexandre, M., Monteverde, F., & Dubois, P. (2005). Supported coordination polymerization: a unique way to potent polyolefin carbon nanotube nanocomposites. *Chemical Communications*, 6, 781-783.
- [20] Park, S., Yoon, W., Lee, B., Kim, J., Jung, Y. H., Do, Y., Paik, H. J., & Choi, I. S. (2006). Carbon Nanotubes as a Ligand in Cp<sub>2</sub>ZrCl<sub>2</sub>-Based Ethylene Polymerization. *Macromolecular Rapid Communication*, 27(1), 47-50.
- [21] Liu, T. X., Phang, I. Y., Shen, L., Chow, S. Y., & Zhang, W. D. (2004). Morphology and mechanical properties of multiwalled carbon nanotubes reinforced nylon-6 composites. *Macromolecules*, 37(19), 7214-7222.
- [22] Siochi, E. J., Working, D. C., Park, C., Lillehei, P. T., Rouse, J. H., & Topping, C. C. Melt processing of SWCNT-polyimide nanocomposite fibers. *Composites Part B*. (2004). , 35(5), 439-446.
- [23] Potschke, P., Fornes, T. D., & Paul, D. R. (2002). Rheological behavior of multiwalled carbon nanotube/polycarbonate composites. *Polymer*, 43(11), 3247-3255.
- [24] Li, C., Zhao, Q., Deng, H., Chen, C., Wang, K., Zhang, Q., Chena, F., & Fua, Q. (2011). Preparation, structure and properties of thermoplastic olefin nanocomposites containing functionalized carbon nanotubes. *Polymer international*, 60(11), 1629-1637.
- [25] Zhang, Z. N., Zhang, J., Chen, P., Zhang, B. Q., He, J. S., & Hu, G. H. (2006). Enhanced interactions between multi-walled carbon nanotubes and polystyrene induced by melt mixing. *Carbon*, 44(4), 692-698.

- [26] Shofner, M. L., Khabashesku, V. N., & Barrera, E. V. (2006). Chemistry of Materials. *Processing and mechanical properties of fluorinated single-wall carbon nanotube-polyethylene composites.*, 18(4), 906-913.
- [27] Mahfuz, H., Adnan, A., Rangari, V. K., & Jeelani, S. (2005). Manufacturing and characterization of carbon nanotube/polyethylene composites. *International Journal of Nanoscience*, 4(1), 55-72.
- [28] Ruan, S. L., Gao, P., & Yu, T. X. (2006). Ultra-strong gel-spun UHMWPE fibers reinforced using multiwalled carbon nanotubes. *Polymer*, 47(5), 1604-1611.
- [29] Shofner, M. L., Khabashesku, V. N., & Barrera, E. V. (2006). *Chemistry of Materials*, 18, 906-913.
- [30] Bahr, J. L., & Tour, J. M. (2001). Processing and mechanical properties of fluorinated single-wall carbon nanotube-polyethylene composites. *Chemistry of Materials*, 13(4), 3823-3824.
- [31] Georgakilas, V., Kordatos, K., Prato, M., Guldi, D. M., Holzinger, M., & Hirsch, A. J. Organic functionalization of carbon nanotubes. *Journal of the American Chemical Society* (2002). , 124(5), 760-761.
- [32] Peng, H., Reverdy, P., Khabashesku, V. N., & Margrave, J. L. (2003). Sidewall functionalization of single-walled carbon nanotubes with organic peroxides. *Chemical Communications*, 362-363.
- [33] Qin, S., Qin, D., Ford, W. T., Resasco, D. E., & Herrera, J. E. (2004). Functionalization of single-walled carbon nanotubes with polystyrene via grafting to and grafting from methods. *Macromolecules*.
- [34] Riggs, J. E., Guo, Z., Carroll, D. L., & Sun-P, Y. (2000). Strong luminescence of solubilized carbon nanotubes. *Journal of the American Chemical Society*, 122(24), 5879-5884.
- [35] Umek, P., Seo, J. W., Hernadi, K., Mrzel, A., Pechy, P., Mihailovic, D. D., & Forro, L. (2003). Addition of carbon radicals generated from organic peroxides to single wall carbon nanotubes. *Chemistry of Materials*, 15(25), 4751-4755.
- [36] Liu, Y. K., Yao, Z. L., & Adronov, A. (2005). Functionalization of single-walled carbon nanotubes with well-defined polymers by radical coupling. *Macromolecules*, 38(4), 1172-1179.
