

# Fabrication and Application of Polymer Composites Comprising Carbon Nanotubes

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**Abstract:** Carbon nanotubes are being used in place of carbon fibers in making composites due to their high strength, high aspect-ratio and excellent thermal and electrical conductivity. Although carbon nanotubes were discovered more than a decade ago, works on preparation of satisfactory composites reinforced by carbon nanotubes have encountered difficulties. This review will discuss some registered patents and relevant papers on the fabrication of carbon nanotube-polymer composites on improving material properties such as electrical conductivity, mechanical strength, and radiation detection which have a broad range of applications in nano-electronic devices, and space and medical elements.

**Keywords:** Carbon nanotubes, polymer, composite, fabrication, conductivity, mechanical strength, radiation, optical activity.

## INTRODUCTION

Conventional fibers made from materials such as alumina, glass, boron, silicon carbide and carbon have been used as fillers in composites. Compared to those fibers, carbon nanotubes (CNTs) have many superior properties such as low-weight, very high aspect ratio, high electrical conductivity, elastic moduli in the TPa range, and much higher fracture strain. These outstanding properties of CNTs make them an attractive candidate for making advanced composite materials with multifunctional features. However, the preparation of satisfactory composites is still a great challenge. An analysis of the registered patents regarding the fabrication of polymer composites containing carbon nanotubes reveals that several fundamental processing challenges such as purification, dispersion, alignment and adhesion of nanotubes and the limitations in interfacial load transfer must be overcome. In addition, another major obstacle to use CNTs as fillers is the high expenses, though it can be only a matter of time to produce CNTs at low cost.

The first section of this paper will review the strategies invented corresponding to the above challenges, with a particular attention to the CNT-polymer composites. Following that, the inventions aimed to increase some specific properties of the composites will be presented. Then some demonstrated applications of the composites will be discussed. Finally, some potential developments for practical applications will be outlined.

## FUNDAMENTAL PROCESSING CHALLENGES

### (i). Purification of Nanotubes

In carbon nanotube production, sublimation and recombination occur and form carbon nanotube soot. Many purification procedures have been developed to remove the inherent contaminants from carbonaceous soot. Patents on purification of CNTs started as early as 1994 [1]. Within the

last decade, over 70 patents have been issued on this topic; an anatomy of patents on purification of CNTs is given in "Carbon Nanotubes Monthly, Feb 2006". However, most of the patented techniques in the 1990s were time consuming, and were only practicable for small quantities. Initially, carbon nanotubes were purified either by treatments with strong chemical oxidants or surfactants or by burning unpurified samples (see e.g. patents [2-5]). These methods have clear disadvantages. For example, chemical oxidants and surfactants tend to break chemical bonds in nanotubes, especially at the tips. Methods involving burning, though can produce better CNTs, often have very poor yield.

In 1999, Davey *et al.* [6] patented a non-destructive and efficient purification method using a coiled polymer to extract nanotubes from their accompanying material with a high yield. In this invention, an organic solvent, toluene, containing poly (m-phenylene-co-2,5-dioctoxy-p-phenylenevinylene) was added to the nanotube soot (Fig. 1a), sonicated in a low power ultrasonic bath and allowed the solid material amorphous carbon to settle to the bottom of the solution (Fig. 1b). The nanotube composite suspension was then decanted from the settled solid. The advantage of this method is that while purifying the nanotubes, a CNT-polymer composite with relatively high electrical conductivity can be produced.

### (ii). Dispersion of Nanotubes when Blended with Polymers

The effective use of CNTs in composite applications depends on the ability to disperse the CNTs uniformly throughout the matrix without reducing their aspect ratio. Due to the van der Waals attraction, nanotubes are held together as bundles and ropes. Thus they have very low solubility in solvents and tend to remain as entangled agglomerates. To overcome the difficulty of dispersion, mechanical/physical methods such as ultrasonication, high shear mixing, surfactant addition, melt blending and chemical modification through functionalization were used. In recent years, researchers have paid much attention to the ultrasonication approach [7-9] for dispersing the nanotubes.

