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Polymer nanocomposites doped with carbon nanotubes

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ABSTRACT

In the large field of nanotechnology, polymer matrix based carbon nanotubes/nanocomposites have become a prominent area of current research and development. We review the present article of polymer nanocomposites research in which the fillers are carbon nanotubes with provide a brief synopsis about carbon nanotubes materials and their suspensions and critique various nanotube/polymer nanocomposites fabrication and modification methods including solution mixing, bulk method, melt mixing, and in situ polymerization with a particular emphasis on evaluating the dispersion state of the nanotubes with discuss mechanical, electrical, morphological and thermal properties separately and how these physical properties depend on the size, aspect ratio, loading, dispersion state. In addition, this article reviews the current understanding of carbon nanotubes/polymer nanocomposites with two particular topics: i) the principles and techniques for carbon nanotubes dispersion and functionalization and ii) the effects of carbon nanotubes dispersion and functionalization on the properties of carbon nanotubes/polymer nanocomposites. Enhanced dispersion of CNTs in the polymer matrix will promote and extend the applications and developments of polymer nanocomposites containing carbon nanotubes. Other properties and potential applications of carbon nanotubes/nanocomposites are also highlighted.

INTRODUCTION

Carbon nanotubes (CNTs), the macromolecular analog of fullerenes, were found by Iijima[1] in 1991. These are arrangements of carbon hexagons formed into tiny tubes. CNTs can be viewed as hollow coaxial cylinders formed of graphite layers with both ends of the cylinder normally capped by fullerene-like structures as shown in Figure 1[2].

There are two kinds of CNTs, single walled carbon nanotubes (SWNTs) formed by a single graphene sheet and multi walled nanotubes (MWNTs) formed with additional graphene sheets wrapped around the SWNT core[3]. The development of CNT research began soon after the macroscopic production of C_{60} and the identification of CNTs in soot deposits formed during plasma arc experiments. CNTs possess unique mechanical and electronic properties depending on their geometry and dimensions. CNTs have very high moduli[4] and are believed to be the lightest and strongest materials so far discovered. Single wall carbon nanotubes with their well-defined atomic structure, their high length to diameter ratio, and their chemical stability constitute one-dimension molecules[5]. SWCNTs exhibit specific electronic properties and can be either metallic or semiconducting depending on their geometry.

Since the discovery of CNTs; they have contributed to the development of studies in the field of physics, chemistry and material sciences. Many works were completed on the structure, properties and potential applications[6]. Many properties of nanotubes are directly influenced by the way of the graphene sheets are wrapped around. Due to their cylindrical geometry and their nanometric scale, CNTs are candidates for potential applications like hydrogen storage[7].

CNTs can be produced by an array of techniques, such as arc discharge, laser ablation and chemical vapor deposition. Production of carbon nanotubes in a controlled way and in large amount encounters problems, which remains to be solved. It is needed to identify all properties of these tubes. However, to fully characterize carbon nanotubes, there are not so many techniques available.

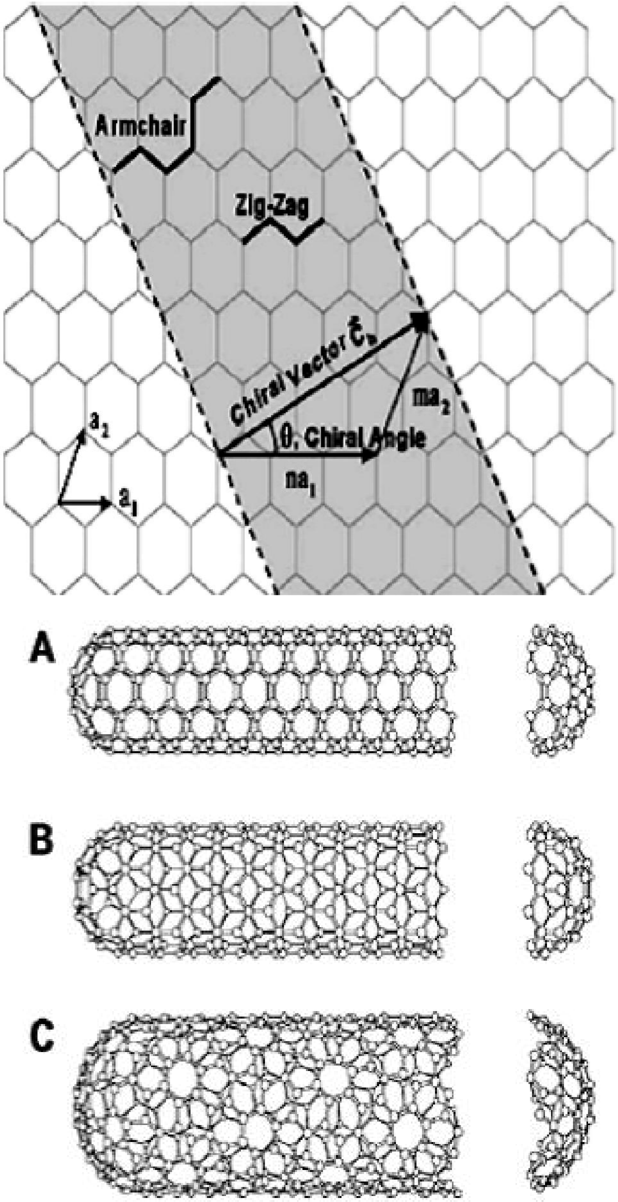

Figure 1 : Schematic diagram showing how a hexagonal sheet of graphene is rolled to form a CNT with different chiralities. (A: armchair; B: zigzag and C: chiral)

This review concerns the methods of fabrications and modifications with the main structural, morphological and mechanical properties of carbon nanotubes/polymer nanocomposites as novel promising materials. The feasible and potential fields of applications of carbon nanotubes are outlined.

Functionalization of carbon nanotubes

Functionalization of CNTs is often discussed in articles reporting dispersion and interaction of CNTs with different materials, but it is difficult to compare data between articles because there are several different procedures and many adaptations. A literature review was made to clarify the differences and advantages on three acids that were used, as well as its procedures[8].