- [37] Shaffer, M. S. P., & Koziol, K. (2002). Polystyrene grafted multi-walled carbon nanotubes. *Chemical Communications*.
- [38] Kong, H., Gao, C., & Yan, D. Y. (2004). Controlled functionalization of multiwalled carbon nanotubes by in situ atom transfer radical polymerization. *Journal of the American Chemical Society*, 126(2), 412-413.
- [39] Baskaran, D., Mays, J. W., & Bratcher, M.S. (2004). Polymer-grafted multiwalled carbon nanotubes through surface-initiated polymerization. *Angewandte Chemie International Edition*.



- [40] Breuer, O., & Sundararaj, U. (2004). Big returns from small fibers. *A review of polymer/carbon nanotube composites*. *Polymer Composites*, 25(6), 630-645.
- [41] Tiwari, I., Singh, K. P., & Singh, M. (2009). An insight review on the application of polymer-carbon nanotubes based composite material in sensor technology. *Russian Journal of General Chemistry*.
- [42] Martínez- Hernández, A.L., Velasco-Santos, C., & Castaño, V.M. (2010). Carbon Nanotubes Composites: Processing, Grafting and Mechanical and Thermal Properties. *Current Nanoscience*, 6(1), 12-39.
- [43] Jin, L., Bower, C. L., & Zhou, O. (1998). *Applied Physics Letters*, 73(9), 1197-1199.
- [44] Coleman, J. N., Cadek, M., Blake, R., Nicolosi, V., Ryan, K. P., & Belton, C. (2004). High-performance nanotube-reinforced plastics: Understanding the mechanism of strength increase. *Advanced Functional Materials*, 14(8), 791-798.
- [45] Cadek, M., Coleman, J. N., Ryan, K. P., Nicolosi, V., Bister, G., & Fonseca, A. (2004). Reinforcement of polymers with carbon nanotubes: The role of nanotube surface area. *Nano Letters*, 4(2), 353-356.
- [46] Cadek, M., Coleman, J. N., Barron, V., Hedicke, K., & Blau, W. J. (2002). Morphological and mechanical properties of carbon-nanotube-reinforced semicrystalline and amorphous polymer composites. *Applied Physics Letters*, 81(27), 5123-5125.
- [47] Andrews, R., Jacques, D., Minot, M., & Rantell, T. (2002). Fabrication of carbon multi-wall nanotube/polymer composites by shear mixing. *Macromolecular. Materials and Engineering*, 287(6), 395-403.
- [48] Breuer, O., & Sundararaj, U. (2004). Big returns from small fibers. *A review of polymer/carbon nanotube composites*. *Polymer Composites*, 25(6), 630-645.
- [49] Potschke, P., Bhattacharyya, A. R., Janke, A., & Goering, H. (2003). Melt mixing of polycarbonate/multi-wall carbon nanotube composites. *Composite Interfaces*, 10(4), 389-404.
- [50] Andrews, R., Jacques, D., Qian, D. L., & Rantell, T. (2002). Multiwall carbon nanotubes: Synthesis and application. *Accounts of Chemical Research*, 35(12), 1008-1017.
- [51] Tang, W., Santare, M. H., & Advani, S. G. (2003). Melt processing and mechanical property characterization of multi-walled carbon nanotube/high density polyethylene (MWNT/HDPE) composite films. *Carbon*, 41(14), 2779-2785.
- [52] Jia, Z., Wang, Z., Xu, C., Liang, J., Wei, B., & Wu, D. (1999). Study on poly(methyl methacrylate)/carbon nanotube composites. *Materials Science and Engineering A*, 271(1), 395-400.
- [53] Bonduel, D., Mainil, M., Alexandre, M., Monteverde, F., & Dubois, P. (2005). Supported coordination polymerization: a unique way to potent polyolefin carbon nanotube nanocomposites. *Chemical Communications*, 41(6), 781-783.

- [54] Bryning, M. B., Milkie, D. E., Islam, M. F., Kikkawa, J. M., & Yodh, A. G. (2005). Thermal conductivity and interfacial resistance in single-wall carbon nanotube epoxy composites. *Applied Physics Letters*, 87(87), 161909-161911.
- [55] Moniruzzaman, M., Du, F., Romero, N., & Winey, K. I. (2006). Increased flexural modulus and strength in SWNT/epoxy composites by a new fabrication method. *Polymer*, 47(1), 293-298.