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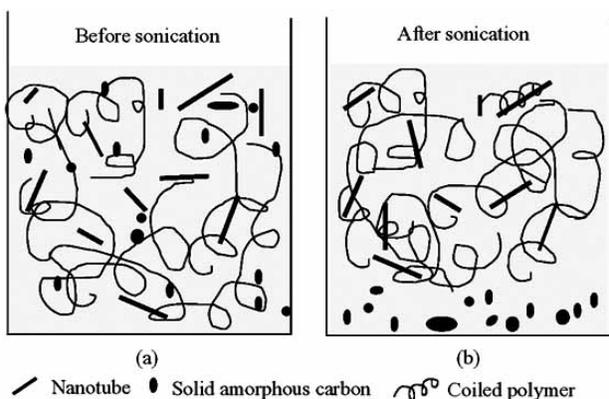


Fig. (1). Schematic of carbon nanotube purification using polymer.

In 2001, Dupire *et al.* patented [10] a method for the production of reinforced polymer, in which both the polymer chains and carbon nanotubes were oriented and dispersed by stretching the nanotube-polymer mixture in a molten state and in a solid state using a high shear mixer. However, the resulting nanocomposites exhibited limited transparency in the visible range. Xiao and Zhang [11] reported a much more effective mechanical method to simultaneously separate and align long entangled CNTs in epoxy matrices. By adding a matrix hardener to the CNT-polymer composite under continuous shear, they found that the viscosity increased and the major CNT separation-alignment achieved at a critical viscosity of  $10^4$  Pa s. Recently, Harmon *et al.* [8] produced conductive and transparent CNT-polymer composites through a combination of dispersion through sonication, in-situ polymerization, dissolution and film casting, in which, the nanotubes were mixed with de-inhibited methyl methacrylate (MMA) and dispersed by sonication. Then by adding an initiator, 1-phenyl-2-hydroxy-2-methyl-1-propanone, MMA was polymerized utilizing UV light/heat/gamma radiation, to produce CNT-PMMA composites.

Although functionalizing nanotube ends with carboxylic groups had been reported in late 1990s, a more direct approach to high degrees of functionalization of nanotubes using diazonium salts was disclosed in 2002 [12]. However, such processes require extraordinary amounts of solvent for the dissolution and dispersion of nanotubes. Margrave *et al.* then disclosed a patent [13] to direct side wall functionalization by fluorination, but the functional group intolerance to organolithium reagents rendered the process incompatible. Recently, aryl halide functionalized CNTs [14] were utilized in anionic polymerization processes to form polymer-CNT materials with improved dispersion ability. In their process, they first reacted aryl halide functionalized CNTs with alkyl-lithium species to replace the aryl-halide bonds by aryl-lithium bonds. After removing the excess alkyl-lithium solution, styrene was added with rapid stirring, and the reaction was terminated with ethanol to produce CNT-polystyrene composite. The mechanism is schematically shown in (Fig. 2), where the introduction of carbanions onto the nanotube surface helps to exfoliate the nanotube

bundle through mutual electrostatic repulsion between nanotubes and provide initiating sites for the polymerization.

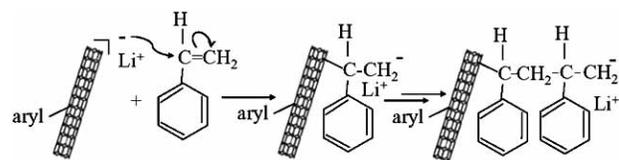


Fig. (2). Schematic of anionic polymerization process.