The addition of functional groups on CNTs is commonly made by immersing it in sulfuric acid (H_2SO_4) and nitric acid (HNO_3) in the range 3:1[9]. According to these researchers, this method inserts carboxyl groups (–COOH) on the surface of nanotubes.

Some researchers[10,11] increased the temperature and/or carried out stirring to accelerate the process of oxidation. The addition of chloridric acid (HCl) later is another method reported by some scientists to adsorb functional groups on the CNTs.

Functionalization using only nitric acid has also been published. Wang et al.[12] functionalized his material by immersing it in nitric acid in ultrasound at 90 °C for 4 h. After wards, he stirred the material until it reached the ambient temperature. Alternative acids were also studied and used to oxidize CNTs. Xie et al.[13] used a mixture of H_2SO_4/HNO_3 (3:1) and H_2O_2 to obtain carboxyl and hydroxyl groups. The use of isolated H_2O_2 is also an option to obtain carboxyl groups.

Some literature were used other acids to oxidize CNTs. Choi et al.[14] used 5-phenoxyisophthalic acid, phosphorous pentoxide (P_2O_5), and polyphosphoric acid (PPA) to graft functional groups onto the surface of CNTs. Shanmugharaj et al.[15] added sulfuric acid and potassium dichromate and placed it at 80 °C for 30 min for the adsorption of –COOH, –OH, and O. In addition to the above mentioned methods, there are still other methodologies that function as alternative routes to functionalize CNT[16].

Despite the chemical functionalization mentioned above, there are other techniques to oxidize the surface of CNTs. Xia et al.[17] functionalized the CNTs using nitric acid and oxygen plasma. He concluded that nitric acid added carboxylic and phenolic groups, whereas the oxidation by plasma inserted a vast amount of carbonyl groups.

Properties of carbon nanotubes

Carbon nanotubes have some distinct electrical properties. One of the important properties of carbon nanotube is that it can exhibit the characteristics of a metal or a semiconductor. Specially, the energy gap is determined by the rolling direction of nanotube.

Nanotubes are the strongest fibers that are currently known. A single-wall nanotube can be up to 100 times stronger than that of steel with the same weight. The Young's Modulus of SWNT is up to 1TPa, which is 5 times greater than steel (230 GPa) while the density is only 1.3 g/cm^3; that means that materials made of nanotubes are lighter. There may also be other applications due to these properties, such as car bumpers, and strong wires. Nanotubes also have a very high aspect ratio. The lengths of nanotubes are usually around 1 μm, while the diameter for SWNT is only 1 nm (50 nm for MWNT). This property makes nanotubes useful for tips and nanowires. In addition, the thermal conductivity (2000 W/m.K) is five times greater than that of copper (400W/m.K)[18].

Production of carbon nanotubes

The physical mechanisms and reactions that cause the formation of carbon nanotubes are still unknown. However, three methods currently exist to fabricate these nanotubes. The three methods are all gas-phase processes that start with a source of carbon that is evaporated from a surface. The three techniques used produce carbon nanotubes are the carbon arc-discharge method, the laser vaporization technique and chemical vapor deposition method[19].

Carbon arc discharge

The arc-discharge method produces good quality multi-wall and single-wall nanotubes. This process produces nanotubes at a greater rate than the pulsed laser vaporization technique. This technique utilizes two graphite electrodes to generate an arc by a high dc current. After arc discharging for a period of time, a carbon rod builds up at the cathode. Carbon nanotube bundles and amorphous carbon both form at the cross section of the rod. Figure 2 shows the setup of the arc-discharge method. This method does not produce clean results due to the existence of these amorphous carbons. Helium gas is present to increase the speed of carbon deposition. Some parameters that are critical in this process are the pressure of the helium, the temperature, and the dc current. Efficient cooling is necessary to form homogenous deposition of carbon nanotubes[20].

The group at University of Montpellier, France perfected the arc-discharge method by using yttrium and nickel metal catalysts. The group produced carbon nanotubes from vapors of carbon containing a small amount of nickel and yttrium catalysts. "An electric arc vaporizes an anode containing the catalysts". An electrical current of 100 amps and 35 volts provide the energy to generate the discharge. The flow system is controlled via gas pressure and is pumped by a mechanical vacuum pump[21].

Laser ablation or vaporization

The pulsed laser vaporization (PLV) of graphite in the presence of an inert gas and catalyst forms single-walled carbon nanotubes. Without the presence of these catalysts, the vaporized graphite would form buckyballs instead. Buckyballs are formed in nature when both ends of the graphite sheet closes. However, in the presence of a catalyst, the graphite layers stays open on one end[22].

PLV of carbon containing metal catalysts produces the purest SWNT. Some factors that determine the amount of carbon nanotubes produced are the amount and type of catalysts, laser power and wavelength, temperature, pressure, type of inert gas present, and the fluid dynamics near the carbon target. The PLV method reduces the amount of amorphous carbon contaminates. The PLV of carbon is an expensive method that avoids the high electric fields involved in the arc-discharge method.

Figure 3 shows the setup. The Argon gas carries the vapors from the high temperature chamber into a water-cooled copper collector positioned downstream the nanotubes self-assemble from the carbon vapors and condense on the walls of the flow tube. The nanotubes produced have a very narrow distribution of diameters. The yield is about 0.3:0.4 grams per hour[23].

Chemical vapor deposition

The chemical vapor deposition (CVD) method deposits hydrocarbon molecules on top of heated catalyst material. The catalyst is usually predeposited on a substrate. Metal catalysts dissociate the hydrocarbon molecules. Figure 4 shows the apparatus of the CVD process. The CVD method produces both single-wall and multi-wall nanotubes. The CVD process uses hydrocarbons as the carbon source. Hydrocarbons flow through the quartz tube where it is heated at a high temperature. The dissociation of the hydrocarbons breaks the hydrogen carbon bond, producing pure carbon molecules. At high temperatures, the carbon form carbon nanotubes. Growth of SWNTs also occurs at a higher temperature than MWNTs. Some advantages of the CVD are low power input, lower temperature range, relatively high purity and possibility to scale up the process[24].