- [56] Zhu, J., Kim, J., Peng, H., Margrave, J. L., Khabashesku, V. N., & Barrera, E. V. (2003). Improving the dispersion and integration of single-walled carbon nanotubes in epoxy composites through functionalization. *Nano Letters*, 3(8), 1107-1113.
- [57] Xia, H., Wang, Q., Li, K., & Hu, G. H. (2004). Preparation of polypropylene/carbon nanotube composite powder with a solid-state mechanochemical pulverization process. *Journal of Applied Polymer Science*, 93(1), 378-386.
- [58] Kasimatis, K. G., Nowell, J. A., Dykes, L. M., Burghardt, W. R., Thillalyan, R., Brinson, L. C., Andrews, R., & Torkelson, J. M. (2005). Morphology, thermal, and rheological behavior of nylon 11/multi-walled carbon nanotube nanocomposites prepared by melt compounding. *Programme Making and Special Events Preprint*, 92, 255-256.
- [59] Regev, O., El Kati, P. N. B., Loos, J., & Koning, C.E. (2004). Preparation of conductive nanotube-polymer composites using latex technology. *Advanced Materials*, 16(3), 248-251.
- [60] Lee, J. U., Huh, J., Kim, K. H., Park, C., & Jo, W. H. (2007). Aqueous suspension of carbon nanotubes via non-covalent functionalization with oligothiophene-terminated poly(ethylene glycol). *Carbon*, 45(5), 1051-1057.
- [61] McAndrew, T., Roger, C., Bressand, E., & Laurent, P. W. (2008). *WO/2008/106572*.
- [62] Vigolo, B., Penicaud, A., Coulon, C., Sauder, C., Pailler, R., Journet, C., Bernier, P., & Poulin, P. (2000). Macroscopic fibers and ribbons of oriented carbon nanotubes. *Science*, 290(5495), 1331-1334.
- [63] Mamedov, A.A., Kotov, N.A., Prato, M., Guldi, D. M., Wicksted, J. P., & Hirsch, A. (2002). Molecular design of strong single-wall carbon nanotube/polyelectrolyte multilayer composites. *Nature Materials*, 1(3), 190-194.
- [64] Calvert, P. (1999). Nanotube composites- A recipe for strength. *Nature*, 399(6733), 210-211.
- [65] Hersam, M.C. (2008). Progress towards monodisperse single-walled carbon nanotubes. *Nature Nanotechnology*.
- [66] Green, M.J. (2010). Analysis and measurement of carbon nanotube dispersions: nano-dispersion versus macrodispersion. *Polymer International*, 59(10), 1319-22.
- [67] Kim, S. W., Kim, T., Kim, Y. S., Choi, H. S., Lim, H. J., Yang, S. J., & Park, C. R. (2012). Surface modifications for the effective dispersion of carbon nanotubes in solvents and polymers. *Carbon*, 50(8), 3-33.

- [68] O'Connell, M.J., Boul, P., Ericson, L. M., Huffman, C., Wang, Y., & Haroz, E. (2001). Reversible water-solubilization of single-walled carbon nanotubes by polymer wrapping. *Chemical Physics Letters*, 342(3), 265-271.
- [69] Star, A., Stoddart, J. F., Steuerman, D., Diehl, M., Boukai, A., & Wong, E. W. (2001). Preparation and properties of polymer-wrapped single-walled carbon nanotubes. *Angewandte Chemie International Edition*, 40(9), 1721-1725.
- [70] Steuerman, D. W., Star, A., Narizzano, R., Choi, H., Ries, R. S., & Nicolini, C. Interactions between conjugated polymers and single-walled carbon nanotubes. *Journal of Physical Chemistry B*. (2002). , 106(12), 3124-3130.
- [71] Star, A., Liu, Y., Grant, K., Ridvan, L., Stoddart, J. F., & Steuerman, D. W. (2003). Noncovalent side-wall functionalization of single-walled carbon nanotubes. *Macromolecules*, 36(3), 553-560.
- [72] Star, A., & Stoddart, J. F. (2002). *Macromolecules*, 35(19), 7516-7520.
- [73] Nativ-Roth, E., Levi-Kalisman, Y., Regev, O., & Yerushalmi-Rozen, R. (2002). On the route to compatibilization of carbon nanotubes. *Journal of Polymer Engineering*, 22(5), 353-368.
- [74] Xia, H. S., Wang, Q., & Qiu, G. H. (2003). Polymer-encapsulated carbon nanotubes prepared through ultrasonically initiated in situ emulsion polymerization. *Chemistry of Materials*, 15(20), 3879-3886.