### (iii). Alignment of Nanotubes when Making Composites

Nanotube alignment is important because it is the only way to maximize the preferred anisotropic behavior of a CNT composite. To date, various techniques such as carbon arc discharge [15], composite slicing [16], film rubbing [17], chemical vapor deposition [18, 19], mechanical stretching of CNT-polymer composites [20] and magnetic orientation [21] have been reported for aligning nanotubes in composites. In fact, approaches to achieve nanotube alignment in composites are dependent on how nanotubes are incorporated into polymer matrices. It seems that the first report on nanotube alignment in composites was in 1994 [16]. They found that slicing the composite when preparing samples for TEM caused partial alignment of CNTs along the shear direction in the cutting planes. deHeer *et al.* [17] made a real attempt in this regard. They fabricated aligned CNT films by drawing a nanotube suspension through a micropore filter and rubbing the tube-coated side of the filter on to a polymer (Delrin or Teflon). Clearly, the drawing and rubbing applied large shear stresses to the CNT films. However, these studies focused on the alignment of CNTs in their bulk aggregates without any attention to polymer compositions. Jin *et al.* [20] fabricated CNT-polymer composites by casting a suspension of CNTs in a solution of a thermo plastic polymer and chloroform. They mechanically stretched the composite by applying load uniaxially at  $100^\circ$  C and found that the CNTs were aligned inside the polymer matrix after unloading at room temperature. Apparently, loading by stretching is different from that of drawing or rubbing; as a matter of fact, stretching still applies shearing to CNTs through the CNT-matrix interfaces. Smith *et al.* [21] magnetically oriented the CNTs based on the difference in magnetic susceptibility between the CNTs and the polymer. However, the magnetic susceptibility of both the polymer and the CNTs was very weak and required very strong magnetic fields ( $\sim 25$  tesla), which is uneconomical for industrial applications. Recently, Xiao and Zhang [11] successfully aligned CNTs in epoxy using continuous shear by optimizing the viscosity of the matrix. Shear is still the key loading in the process.

### FABRICATION OF COMPOSITES WITH IMPROVED MATERIAL PROPERTIES

Several processing methods are available for producing polymer-CNT composites based on the polymer being used. For example, the most common solution processing method is unsuitable for polymers that are insoluble. For thermoplastic polymers, melt processing method is a common alternative. For thermosetting polymers such as epoxy, a hardener is used for curing. For insoluble and thermally

unstable polymers, chemical processing is often used, which involves *in-situ* polymerization or covalent functionalization of CNTs with polymer molecules. Various CNT-polymer composites have been fabricated to improve the material properties such as electrical conductivity, mechanical strength, radiation detection, optical activity etc. Among these, improving the first two properties have been examined and reported to a greater extent.

### (i). Electrically Conductive Composites

Many researchers have tried to incorporate CNTs in polymer matrices to tailor electrical properties suitable for different applications such as for electronic goods, semiconductor components, and circuit boards, because different applications normally require specific levels of conductivity. For instance to confer protection against electrostatic discharge, a low level of conductivity (i.e. high level of resistivity ranging from  $10^4$  -  $10^8$  ohm/cm) is enough whereas to protect against electromagnetic interference as well as to prevent the emission of interfering radiation, resistivity of  $10^4$  ohm/cm is needed. Except for the method of Blanchet-Fincher *et al.* [22], all the others, although a high weight percentage of CNTs has been used, can produce a maximum conductivity of only 5 S/cm, which is well below the required conductivity in electronic applications.

Niu *et al.* [23] revealed a method for the preparation of mechanically strong yet electrically conductive polyvinylidene fluoride, (PVDF)-CNT composite by two different methods. In solution method, PVDF was first dissolved in a solvent such as acetone, CNTs were then added into the solution and sonicated. The composite was then precipitated with a precipitating component such as water, filtered and dried. In melt compounding method, PVDF was mixed with CNTs in a mixer at high temperatures to melt and compound PVDF into CNTs to form the composite. They found that the composite prepared by the solution method were better electrical conductors than that by the melt compounding method. They claimed that this composite had a higher level of conductivity than other known polymer composites, using as little as 13 wt% of CNTs to achieve a conductivity close to pure CNT mats. Moreover, they reported that the conductivity might be adjusted by varying the CNT loading to meet the required value for a specific application. According to their results, the resistivity (i.e. the reciprocal of conductivity) varied with the nanotube loading, as illustrated in Fig. (3), dropped significantly as the CNT concentration increased (to ~3 wt%).

McElrath *et al.* [24] made a polymer-CNT composite comprising at least one polar polymer with electrical and/or thermal conductivity enhanced over that of polymer alone. They found that the electrical conductivity enhancement depends on the weight fraction of the SWNTs in the composite and that the conductivity of a 50 wt% SWNT was ~5 S/cm which is 6 orders higher than that ( $3 \times 10^{-6}$  S/cm) of the pure polymer, although it is still well below the value required for practical applications.