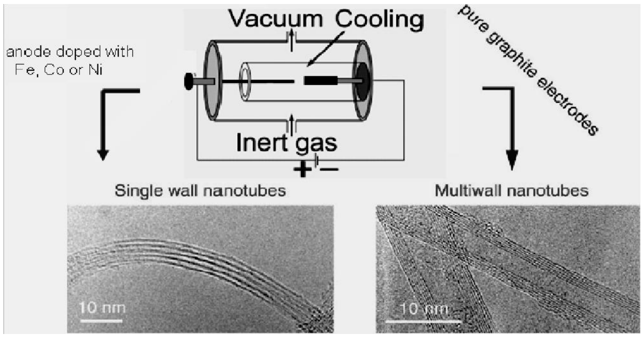

Figure 2 : Carbon arc discharge method

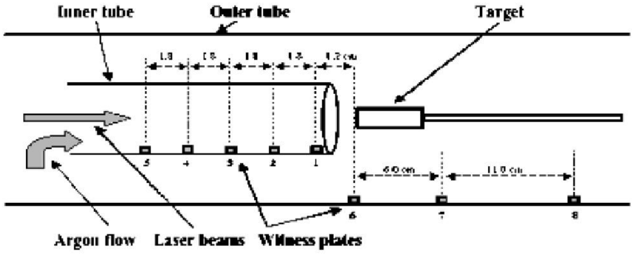

Figure 3 : Laser vaporization apparatus

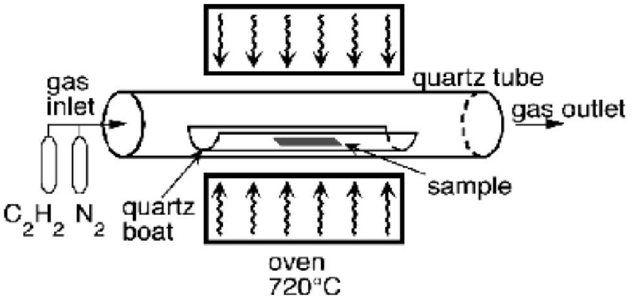

Figure 4 : Apparatus of the CVD process

Nanocomposites

Polymer nanocomposites

Polymer nanocomposites consist of a polymeric material (e.g., thermoplastics, thermosets, or elastomers) and a reinforcing nanoscale material. In the simplest case, appropriately adding nanoparticulates to a polymer matrix can enhance its performance, often in very dramatic degree, by simply capitalizing on the nature and properties of the nanoscale filler, these materials are better described by the term nano-filled polymer composites. This strategy is particularly effective in yielding high performance composites, when good dispersion of the filler is achieved and the properties of the nanoscale filler are substantially different or better than those of the matrix, for example, reinforcing a polymer matrix by much stiffer nanoparticles of ceramics, clays, or carbon nanotubes. Alternatively, the enhanced properties of high performance nanocomposites may be mainly due to the high aspect ratio and/or the high surface area of the filler since nanoparticulates have extremely high surface area to volume ratios when good dispersion is achieved[25].

The structural, mechanical, electrical, thermal, optical, electrochemical, catalytic properties of the nanocomposite will differ markedly from that of the component materials. Size limits for these effects have been proposed <5 nm for catalytic activity, <20 nm for making a hard magnetic material soft, <50 nm for refractive index changes, and <100 nm for achieving superparamagnetism, mechanical strengthening or restricting matrix dislocation movement[26].

Nanocomposites are found in nature, for example in the structure of the abalone shell and bone. The use of nanoparticle-rich materials long predates the understanding of the physical and chemical nature of these materials.

Nanoscale dispersion of filler or controlled nanostructures in the composite can introduce new physical properties and novel behaviours that are absent in the unfilled matrices, effectively changing the nature of the original matrix[27].

There are many factors that affect the polymer nanocomposite properties:

- Synthesis methods such as melt compounding, solvent blending, in-situ polymerization, and emulsion polymerization,

- Polymer nanocomposite morphology,
- Types of nanoparticles and their surface treatments,
- Polymer matrix such as crystallinity, molecular weight, polymer chemistry, and whether thermoplastic or thermosetting

Fabrication and modification of carbon nanotubes with polymers

Fabrication methods have focused on improving nanotube dispersion because better nanotube dispersion in the polymer matrices has been found to improve properties. Similar to the case of nanotube/solvent suspensions, pristine 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. The quality of nanotubes dispersion in polymer matrices should be evaluated over a range of length scales and can be accomplished using a selection of these imaging methods: optical microscopy, Raman imaging, scanning electron microscopy, and transmission electron microscopy[28].

The modification of CNTs by polymers may be divided into two categories, involving either non-covalent or covalent bonding between CNT and polymer. Non-covalent CNT modification concerns the physical adsorption and/or wrapping of polymers to the surface of the CNTs. The graphitic sidewalls of CNTs provide the possibility for π-stacking interactions with conjugated polymers, as well as organic polymers containing heteroatoms with free electron pair[29].

The advantage of non-covalent functionalization is that it does not destroy the conjugated system of the CNT sidewalls, and therefore it does not affect the final structural properties of the material.

The second modification is the covalent chemical bonding (grafting) of polymer chains to CNTs, where strong chemical bonds between nanotubes and polymers are established.

Two main strategies for the covalent grafting of polymers to nanotubes have been reported: “grafting to” and “grafting from”.

“Grafting to” method

The “grafting to” method means that the readymade polymers with reactive end groups reacted with the functional groups on the nanotube surfaces. It is the reaction between the surface groups of nanotubes and readymade polymers with physical adsorption or covalent attachment mechanisms.

An advantage of the “grafting to” method is that pre-formed commercial polymers of controlled molecular weight and polydispersity can be used. The main limitation of the technique is that initial binding of polymer chains sterically hinders diffusion of additional macromolecules to the CNT surface, leading to a low grafting density. Also, only polymers containing reactive functional groups can be used.

A disadvantage of this method is that the grafted polymer content is limited because of the relatively low reactivity and high steric hindrance of macromolecules.

The grafting of both oxidized SWCNTs and MWCNTs with a polystyrene (PS) was reported by Hill and co-workers[30], where a solution of poly(styrene-co-p-(4-(4-vinylphenyl)-3-oxobutanol)) (PSV) in tetrahydrofuran (THF) was mixed with acyl chloride-activated nanotubes.