- [75] Li, X., Qin, Y., Picraux, S. T., & Guo-X, Z. (2011). Noncovalent assembly of carbon nanotube-inorganic hybrids. *Journal of Material Chemistry*, 21(21), 25-47.
- [76] Sahoo, N. G., Rana, S., Cho, J. W. L. S. H., & Chan, Li. (2010). Polymer nanocomposites based on functionalized carbon nanotubes. *Progress in Polymer Science*, 35(7), 837-867.
- [77] Kitano, H., Tachimoto, K., & Anraku, Y. J. (2007). Functionalization of single-walled carbon nanotube by the covalent modification with polymer chains. *Journal of Colloid and Interface Science*, 306(1), 28-33.
- [78] Park, H., Zhao, J., & Lu, J. P. (2006). Effects of sidewall functionalization on conducting properties of single wall carbon nanotubes. *Nano Letters*, 6(5), 916-9.
- [79] Han, S. J., Kim, B., & Suh, K. D. (2007). Electrical properties of a composite film of poly(acrylonitrile) nanoparticles coated with carbon nanotubes. *Macromolecular Chemistry and Physics*, 208(4), 377-383.
- [80] Zhou, C., Wang, S., Zhang, Y., Zhuang, Q., & Han, Z. (2008). situ preparation and continuous fiber spinning of poly(p-phenylene benzobisoxazole) composites with oligo-hydroxyamide-functionalized multi-walled carbon nanotubes. *Polymer*, 49(10), 2520-2530.

- [81] Baskaran, D., Mays, J. W., & Bratcher, M.S. (2005). Polymer adsorption in the grafting reactions of hydroxyl terminal polymers with multi-walled carbon nanotubes. *Polymer*, 46(14), 5050-5057.
- [82] Zhao, B., Hu, H., Yu, A., Perea, D., & Haddon, R. C. (2005). Synthesis and characterization of water soluble single-walled carbon nanotube graft copolymers. *Journal of American Chemical Society*, 127(22), 8197-8203.
- [83] Zhang, N., Xie, J., Guers, M., & Varadan, V. K. *Chemical bonding of multiwalled carbon nanotubes to polydimethylsiloxanes and modification of the photoinitiator system for micro-stereolithography processing.*
- [84] Qin, S., Qin, D., Ford, W. T., Resasco, D. E., & Herrera, J. E. (2004). Functionalization of Single-Walled Carbon Nanotubes with Polystyrene via Grafting to and Grafting from Methods. *Macromolecules*, 37(3), 752-757.
- [85] Li, H., Cheng, F., Duft, A. M., & Adronov, A. (2005). Functionalization of single-walled carbon nanotubes with well-defined polystyrene by "click" coupling. *Journal of American Chemical Society*, 127(41), 14518-24.
- [86] Huang, H. M., Liu, I. C., Chang, C. Y., Tsai, H. C., Hsu, C. H., & Tsiang, R. C. C. (2004). Preparing a polystyrene-functionalized multiple-walled carbon nanotubes via covalently linking acyl chloride functionalities with living polystyryllithium. *Journal of Polymer Science Part A: Polymer Chemistry*, 42(22), 5802-5810.
- [87] Lou, X., Detrembleur, C., Pagnouille, C., Sciannamea, V., & Jerome, R. (2004). Grafting of alkoxyamine end-capped (co)polymers onto multi-walled carbon nanotubes. *Polymer*, 45(18), 6097-6102.
- [88] Viswanathan, G., Chakrapani, N., Yang, H., Wie, B., Chung, H., & Cho, K. (2003). Single-step in situ synthesis of polymer-grafted single-wall nanotube composites. *Journal of American Chemical Society*, 9258-9259.
- [89] Liu, Y., Wu, D. C., Zhang, W. D., Jiang, X., He, C. B., & Chung, T. S. (2005). Polyethylenimine-grafted multiwalled carbon nanotubes for secure noncovalent immobilization and efficient delivery of DNA. *Angewandte Chemie-International Edition*, 44(30), 4782-4785.
- [90] Bonduel, D., Mainil, M., Alexandre, M., Monteverde, F., & Dubois, P. (2005). Supported coordination polymerization: a unique way to potent polyolefin carbon nanotube nanocomposites. *Chemical Communication*, 6, 781-783.
- [91] Park, J. J., Park, D. M., Youk, J. H., Yu, W. R., & Lee, J. (2010). Functionalization of multi-walled carbon nanotubes by free radical graft polymerization initiated from photoinduced surface groups. *Carbon*, 48(10), 2899-2905.