Recently Charati *et al.* [25] revealed a method for manufacturing conductive composites for material-handling, electronic devices (computers, printers etc.) and automotive components that require electrostatic dissipation and

electromagnetic shielding while retaining the advantages of

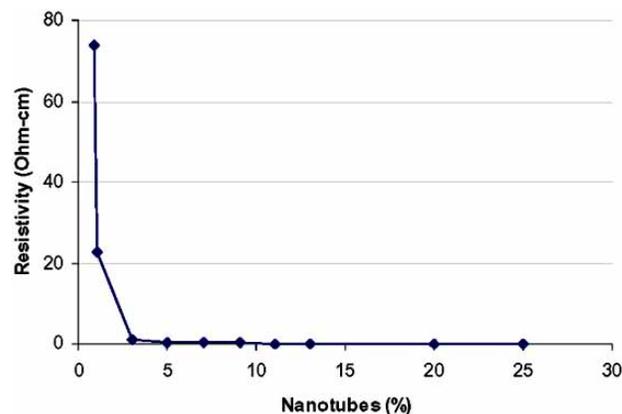


Fig. (3). Variation of CNT-PVDF composite resistivity with CNT loading.

mechanical properties. This was prepared by blending an organic polymer precursor (i.e. reactive species that are monomeric, oligomeric or polymeric that can undergo additional polymerization) with single wall CNT and polymerizing the polymer precursor to form an organic polymer. In their method they first sonicated an organic polymer precursor (e.g. poly(arylene ether)) together with the SWNTs in an ultrasonicator to disperse the SWNTs and then polymerized the organic polymer precursor using shear and elongational forces. They claimed that in this way, at least a portion of the CNTs could be functionalized either at the side wall or hemispherical ends.

Highly conductive polymers have been limited in practical applications as they are chemically unstable in use and unsuited for solution or melt processing. Among the conductive polymers, polyaniline (PANI) is known to be chemically stable and readily soluble in environmentally friendly solvents. Protonic acid doped emeraldine nitrogen base salt of PANI is the most highly conductive form with conductivity of 5 S/cm, which is well below the  $10^2$  S/cm threshold conductivity required for widespread utility in electronics. Blanchet-Fincher *et al.* [22] disclosed a method for the preparation of a composite comprising nitrogen base salt of emeraldine form of PANI and CNTs that exhibited electronic conductivities of  $10^2$  S/cm while retaining the desirable chemical stability of PANI. In their invention, the emeraldine form of PANI (Fig. 4a) was treated with an organic acid such as dodecylbenzenesulfonic acid (DBSA) at a temperature of 80-150°C in a solvent such as toluene; the composite was formed by mixing the resulting salt solution (i.e. nitrogen base salt, (Fig. 4b) with CNTs dispersed in the same solvent. By examining specimens with different wt% of CNTs, they found that the most preferred concentration of CNTs was 1-5 wt%. Thus they achieved a high conductivity with a small wt% of CNTs. At concentrations below 0.5 wt%, increase in conductivity was very little and at concentrations above 30 wt%, physical properties of the composites were adversely affected. They used the above composite as a

conductive pathway, produced by laser thermal transfer imaging, in electronic circuits.

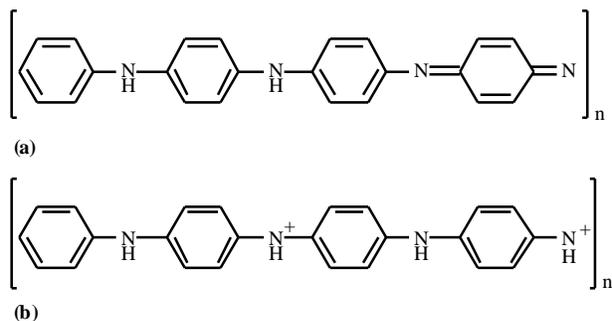


Fig. (4). (a) Emeraldine base form of PANI (b) Emeraldine salt form of PANI.