According to thermogravimetric analysis (TGA), the CNT contents in the PSV-functionalized SWCNT and MWCNT samples are approximately 12% and 18%, respectively. Similarly, Guojian and co-workers[31] grafted a styrene–maleic anhydride onto MWCNTs and the modified material was incorporated into polyvinyl chloride (PVC) matrix. Mechanical testing showed significant enhancements of the elongation at break and the impact strength. Alternatively, the reaction of hydroxy-terminated PS with thionyl chloride treated MWCNTs was performed by Baskaran et al.[32], resulting in a hybrid containing 86 wt% of CNTs.

Polyvinyl alcohol was grafted by esterification reactions of oxidized SWCNTs and MWCNTs. Riggs et al.[33] reported the grafting of polyvinyl acetate-co-vinyl alcohol via ester linkages to acyl-activated SWCNTs for measurement of the optical properties of the prepared modified nanotubes. Other PVA-based copolymer used for functionalization of nanotubes was polyethylene-co-vinyl alcohol under carbodiimide-activated esterification reaction conditions[34].

Nuclear magnetic resonance (NMR) spectra showed that nanotube content in the SWCNT-EVOH is about 14 wt%, whereas thermogravimetric analysis showed 10 wt%. Silicone-functionalized CNT derivatives were prepared by opening terminal epoxy groups of functionalized polydimethylsiloxanes (PDMS) by the carboxylic groups of acid-treated MWCNTs. The prepared composite contained about 85 wt% of CNTs. The derivative was found to be homogeneous and viscous, almost tar-like, liquid at room temperature. It was dispersible at high concentrations (10 mg/ml) in toluene. Its fluid-like nature is suitable for applications in ink-jet printing technology[35].

The esterification reaction was used for grafting polyethylene glycol (PEG) chains to acyl chloride-activated SWCNTs. Such modified nanotubes were found to modulate neurite outgrowth, indicating a potential application in nerve regeneration. In the absence of solvent medium, a grafting reaction of hydroxy-terminated PEG with thionyl chloride treated MWCNTs was performed at temperatures above the melting point of the polymer[36].

However, grafting efficiency was low, as the TGA analysis showed the presence of 93 wt% of nanotubes. Both oxidized SWCNT and MWCNT material were targeted for carbodiimide-activated esterifications with a derivatized polyimide endcapped with alkoxysilane groups or having pendant hydroxyl groups[37]. Based on the NMR signal integrations in reference to standard, the CNT content in the sample was estimated to be about 35 wt%. A similar approach was used in the case of a poly(N-vinyl carbazole) copolymer containing pendant hydroxyl groups (PVKV) which was grafted to oxidized SWCNTs under typical reaction conditions for the esterification via acyl-activation reaction.

The CNT content in the sample was estimated to be ~20 wt%. Wang and Tseng prepared segmented polyurethanes carrying carboxyl groups in the chain extender, with this polymer undergoing esterification reaction with acyl chloride-activated MWCNTs. According to TGA data, the CNT content was up to 67 wt%. It was found that longer acid treatment time in the CNT material resulted in a higher grafted amount of polymer chains[38].

Grafting reactions of hydroxyl terminated polymethyl methacrylate and poly[(ethyl methacrylate- co-2-hydroxyethyl methacrylate] with acyl chloride-activated MWCNTs were carried out in different solvents at various temperatures[39]. It was found that at higher temperatures and longer reaction times favored the grafting reaction. Increasing the concentration ratio of hydroxyl groups to acid-chloride groups did not improve the grafting efficiency. Other examples of esterification reactions include the grafting of poly(bisphenol-A-co-epichlorohydrin) chains to oxidized MWCNTs by a reactive blending process and the grafting of hyperbranched polyester based on 2, 2-bis (methylol) propionic acid to the surfaces of MWCNTs[40].

“Grafting from” method

The ‘‘grafting from’’ method means the reactive groups were covalently attached to the nanotube surfaces and then the polymers graft from the reactive groups. It is the reaction between the reactive groups in the surfaces of nanotubes and monomers.

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. In addition, nanotube–polymer composites with quite high grafting density can be prepared. However, this method requires strict control of the amounts of initiator and substrate as well as accurate control of conditions required for the polymerization reaction. To demonstrate this approach, the well known living polymerization approaches have been employed in recent years because of their tolerance to a wide variety of functional groups in the monomer units[41].

Carbon nanotubes/polymer nanoomposites processing

To maximize the advantage of CNTs as effective reinforcement for high strength polymer composites, the CNTs should not form aggregates and must be well dispersed to enhance the interfacial interaction with the matrix. Several processing methods available for fabricating CNT/polymer composites based on either thermoplastic or thermosetting matrices. They mainly include solution mixing, in situ polymerization; melt blending and chemical modification processes.

Although inherently different processing routes have been attempted, they all address important issues that affect composite properties, such as exfoliation of CNT bundles and ropes, homogeneous dispersion of the individual tubes into the matrix, alignment and interfacial bonding. The effective utilization of CNT material in composite applications depends strongly on their ability to be dispersed individually and homogeneously within a matrix. Some processing methods for CNT-based composites are described below[42].

Solution method

This is the most common method for fabricating polymer nanocomposites because it is both amenable to sample sizes and effective. Solution blending involves three major steps: i) disperse nanotubes in a suitable solvent, ii) mix with the polymer (at room temperature or elevated temperature), and iii) recover the composite by precipitating or casting a film.

The general protocol for all solution processing methods includes the dispersion of CNT powder in a liquid medium by vigorous stirring and/or sonication, mixing the CNT dispersion with a polymer solution and controlled evaporation of the solvent with or without vacuum conditions. In general, the most efficient dispersion of tubes during the first step is achieved by bath or tip sonication.

Regarding thermosetting epoxy matrices, an early example of solution-based composite formation was described by Ajayan et al.[43]. In this work, MWCNTs were dispersed in ethanol by sonication and mechanically mixed with a mixture of epoxy monomer and curing agent. After evaporation of the volatile solvent, the CNT–epoxy mixture was poured into capsular molds and then cured. Electron microscopy images showed that slicing the composite material caused partial alignment of the CNTs on the cut surface.