- [92] Yao, Z., Braid, N., Botton, G. A., & Adronov, A. (2003). Polymerization from the surface of single-walled carbon nanotubes- Preparation and characterization of nanocomposites. *Journal of American Chemical Society*, 125(51), 16015-16024.

- [93] Kong, H., Gao, C., & Yan, D. (2004). Controlled functionalization of multiwalled carbon nanotubes by in situ atom transfer radical polymerization. *Journal of American Chemical Society*, 126(2), 412-413.
- [94] Wang, M., Pramoda, K. P., & Goh, S. H. (2005). Enhancement of the mechanical properties of poly (styrene-co-acrylonitrile) with poly(methyl methacrylate)-grafted multiwalled carbon nanotubes. *Polymer*, 46(25), 11510-11516.
- [95] Baskaran, D., Mays, J. W., & Bratcher, MS. (2004). Polymer-grafted multiwalled carbon nanotubes through surface-initiated polymerization. *Angewandte Chemie-International Edition*, 43(16), 2138-2142.
- [96] Shanmugharah, A. M., Bae, J. H., Nayak, R. R., & Ryu, S. H. (2007). Preparation of poly(styrene-co-acrylonitrile)-grafted multiwalled carbon nanotubes via surface-initiated atom transfer radical polymerization. *Journal of Polymer Science Part A-Polymer Chemistry*, 45(3), 460-470.
- [97] Cui, J., Wang, W. P., You, Y. Z., Liu, C., & Wang, P. (2004). Functionalization of multiwalled carbon nanotubes by reversible addition fragmentation chain-transfer polymerization. *Polymer*, 45(26), 8717-8721.
- [98] Hong, C. Y., You, Y. Z., & Pan, C. Y. (2005). Synthesis of water-soluble multiwalled carbon nanotubes with grafted temperature-responsive shells by surface RAFT polymerization. *Chemistry of Materials*, 17(9), 2247-2254.
- [99] Wang, G. J., Huang, S. Z., Wang, Y., Liu, L., Qiu, J., & Li, Y. (2007). Synthesis of water-soluble single-walled carbon nanotubes by RAFT polymerization. *Polymer*, 48(3), 728-733.
- [100] Datsyuk, V., Guerret-Piecourt, C., Dageou, S., Billon, L., Dupin, J. C., & Flahaut, E. (2005). Double walled carbon nanotube/polymer composites via in-situ nitroxide mediated polymerisation of amphiphilic block copolymers. *Carbon*, 43(4), 873-876.
- [101] Zhao, X. D., Fan, X. H., Chen, X. F., Chai, C. P., & Zhou, Q. F. (2006). Surface modification of multiwalled carbon nanotubes via nitroxide-mediated radical polymerization. *Journal of Polymer Science Part A-Polymer Chemistry*, 44(15), 4656-4667.
- [102] Dehonor, M., Masenelli-Varlot, K., Gonzalez-Montiel, A., Gauthier, C., Cavaille, J. Y., & Terrones, H. (2005). Nanotube brushes: Polystyrene grafted covalently on CN<sub>x</sub> nanotubes by nitroxide-mediated radical polymerization. *Chemical Communications*, 42, 5349-5351.
- [103] Fan, D. Q., He, J. P., Tang, W., Xu, J. T., & Yang, Y. L. (2007). Synthesis of polymer grafted carbon nanotubes by nitroxide mediated radical polymerization in the presence of spin-labeled carbon nanotubes. *European Polymer Journal*, 43(1), 26-34.
- [104] Kaminsky, W. (2008). Trends in polyolefin chemistry. *Macromolecular Chemistry and Physics*, 209(5), 459-466.

- [105] Mokashi, V. V., Mokashi, V. V., Qian, D., & Liu, Y. J. A. (2007). study on the tensile response and fracture in carbon nanotube-based composites using molecular mechanics. *Composites science and technology*, 67(3-4), 530-540.
- [106] Tang, W. Z., Santare, M. H., & Advani, S. G. (2003). Melt processing and mechanical property characterization of multi-walled carbon nanotube/high density polyethylene (MWNT/HDPE) composite films. *Carbon*, 41(14), 2779-2785.
- [107] Yang, B. X., Pramoda, K. P., Xu, G. Q., & Goh, S. H. (2007). Mechanical reinforcement of polyethylene using polyethylene-grafted multiwalled carbon nanotubes. *Advanced Functional Materials*, 17(13), 2062-2069.