### (ii). Mechanically Reinforced Composites

Fundamental issues such as large aspect ratio, good dispersion, good alignment and interfacial stress transfer are required for effective reinforcement. Among these, the interfacial stress transfer, characterized by the applied shear stress at which the interface fails, is the most important. CNTs have atomically smooth non-reactive surfaces and as such there is a lack of interfacial bonding between the CNT and the polymer chains that limits stress transfer. Chemical modification and functionalization of CNTs, which can provide bonding sites to the polymer matrix, were shown to be a feasible solution. Quantum mechanics and molecular dynamics calculations supported this approach [26-29]. Various methods such as solution processing, melt processing, and chemical processing gave polymer-CNT composites with interfacial shear strength ranging from 50-500 MPa. These reinforced composites have numerous possible applications in ultra-light weight space structures, making bullet proof vests, sporting goods etc.

In 2005, Margrave *et al* [30] presented a method of integrating CNTs into epoxy polymer via chemical functionalization of CNTs. First they treated SWNTs with concentrated  $H_2SO_4/HNO_3$  mixture and functionalized them by fluorination. The functionalized CNTs were then dispersed in solvents like *N, N*-dimethylformamide/ tetrahydrofuran; epoxy resin was added and the solvent was removed by evaporation. The resulting solvent-free mixture was treated with curing agents such as primary or secondary amines that react with the fluorine on the CNTs and form CNTs with amine groups on the side wall, which then react with the epoxide rings on the epoxy resin and form covalent bonds with the polymer. They confirmed the occurrence of the above reactions using infra-red and Raman spectroscopy. By performing tensile tests, they found that the composite with 1wt% functionalized CNTs showed an increase of 18% and 24% in tensile strength and modulus respectively over the epoxy composites with unfunctionalized CNTs and a 30% increase in tensile modulus over pure epoxy resin.

Kumar *et al.* [31] revealed a method for making composite comprising dispersed CNTs aligned with rigid-rod polymers formed by *in-situ* polymerization from the polycondensation of diamine and diacid monomers. These composites were characterized by high tensile strength, high modulus, stiffness and thermal stability. They also showed that the tensile modulus, tensile strength and elongation to break of composite having 10 wt% CNT increased by 20, 60 and 40% respectively compared to the polymer. However, there was no claim of covalent bond formation at the interface.

In a patent by Alba [32], the CNTs were joined to the polymer through the use of a bonding agent that mechanically coupled the polymer chains to the CNTs. Alba claimed that the bonding agent is non-covalently bonded (for e.g. pi-bonding) to the CNTs in a manner that retains substantially all of the properties of CNTs.

Shambaugh *et al.* [33] recently disclosed a method for producing SWNT-polypropylene composite, by combining the uniformly dispersed nanotube/solvent mixture with polypropylene matrix/solvent mixture to form nanotube/solvent/matrix mixture. After removing the solvent, they heated the nanotube/matrix mixture to a temperature above the melting point of the matrix material, passed it through an orifice to form an extrudate and drawn it to form fiber. They found that the composite fiber with 1 wt% of CNTs showed more than 50% increase in tensile strength over a fiber drawn from matrix material alone. This substantial increase in strength was believed to be due to a uniform dispersion of CNTs in the matrix material.

The above results show that not only the interfacial bonding but also the type of polymer and the conditions used in making the composite are important to produce a strong composite.

### (iii). Radiation Detection Composites

Radiation shielding materials have been developed to protect personnel and equipment from the damaging effects of radiation including galactic cosmic radiation (GCR). Currently polyethylene (PE) is used in space applications for shielding GCR. However, its use is limited to low temperature applications. Recently Harmon *et al.* [34] disclosed a patent for the synthesis of transparent composites composed of SWNTs incorporated into poly (4-methyl-1-pentene), or PMP in abbreviation, for space vehicles, space stations as well as in the biomedical arts and atom splitting research. When compared to PE, PMP exhibits superior strength, thermal and optical properties, and has a melt temperature of 235°C (compared to 136°C for PE) which extends the temperature range for shielding radiation. Moreover, PMP is transparent in the visible region of electromagnetic spectrum and can be modified by doping with an organic dye having at least one phenyl ring. Harmon *et al.* claimed that the composites prepared with doped polymers are useful in thermo-luminescent detection where high energy particles and radiation excite pi-electrons in the phenyl rings of the organic dyes and emit photons on relaxing to the ground state which can be transported to photodetectors and counted. In this way, the radiation

environment of the shielding materials can be continuously monitored.