Concerning the fabrication of CNT-based composites with thermoplastic matrices, Jin et al.[44] have reported a similar method consisting of solution mixing, casting and drying. The chosen polymer, polyhydroxy-aminoether was dissolved in the arc discharge-grown CNTs in chloroform under sonication. The suspension was then poured into a Teflon mold and dried under ambient conditions for a certain time. Mechanical stretching of thin strips of the composite at 100 °C was found to cause orientation of tubes in the axis of tension. Slight processing variations were used in most subsequent studies. Shaffer and Windle[45] dispersed chemically oxidized catalytic MWCNTs in water. The material was carefully blended with solutions of PVA in water to give composite dispersions which could be drop-cast to form films with up to 60 wt% nanotubes.

In an alternative processing method, Geng and coworkers[46] utilized a roll-casting technique to prepare composite films of poly ethylenoxide embedded with fluorinated CNTs. The roll-cast system comprises two opposing parallel rollers with a gap distance that can be adjusted. A suspension of a CNT/polymer mixture was slowly dropped onto one roller when rotating, while a solid film was formed after evaporation of the solvent.

In order to succeed rapid evaporation of solvent during the suspension casting process, Safadi et al.[47] have used the spin coating technique. The authors elucidated the basic relationships between simple casting and spin casting conditions, concluding that the processing method employed had no effect on the mechanical/electrical properties of the composite.

Since the casting/evaporation process results in the reagglomeration of CNTs within the composite film, Du and co-workers[48] proposed an alternative approach for fabricating composites with individually dispersed CNTs, the so called coagulation. After the solution mixing step, a CNT/PMMA suspension was dripped into a large excess of bad solvent (water) in order to induce instant precipitation of the polymer chains. The precipitating chains entrapped the carbon nanostructures and prevented them from bundling again. After filtration and drying in vacuum, nanocomposites were obtained with homogeneously distributed CNTs.

In order to periodically functionalize CNT sidewalls using controlled polymer crystallization process, the hotcoagulation method was developed for the fabrication of CNT/polyethylene (PE) composites. First, the polymer was dissolved in an organic solvent at temperatures approaching its melting point. Subsequently, the CNT material was suspended in the same medium using ultrasonication in a hot bath and the hot polymer solution was added to the nanotube suspension. After further sonication, the mixture was brought to the crystallization temperature Tc at which point the polymer crystallized on the CNT surface, forming shish-kebab structures[49].

Bulk mixing method

Milling is a mechanical process that leads to local generation of high pressure as a result of collisions throughout the grinding media. Concerning applications in CNT nanotechnology, this method has been used to shorten the lengths of carbon nanostructures. A solid state mechanochemical process, namely pan milling, was used to prepare a CNT/polypropylene composite powder. This powder was subsequently melt-mixed with a twin-roll masticator to obtain a homogeneous composite. The length of the CNTs was reduced from a few micrometers to ~500 nm[50].

Similarly, high energy ball milling was utilized to incorporate CNTs into polymer matrices. In this way, a satisfactory level of dispersion of CNTs into the polymer matrix was obtained, resulting in an improvement of the physical properties of the samples. In addition, a mechanical–chemical high-speed vibration milling technique was applied for solubilizing CNTs in various media due to the formation of non-covalent-type complexes with species, such as cyclodextrins[51].

Melt mixing method

Melt blending uses high temperature and high shear forces to disperse nanotubes in a polymer matrix and is most compatible with current industrial practices. However, relative to solution blending methods, melt blending is generally less effective at dispersing nanotubes in polymers and is limited to lower concentrations due to the high viscosities of the composites at higher nanotube loadings. Due to the fact that thermoplastic semicrystalline polymers soften when heated above their melting point, melt processing has been a very valuable technique for the fabrication of CNT-based composites. In addition, the method is suitable for polymers that cannot be processed with solution techniques due to their insolubility in common solvents.

In general, melt processing involves the blending of polymer melt with CNT material by application of intense shear forces. Depending on the final morphology/shape of the composites, the bulk samples can then be processed by several techniques, such as extrusion. An early study on the melt mixing of SWCNTs and PMMA matrix was carried out by Haggenmueller and co-workers[52]. CNTs and PMMA were first blended in dimethylformamide (DMF) and the resulting suspension was casted onto Teflon dishes and dried. The resultant films were broken up in small pieces and hot pressed to form a new film. This was then broken up and hot pressed, a process that was repeated as many as 25 times.

Jin and co-workers[53] have melt-blended MWCNTs and PMMA in a laboratory mixing molder at a speed of 120rpm (blending temperature ~200 °C). The mixed samples were then compressed under pressure at 210 C using a hydraulic press to yield composite films. Electron microscopy images showed that the nanotubes are well dispersed in the polymer matrix. Concerning the upscaled fabrication of composites, Potschke et al.[54] have fabricated 1 kg batches of MWCNTs/polycarbonate composites by melt extrusion and compression molding.

Rheology measurements of the composites at 260 °C showed that viscosity increases significantly with increasing CNT concentration, especially for CNT weight fractions above 2%.

In situ polymerization method

This fabrication strategy starts by dispersing nanotubes in monomer followed by polymerizing the monomers. As with solution blending, functionalized nanotubes can improve the initial dispersion of the nanotubes in the liquid (monomer, solvent) and consequently in the composites. Furthermore, in situ polymerization methods enable covalent bonding between functionalized nanotubes and the polymer matrix using various condensation reactions.

The main advantage of this method is that it produces polymer grafted tubes, mixed with free polymer chains. Moreover, due to the small size of monomeric molecules, the homogeneity of the resulting composite adducts is much higher than mixing CNTs and polymer chains in solution. In this sense, the method allows the preparation of composites with high CNT weight fraction.

Gojny et al.[55] studied the dispersion of CNTs into viscous epoxy monomers via a common shear mixing technique that is, calendering. In a first step, the nanoparticles were manually mixed into the resin while in the following step they were homogeneously dispersed using of a three-roll calender. A first primary dispersion of the agglomerates could be achieved by the knead-vortex between the rolls, while the final exfoliation and dispersion of the CNTs occurs in the area between the rolls. The suspension was collected and then mixed with the curing agent to obtain a homogeneous composite.