- [108] Shofner, M. L., Khabashesku, V. N., & Barrera, E. V. (2006). Processing and mechanical properties of fluorinated single-wall carbon nanotube-polyethylene composites. *Chemistry of Materials*, 18(4), 906-913.
- [109] Mahfuz, H., Adnan, A., Rangari, V. K., & Jeelani, S. (2005). Manufacturing and Characterization of Carbon Nanotube/Polyethylene Composites. *International Journal of Nanoscience*, 4(1), 55-72.
- [110] Ruan, S., Gao, P., & Yu, T. X. (2006). Ultra-strong gel-spun UHMWPE fibers reinforced using multiwalled carbon nanotubes. *Polymer*, 47(5), 1604-1611.
- [111] Tong, X., Liu, C., Cheng, H. M., Zhao, H., Yang, F., & Zhang, X. (2004). Surface Modification of Single-walled Carbon Nanotubes with Polyethylene via in situ Ziegler-Natta Polymerization. *Journal of Applied Polymer Science*, 92(6), 3697-3700.
- [112] Funk, A., & Kaminsky, W. (2007). Polypropylene carbon nanotube composites by in situ polymerization. *Composites Science and Technology*, 67(5), 906-915.
- [113] Bonduel, D., Bredeau, S., Alexandre, M., Monteverde, F., & Dubois, P. (2007). Supported metallocene catalysis as an efficient tool for the preparation of polyethylene/carbon nanotube nanocomposites: effect of the catalytic system on the coating morphology. *Journal of Materials Chemistry*, 17(22), 2359-2366.
- [114] Dong, J. Y., & Hu, Y. (2006). Design and synthesis of structurally well-defined functional polyolefins via transition metal-mediated olefin polymerization chemistry. *Coordination Chemistry Reviews*.
- [115] Russell, K.E. (2002). Free radical graft polymerization and copolymerization at higher temperatures. *Progress in Polymer Science*, 27(6), 1007-1038.
- [116] Chung, T.C. (2002). Synthesis of functional polyolefin copolymers with graft and block structures. *Progress in Polymer Science*, 27(1), 39-85.
- [117] Moad, G. (1999). The synthesis of polyolefin graft copolymers by reactive extrusion. *Progress in Polymer Science*, 24(1), 81-142.
- [118] Hetteema, R., Van Tol, J., & Janssen, L. P. B. M. (1999). In-situ reactive blending of polyethylene and polypropylene in co-rotating and counter-rotating extruders. *Polymer Engineering and Science*, 39(9), 1628-1641.

- [119] Akbar, S., Beyou, E., Cassagnau, P., Chaumont, P., & Farzi, G. (2009). Radical grafting of polyethylene onto MWCNTs: A model compound approach. *Polymer*, 50(12), 2535-2543.
- [120] Badel, T., Beyou, E., Bounor-Legare, V., Chaumont, P., Flat, J. J., & Michel, A. (2007). Melt grafting of polymethyl methacrylate onto poly(ethylene-co-1-octene) by reactive extrusion: Model compound approach. *Journal of Polymer Science Part A-Polymer Chemistry*, 45(22), 5215-5226.
- [121] Johnston, R.T. (2003). Monte Carlo simulation of the peroxide curing of ethylene elastomers. *Rubber Chemistry and Technology*, 76(1), 174-201.
- [122] Johnston, R.T. (2003). Modelling peroxide crosslinking in polyolefins. *Sealing Technology*, 76(2), 6-9.
- [123] Osswald, S., Havel, M., & Gogotsi, Y. (2007). Monitoring oxidation of multiwalled carbon nanotubes by Raman spectroscopy. *Journal of Raman Spectroscopy*, 38(6), 728-736.
- [124] Pastine, S. J., Okawa, D., Kessler, B., Rolandi, M., Llorente, M., Zettl, A., & Frechet, J. M. J. (2008). A facile and patternable method for the surface modification of carbon nanotube forests using perfluoroarylazides. *Journal of the American Chemical Society*, 130(13), 4238-4239.
- [125] Park, M.J., Lee, J. K., Lee, B.S., Lee-W, Y., Choi, I. S., & Lee-G, S. (2006). Covalent Modification of Multiwalled Carbon Nanotubes with Imidazolium-Based Ionic Liquids. *Effect of Anions on Solubility. Chemistry of Materials*, 18, 1546-51.