#### (iv). Optically Active Composites

Organic materials allow much faster signal processing because of their much greater state change rate and ease of hybridization change. However, producing polymeric materials in a robust opto-electronic fashion creates problems such as sensitivity to intensity within the polymer, long term instabilities due to photochemical effects and low thermal electrical conductivity that are necessary for transport. Polyimide polymers have long been used to fabricate optical waveguides on chips. In 2004, Zhao *et al.* [35] disclosed a patent for an ultra-fast, high-sensitivity, all-optical switch made from SWNT-polymer composites consisting 0.1 wt% CNTs and polyimide. All-optical systems avoid repeated conversions between electrical and optical signals and they are faster. They claimed that the fabricated material was a substantially transparent, third-order nonlinear optical material and the switch had a switching speed of 1 ps, for light with a wavelength of about 1.55  $\mu\text{m}$ .

Woo *et al.* [36] showed that the organic light emitting diode, fabricated from poly (m-phenylene vinylene-co-2,5-dioctoxy-p-phenylene vinylene), PmPV and SWNT (~0.1 wt%), increased oscillator strength in green radiation by about 700% as compared to PmPV alone. From this they concluded that SWNTs in the composite were responsible for blocking hole transport by forming hole traps in the polymer matrix. This non-linear optical effect could be employed to protect optical sensors from high intensity laser beams and in developing new light sensitive shields for helmets.

### APPLICATIONS OF CNT-POLYMER COMPOSITES

Diverse applications in electronics, medicine, defense and aerospace have been envisioned due to the remarkable improvement on the material properties. This section will review some of their applications.

#### (i). Actuators

Materials such as shape-memory alloys or liquid crystal elastomers exhibit a latent ability to actuate under the right conditions whereas other systems require the blending of two or more materials to impart a new physical response leading to the actuation process. Recently, polymer nanocomposites appeared as the subject of mechanical actuation studies, but most of them concentrated on accentuating the already present features of the host matrix by adding nanotubes. In 2003, Courty *et al.* [37] reported a novel actuator response driven by an electric field due to the presence of multi-walled CNTs in nematic elastomer, polysiloxane. They produced a composite material with embedded and aligned CNTs with an effective dielectric anisotropy, many orders of magnitude higher than in the usual liquid crystals. Koerner *et al.* [38] fabricated multi-walled CNT-polydimethylsiloxane composite that produced a mechanical response to the infrared radiation. They reported that the sample spontaneously contracted and elongated on irradiation. They further showed that the mechanical response is due to photon absorption and not because of the trivial heating of the materials due to

irradiation. However, the nature of the actuator mechanism is not known.

Ounaies *et al.* [39] developed technique for making actuating composite materials with polarizable moieties (eg. polyimide) and CNTs. With the aid of an *in-situ* polymerization under sonication and stirring, they achieved an increase of dielectric constant from 4.0 to 31 with a 0.1% volume fraction of SWNTs.

#### (ii). Sensors

Sensing gas molecules is critical to environmental monitoring, space missions and industrial, agricultural and medical applications. For instance, the detection of NO<sub>2</sub> and CO is important to monitor environmental pollution; detection of NH<sub>3</sub> is required in industrial and medical environments. Kong *et al.* [40] demonstrated chemical sensors based on individual SWNTs. They found that the electrical resistance of a semi-conducting SWNT changed dramatically upon exposure to gas molecules such as NO<sub>2</sub> or NH<sub>3</sub>. The existing electrical sensor materials including carbon black-polymer composites operate at high temperatures for substantial sensitivity whereas the sensors based on SWNT exhibited a fast response and higher sensitivity at room temperature. A few patents have demonstrated the use of CNT-polymer composite as sensors.