Characterization methods

Morphological and structural characterizations

Fullerenes, which are carbon compounds and similar to CNTs, are closed spheres composed of pentagons and hexagons. Their curvatures are given by the organization of these pentagons and hexagons. In carbon nanotubes, the Stone–Wales transformation is obtained by a reversible diatomic interchange. The resulting structure is formed of two pentagons and two heptagons in pair. This transformation induces a new defect in CNTs: the heptagon which allows for concave areas within the nanotube. Thus, there is a not only straight tube with hemispherical caps and many equilibrium shapes can be obtained. Electronic and mechanical properties of CNTs are unique[56].

However, to achieve these properties, the CNTs must be chemically processed in order to purify and bring appropriate functionalizations. Typical treatments involve the use of oxidative methods with nitric acids. The caps at both ends of the CNTs are removed and defects such as carboxylic acid groups on surface are revealed by these purification technique. The properties of the nanotubes are influenced by these defects sites on the walls and at the ends. A determination of the concentration of these defects would be helpful for nanotubes properties characterizations. The concentration of the carboxylic acid groups formed by purification treatments could be determined by various methods: i) the determination of gases concentrations at high temperatures could be used as described by Mawhinney et al.[57] with CO and CO_2; ii) calibrated energy-dispersive X-ray spectroscopy allows investigation of the atomic oxygen percentage and the determination of the atomic oxygen percentage provides an estimation of the amount of chemically bonded compounds containing oxygen such as carboxylic groups; iii) chemical titration methods are also performed to macroscopically estimate the defect density of tubes.

In order to investigate the morphological and structural characterizations of nanotubes, a reduced number of techniques could be used. However, only few techniques are able to characterize CNTs at the individual level such as scanning tunneling microscopy (STM) and transmission electronic microscopy (TEM) (Figure 5). X-ray photoelectron spectroscopy is helpful in order to determine the chemical structure of nanotubes while neutron and X-ray diffraction, infrared and Raman spectroscopy are mostly global characterization techniques.

Mechanical properties

Incorporation of CNTs into a polymer matrix can potentially provide structural materials with dramatically increased modulus and strength. For example, adding 1 wt.% MWCNTs in the PS/MWCNT composite films by the solution-evaporation method, results in 36–42 and 25% improvements in tensile modulus and break stress, respectively. Biercuk et al.[58] have observed a monotonic increase of resistance to indentation (Vickers hardness) by up to 3.5 times on adding 2 wt.% SWCNTs in epoxy resin. Cadek et al.[59] also found that adding 1 wt.% MWSNTs to PVA increased the modulus and hardness by 1.8 times and 1.6 times, respectively.

The homogeneous dispersion and alignment of CNTs in polymer matrices are significant to enhance the effectiveness of reinforcement. For example, for PMMA/MWCNT composites containing 1 wt.% MWCNT, the storage modulus at 90 °C is increased by an outstanding 135% due to the homogeneous dispersion enhanced by in situ polymerization. The tensile strength and modulus of melt drawn PS/MWCNT composite films are, respectively, increased by 137 and 49% compared to the drawn PS film[60].

In general, inclusion of CNTs in polymer matrices leads to reductions in impact toughness of composites and there is an additional effect due to the orientation of the CNTs. However, opposite effects are also reported, which claim an improvement in toughness. For example, Ruan et al.[61] have shown that, with 1 wt.% MWCNTs in PVA, the toughness (that is, area under tensile stress–strain curve) was increased 150% and ductility by 104% due to the enhanced chain mobility in PVA induced by MWCNTs. Similarly, Weisenberger et al.[62] found that addition of 1.8 vol.% MWCNTs enhanced the energies to yield and to break by about 80% for an aligned polyacylonitrile/MWCNT fiber. Dalton et al.[63] prepared super-tough PVA/SWCNT composite fiber containing 60 wt.% SWCNTs caused by slippages between SWCNT bundles. Assouline et al.[64] found that addition of 1 wt.% MWCNTs in polypropylene (PP) matrix increased the composite toughness due to the fibrillar crystal structure of PP induced by MWCNTs.