- [126] Akbar, S., Beyou, E., Chaumont, P., & Mélis, F. (2010). Effect of a Nitroxyle-Based Radical Scavenger on Nanotube Functionalisation with Pentadecane. *A Model Compound Study for Polyethylene Grafting onto MWCNTs, Macromolecular Chemistry and Physics*, 211(22), 2396-2406.
- [127] Mylvaganam, K., & Zhang, L. C. (2004). Nanotube functionalization and polymer grafting: An ab initio study. *Journal of Physical Chemistry B*, 108(39), 5217-5220.
- [128] Akbar, S., Beyou, E., Chaumont, P., Mazzolini, J., Espinosa, E., D'Agosto, F., & Boisson, C. (2011). Synthesis of Polyethylene-Grafted Multiwalled Carbon Nanotubes via a Peroxide-Initiating Radical Coupling Reaction and by Using Well-Defined TEMPO and Thiol End-Functionalized Polyethylenes. *Journal of Polymer Science Part A: Polymer Chemistry*, 49(4), 957-965.
- [129] Farzi, G., Akbar, S., Beyou, E., Cassagnau, P., & Mélis, F. (2009). Effect of radical grafting of tetramethylpentadecane and polypropylene on carbon nanotubes' dispersibility in various solvents and polypropylene matrix. *Polymer*, 50(25), 5901-5908.
- [130] Lopez, R. G., Boisson, C., D'agosto, F., Spitz, R., Boisson, F., Bertin, D., & Tordo, P. (2004). Synthesis and characterization of macroalkoxyamines based on polyethylene. *Macromolecules*, 37(10), 3540-3542.



- [131] Lopez, R. G., Boisson, C., D'agosto, F., Spitz, R., Boisson, F., Gigmes, D., & Bertin, D. (2007). Catalyzed chain growth of polyethylene on magnesium for the synthesis of macroalkoxyamines Application to the production of block copolymers using controlled radical polymerization . *Journal of Polymer Science, Part A: Polymer Chemistry*, 45(13), 2705-2718.
- [132] Mazzolini, J., Espinosa, E., D'Agosto, F., & Boisson, C. (2010). Catalyzed chain growth (CCG) on a main group metal: an efficient tool to functionalize polyethylene. *Polymer Chemistry* , 1(6), 793-800.
- [133] D'Agosto, F., & Boisson, C. (2010). A RAFT Analogue Olefin Polymerization Technique Using Coordination Chemistry. *Australian Journal of Chemistry*, 63(8), 1155-1158.
- [134] Mazzolini, J., Mokthari, I., Briquet, R., Boyron, O., Delolme, F., Monteil, V., Gigmes, D., Bertin, D., D'Agosto, F., & Boisson, C. (2010). Thiol-End-Functionalized Polyethylenes. *Macromolecules*, 43(18), 7495-7503.
- [135] Hawker, C. J., Bosman, A. W., & Harth, E. (2001). New polymer synthesis by nitroxide mediated living radical polymerizations. *Chemical Review*, 101(12), 3661-3688.
- [136] Lou, X., Detrembleur, C., Sciannamea, V., Pagnouille, C., & Jerome, R. (2004). Grafting of alkoxyamine end-capped (co)polymers onto multi-walled carbon nanotubes. *Polymer*, 45(18), 6097-6102.
- [137] Liu, Y., Yao, Z., & Adronov, A. (2005). Functionalization of single-walled carbon nanotubes with well-defined polymers by radical coupling. *Macromolecules*, 38(4), 1172-1179.
- [138] Wang, H. C., Li, Y., & Yang, M. (2007). Sensors for organic vapor detection based on composites of carbon nonotubes functionalized with polymers. *Sensors and Actuators B-Chemical*, 124(2), 360-367.
- [139] Wang, Y., Wu, J., & Wei, F. (2003). A treatment method to give separated multi-walled carbon nanotubes with high purity, high crystallization and a large aspect ratio. *Carbon*, 41(15), 2939-2948.
- [140] Lee, S. H., Cho, E., Jeon, S. H., & Youn, J. R. (2007). Rheological and electrical properties of polypropylene composites containing functionalized multi-walled carbon nanotubes and compatibilizers. *Carbon*, 45(14), 2810-2822.
- [141] Wang, Y., Wen, X., Wan, D., Zhang, Z., & Tang, T. (2012). Promoting the responsive ability of carbon nanotubes to an external stress field in a polypropylene matrix: A synergistic effect of the physical interaction and chemical linking. *Journal Material Chemistry*, 22, 3930-3938.
- [142] Zheng, J., Zhu, Z., Qi, j., Zhou, Z., Li, P., & Peng, M. (2011). Preparation of isotactic polypropylene-grafted multiwalled carbon nanotubes (iPP-g-MWNTs) by macroradical addition in solution and the properties of iPP-g-MWNTs/iPP composites. *Journal Material Science*, 46, 648-658.

- [143] Jancar, J., Douglas, J. F., Starr, F. W., Kumar, S. K., Cassagnau, P., Lesser, A. J., Sternstein, S. S., & Buehler, M. J. (2010). Current issues in research on structure-property relationships in polymer nanocomposites. *Polymer*, 51(15), 3321-3343.
- [144] Cassagnau, P. (2008). Melt rheology of organoclay and fumed silica nanocomposites. *Polymer*.
- [145] Moreira, L., Fulchiron, R., Seytre, G., Dubois, P., & Cassagnau, P. (2010). Aggregation of Carbon Nanotubes in Semidilute Suspension. *Macromolecules*, 43(3), 1467-1472.
- [146] Hobbie, E.K. (2010). Shear rheology of carbon nanotube suspensions. *Rheologica Acta*.
- [147] Marceau, S., Dubois, P., Fulchiron, R., & Cassagnau, P. (2009). Viscoelasticity of Brownian Carbon Nanotubes in PDMS Semidilute Regime. *Macromolecules*, 42(5), 1433-1438.
- [148] Mitchell, C. A., Bahr, J. L., Arepalli, S., Tour, J. M., & Krishnamoorti, R. (2002). Dispersion of functionalized carbon nanotubes in polystyrene. *Macromolecules*, 35(23), 8825-8830.
- [149] Pujari, S., Ramanathan, T., Kasimatis, K., Masuda, J., Andrews, R., Torkelson, J. M., Brinson, L. C., & Burghardt, W. R. (2009). Preparation and Characterization of Multi-walled Carbon Nanotube Dispersions in Polypropylene: Melts Mixing versus Solid-State Shear Pulverization. *Journal of Polymer Science, Part B: Polymer Physics*, 47(14), 1426-1436.
- [150] Hong, J. S., Hong, I. G., Lim, H. T., Ahn, K. H., & Lee, S. J. (2012). In situ lubrication dispersion of Multi-walled carbon nanotubes in Polypropylene melts. *Macromolecular Material Engineering*, 297(3), 279-287.
- [151] Wu, D., Sun, Y., Wu, L., & Zhang, M. (2008). Linear Viscoelasticity Properties and Crystallisation Behavior of Multi-Walled Carbon Nanotube/Polypropylene Composites. *Journal of Applied Polymer Science*, 108(3), 1506-1513.
- [152] Wu, D., Sun, Y., & Zhang, M. (2009). Kinetics Study on Melt Compounding of Carbon Nanotube/Polypropylene Nanocomposites. *Journal of Polymer Science, Part B: Polymer Physics*, 47(6), 608-618.
- [153] Jin, S. H., Kang, C. H., Yoon, K. H., Bang, D. S., & Park, Y. B. (2009). Effect of Compatibilizer on Morphology, Thermal and Rheological Properties of Polypropylene/Functionalized Multi-walled Carbon Nanotubes composite. *Journal of Applied Polymer Science*, 111(2), 1028-1033.
- [154] Menzer, K., Hrausee, B., Boldt, R., Kretschmar, B., Weidisch, R., & Potschke, P. (2011). Percolation Behaviour of multiwalled carbon nanotubes of altered length and primary agglomerate morphology in melt mixed isotactic polypropylene-based composites. *Composite Science and Technology*, 71(16), 1936-1943.
- [155] Hemmati, M., Rahimi, G. H., Kaganj, A. B., Sepehri, S., & Rashidi, A. M. (2008). Rheological and Mechanical Characterization of Multi-walled Carbon Nanotubes/Poly-

propylene Nanocomposites. *Journal of Macromolecular Science, Part B: Physics*, 47(6), 1176-1187.

- [156] Prashantha, K., Soulestin, J., Lacrampe, M. F., Krawczak, P., Dupin, G., & Claes, M. (2009). Masterbatch-based multi-walled carbon nanotube filled polypropylene nanocomposites: Assessment of rheological and mechanical properties. *Composite Science and Technology*, 69(11-12), 1756-1763.
- [157] Palza, H., Reznik, B., Kappes, M., Hennrich, F., Naue, I. F. C., & Wilhelm, M. (2010). Characterization of melt flow instabilities in polyethylene/carbon nanotube. *Polymer*, 51(16), 3753-3761.