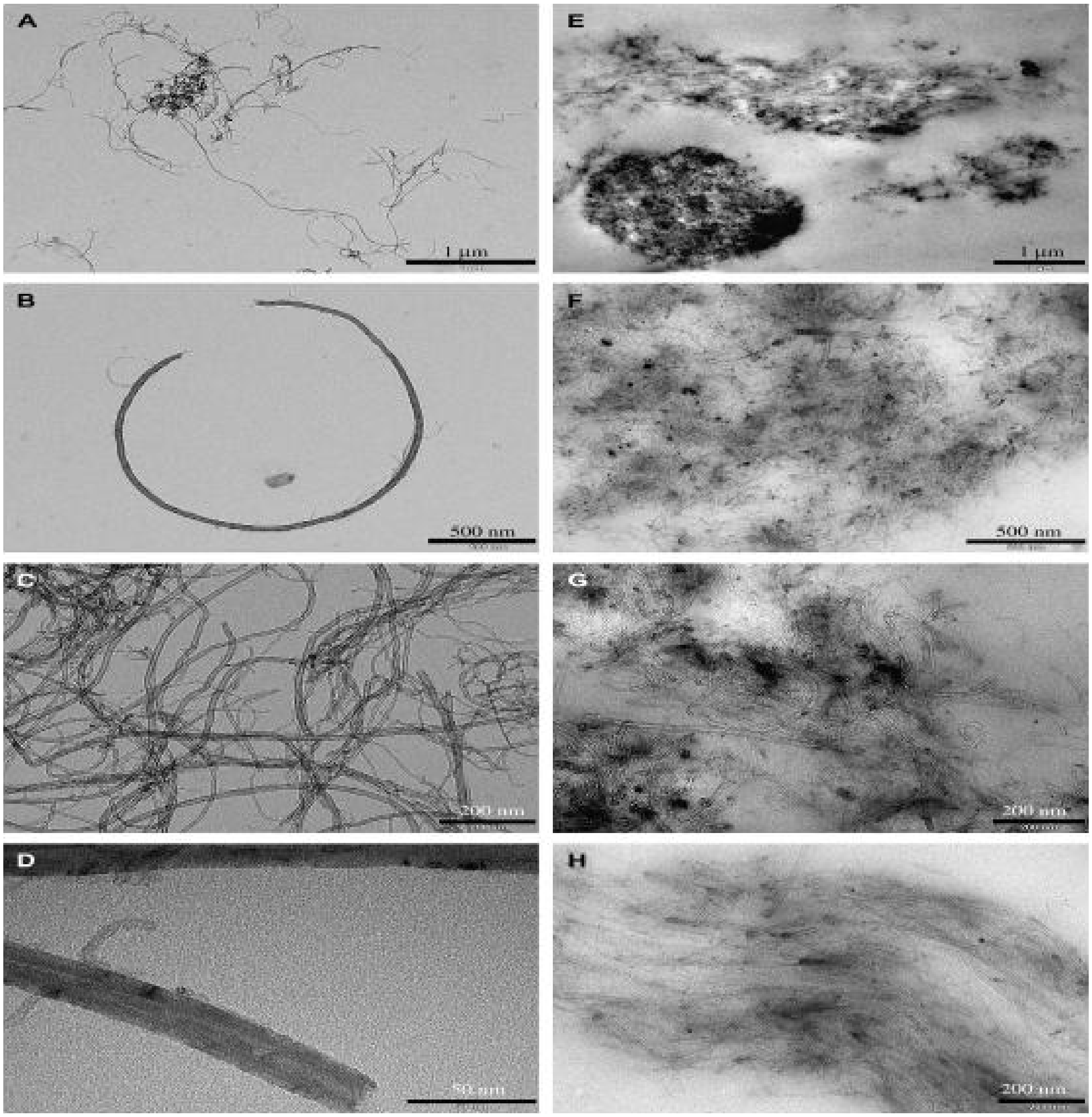

Figure 5 : TEM images. A-D: pure MWNTs; E-H: MWNT/polymer composite

Recently, Blake et al.[65] modified butyl-lithium-functionalized MWCNTs with chlorinated polypropylene (CPP) to produce nanotubes covalently bonded to chlorinated polypropylene (MWCNT/CPP), and compounded the CPP/MWCNT with the CPP/ tetrahydrofuran (THF) solution to obtain CPP/ MWCNT composites. They claimed that as the MWCNT content was increased to 0.6 vol.%, the modulus increased by three times compared to pure CPP from 0.22 to 0.68 GPa, and both tensile strength and toughness (measured by the area under the stress–strain curve) increased by 3.8 times (from 13 to 49 MPa) and 4 times (from 27 to 108 J/g), respectively. These results show that the covalent functionalization of CNTs enables both efficient dispersion and excellent interfacial stress transfer[66].

Photoluminescence spectroscopy

As already described, the SWNTs could be considered either as metallic or semiconducting type. The gap energy of the semiconducting tubes is related to the chirality and is approximately proportional to the inverse of the tube diameter[67]. Photoluminescence from the recombination electron–hole pairs at the band gap has to be expected. However, as noticed by Obraztsova et al., theSWNTs are generally grouped in bundles. In a bundle, nanotubes interact between each others with Van derWaals force. Few nanotubes in these bundles are metallic and are similar to non-radiative channels. The luminescence of the semiconducting tubes in these bundles is relaxed inside these channels. Often, due to this interaction between semiconducting and metallic nanotubes, no photoluminescence signal is obtained. In order to observe the photoluminescence phenomenon, the bundles must be separated into individual tubes. Some treatments could be used to achieve this separation[68].

Thermal properties

The addition of CNTs could increase the glass transition, melting and thermal decomposition temperatures of the polymer matrix due to their constraint effect on the polymer segments and chains. It is important to improve the thermal endurance of polymer composites. Thus, with a surfactant, adding 1 wt.% CNTs to epoxy increases the glass transition temperature from 63 to 88 °C[69].

Similarly, with 1 wt.% well-dispersed SWCNTs, the glass transition temperature of PMMA is increased by ~40 °C[70]. Because CNTs act as nucleation sites in the matrix, their inclusion enhances polymer crystallization and increases the melting temperature. Kashiwagi et al.[71] found that the thermal decomposition temperature of PP at peak weight loss in nitrogen was increased with 2 vol.% MWCNTs.

Also, the incorporation of CNTs could improve the thermal transport properties of polymer composites due to the excellent thermal conductivity of CNTs. This offers an opportunity for polymer/CNT composites for usages as printed circuit boards, connectors, thermal interface materials, heat sinks, lids and housings, and high-performance thermal management from satellite structures down to electronic device packaging. Biercuk et al.[72] found that 1 wt.% un-purified SWCNTs in epoxy showed a 70% increase in thermal conductivity at 40 K, rising to 125% at room temperature. Choi et al.[73] observed that the thermal conductivity of epoxy increased by up to 300% with 3 wt.% SWCNTs.

Electrical and electrochemical properties

The first realized major commercial application of carbon nanotubes is their use as electrically conducting components in polymer composites. It is reported that Plastics has been using CNTs in PPO/PA blend for automotive mirror housings for Ford to replace conventional micron-size conducting fillers, which would require loadings as high as 15 wt.% to have a satisfactory anti-static property but which would impart poor mechanical properties and a high density to the composite[74].

Coleman et al.[75] showed that the electric conductivity of poly p-phenlyenevinylene-co-2,5-dioctoxy-m-phenylenevinylene polymer could be dramatically increased by up to ten orders of magnitude when 8 wt.% CNTs were added, indicative of percolating behavior. The in situ polymerized PA/SWCNT composite films exhibited significant conductivity enhancement (10 orders) at a very low loading (0.1 vol.%) without significantly sacrificing optical transmission.

Since their mechanical properties and thermal stability were also improved by addition of SWCNTs, they are potentially useful in a variety of aerospace and terrestrial applications. Again, alignment of CNTs affects the electrical properties of polymer/CNT nanocomposites. Thus, in epoxy/MWCNT nanocomposites with MWCNTs aligned under a 25 T magnetic field leads to a 35% increase in electric conductivity compared to those similar composites without magnetic aligned CNTs. Improvements on the dispersion and alignment of CNTs in a polymer matrix could decrease the percolation threshold value. Recently, supercapacitors are attracting great attention because of their high capacitance and potential applications in electronic devices. It has been reported that the performance of supercapacitors with MWCNTs deposited with conducting polymers as active materials is greatly enhanced compared to electric double-layer supercapacitors with CNTs due to the Faraday effect of the conducting polymer. Besides these, polymer/CNT nanocomposites could have many potential applications in electrochemical actuation, electromagnetic interference shielding, wave absorption, electronic packaging, self-regulating heater and resistors[76].

Optical and photovoltaic properties

Nonlinear optical organic materials, such as dyes and phthalocyanines, provide optical limiting properties for photonic devices to control light frequency and intensity in a predictable manner. However, these are narrow band optical materials. Carbon nanotubes, both

SWCNTs and MWCNTs, have been studied. O'Flaherty et al.[77] noted that the optical limit saturated at carbon nanotubes exceeding 3.8 wt.%, relative to the polymer mass. Goh et al.[78] found that the aqueous MWCNT suspension showed only week optical limit towards laser at 532 nm operating at 20 Hz, but its mixture with double-C_{60}-end-capped poly ethylene oxide solution displayed enhanced optical limiting responses at 532 and 1064 nm. Polymer/CNT composites could also be used to protect human eyes, optical elements, optical sensors and optical switching. Chen et al.[79] demonstrated the ultra-fast optical switching property of polyimide /SWCNT composites at 1.55 mm.

Applications of CNT/ polymer nanocomposites

CNT have been proposed for many potential applications including conductive and highstrength composites; energy storage and energy conversion devices; sensors; field emissionn displays and radiation sources; hydrogen media; and nanometer-sized semiconductor devices, probes, and interconnects, etc.[80]. Polymer/CNT nanocomposites are expected to have good processability of the polymers and high mechanical and functional properties of the CNTs. Continuing advances on dispersion and alignment of CNTs in polymer matrices will further promote developments in and expand the range of applications of these nanocomposites.

The field of CNTs–polymer nancomposites is currently undergoing rapid developments. Over the last few years it has been demonstrated that polymers can serve as efficient tools for engineering the interfacial behavior of CNT without damaging the unique properties of the individual tube. Polymers were shown to be efficient tools for dispersing, separating, assembling and organizing CNT in different media.

Sensors

The electrical resistance of a semiconductor SWNT changes dramatically when exposed to gaseous molecules. This unusual property makes it useful for chemical sensors. Nanotubes act as the wire between two electrodes so that changes in conductance can be measured[81].

Lighting elements

Nanotubes/polymer are excellent electron sources, thus they are useful in the creation of light elements. The electrons produced by nanotubes are used to bombard a surface coated with phosphor in order to produce light. The brightness of this light is usually 2 times brighter than conventional lighting elements (due to the high electron efficiency)[82].

A potentially important application of CNTs is in polymer-based light-emitting devices. The advantages for organic light-emitting diodes (LEDs) based on conjugated polymers are low cost, low operating voltage, excellent processability and flexibility. However, their low quantum efficiency and stability have limited their applications and developments. Riggs et al.[83] observed strong luminescence of soluble polymer grafted CNTs. Ago et al.[84] revealed the electronic interaction between CNTs and photo-exited polymers, such as poly p-phenylene vinylene (PPV), and proposed "hole collecting" properties of MWCNTs from PPV at the composite interface via the non-radiative energy transfer of singlet excitons from PPV to MWCNTs. Woo et al.[85] found that SWCNTs in poly(m-phenylene vinylene-co-2,5-dioctoxy-p-phenylene vinylene) (PmPV) were responsible for blocking hole transport in the composite by forming hole traps in the polymer matrix induced by image charge effects between SWCNTs and the charge carriers. When the PmPV/MWCNT composite is used as an electron-transport layer in LEDs based on poly(2,5-dimethoxy-1,4-phenylenevinylene-2-methoxy-5(20-ethylhexyloxy)-1,4-phenylene-vinylene, the brightness of LEDs is greatly enhanced due to the low potential barrier reduced by the incorporation of CNTs in the PmPV/MWCNT composite. Kim et al.[86] observed that the device qualities, such as external quantum efficiency, were improved by 2–3 times for up to 0.2 wt.% SWCNTs in LEDs.

Hydrogen storage

Another property of carbon nanotubes/polymer is their ability to quickly adsorb high densities of hydrogen at room temperature and atmospheric pressure. The research group at the National Renewable Energy Laboratory already confirms that SWNTs are capable of storing hydrogen at densities of more than 63kg/m^3. Researchers have found that the interaction of hydrogen and SWNT is between the Van der Waals force of the

SWMT and the chemical bonds of the hydrogen molecule (as opposed to being due to hydrogen dissociation)[87].

Memory device

Because of its ability to store information as a single electronic charge, nanotubes have the potential to be used in the design of memory devices. A single electron is discrete, and thus needs less energy in order to change the state of the memory. Such a design would also take advantage of the high mobility of SWMT, which is ten times greater than that of silicon.

CONCLUSIONS

In this article review, we provide an overview of the research in polymer nanocomposites containing carbon nanotubes and insights to the factors that will ultimately control their properties. Given that much of the research on nanotube/polymer nanocomposites is application driven is an integral part of this research area. The following points are evident about nanotube/polymer composites:

- The properties of nanotube/polymer composites depend on a multitude of factors that include the type (SWNT, MWNT), chirality, purity, and dimensions (length and diameter) of the nanotubes, nanotube loading, dispersion state and alignment of nanotubes in the polymer matrix, and the interfacial adhesion between the nanotube and the polymer matrix. These factors should be taken into account when reporting, interpreting, and comparing results from nanotube/polymer composites.
- Functionalization of nanotubes provides a convenient route to improve dispersion and modify interfacial properties that may in turn improve the properties of nanocomposites, especially mechanical properties. The significant progress in nanotubes functionalization chemistry in recent years ensures that this approach will become more prevalent.
- Quantifying nanotube dispersion in polymers (and solvents) is an inherently challenging problem because it involves a range of length scales, and thereby multiple experimental methods are required. Nanotubes have clearly demonstrated their capability as conductive fillers in polymer nanocomposites.
- The physical properties of nanotube/polymer composites can be interpreted in terms of nanotube networks, which are readily detected by electrical and rheological property measurements. The nanotube network also significantly increases the viscosity and the electrical conductivity of the polymer and slows thermal degradation.

In the feature more straightforward processibility for technological applications are accessible.

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