Ajayan *et al.* [41] developed a controlled method of producing free-standing nanotube-polymer composite films that can be used to form nanosensor, which contains at least one conductive channel comprising an array of substantially aligned carbon nanotubes embedded in a matrix material (e.g. poly (dimethylsiloxane)). This material can be used to determine a real time physical condition of a material, such as monitoring the physical condition of an airplane wing or chassis while the airplane is in flight.<sup>1</sup>

### CURRENT & FUTURE DEVELOPMENTS

Although, the nanotube-polymer composites showed improved properties, there have not been many industrial successes yet. In order to realize the potential applications of these composite materials some work must be done on developing mass production techniques for CNTs with reasonable costs. Current production rate is only enough for doing research and build a knowledge base on the CNT-polymer composite properties. The most critical factor is the production cost. Until this is reduced to a competitive level with the existing materials used in composite production, large scale use of CNTs is unlikely. Arc discharge, laser ablation, solar, plasma and chemical vapor deposition (CVD) have been the main methods used for CNT production. Among these, the first three processes correspond to high temperature methods and reached their limit in production rate. In 2004, Fabry *et al.* [43] of TIMCAL Belgium published a new approach with the plasma process known as 3-phase AC plasma technology for the continuous mass production of CNTs. CVD is the simple and economic technique. Recently Zhang *et al.* [44] claimed that they had

<sup>1</sup> Ito *et al.* [42] disclosed a patent on conductive polymer thin film complex which claimed such a film with an electrode can be used in a light sensor. As this patent is in Japanese language, we are unable to give further information.

developed a novel oxygen assisted hydrocarbon CVD method to afford large scale ultra-high-yield growth of SWNTs. Iwasaki *et al.* [45] synthesized millimeter long vertically aligned CNTs by an improved CVD technique. Mayya *et al.* [46] synthesized diameter controlled CNTs by modified CVD technique. These works show that mass production of long, uniform, aligned CNTs with low cost could become operative in the near future. A good example is that nanotubes have now become available in the market in large quantities (e.g. in kilo grams).

The second task is to optimize the CNT-polymer composite. To achieve this, CNTs must have high aspect ratios, be well purified, well dispersed and aligned in the polymer matrix. They must also have good interfacial properties with matrix. To maintain high aspect ratio, the CNTs must be long and small in diameter. However, longer tubes are hard to disperse and if the diameter becomes too small, although it would give greater surface area, the maximum CNT loading level will be compromised. Therefore the length and the diameter must be optimized (see e.g., [47]). Although several methodologies have already been published in the literature to optimize other steps as discussed in the previous sections, one should aim to combine them in one synthesis. This cannot be done by simply picking up the best technique in the literature, and carrying out the procedures one after the other. For example if one uses the functionalization technique to disperse the nanotubes, their electronic and photonic properties would degrade due to the introduction of  $sp^3$  hybridized carbon defects.

The third task, but not the last, is to understand the mechanisms involved in the methods used to improve the composite material properties. This will help to select the appropriate polymers and the CNTs with suitable parameters and thereby optimize the processes.

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#### REFERENCES

- [1] Hidefumi, H., Toomasu, E.: JP6228824 (1994).
- [2] Hidefumi, H., Toomasu, E.: JP7048110 (1995).
- [3] Uchida, K., Yumura, M., Oshima, S., Kuriki, Y., Yatsuse, K., Igasaki, F.: JP7048111 (1995).
- [4] Hidefumi, H., Toomasu, E.: JP8012310 (1996), US5698175 (1997).
- [5] Smalley, R. E., Colbert, D. T., Dai, H., Liu, J., Rinzler, A. G., Hafner, J. H., Smith, K., Guo, T., Nikolaev, P., Thess, A.: WO9839250 (1998).
- \*[6] Davey, A., Curran, S., Blau, W.: EP0949199 (1999), US20036576341 (2003).
- [7] Glatkowski, P. J., Landrau, N., Landis, D.H., Piche, J. W., Conroy, J. L.: US20067118693 (2006).
- [8] Harmon, J. P., Clayton, L. M., Muisener, P.: US20067094367 (2006).
- [9] Smalley, R. E., Hauge, R. H., Kittrell, W. C., Sivarajan, R., Strano, M. S., Bachilo, S. M., Weisman, R. B.: US20067074310 (2006).
- [10] Dupire, M., Michel, J.: US20016331265 (2001).
- [11] Xiao KQ, Zhang LC. Effective separation and alignment of long entangled carbon nanotubes in epoxy. *J Mat Sci* 2005; 40: 6513-6516.
- [12] Tour, J. M., Bahr, J., Yang, J.: WO/2002/060812 (2002).
- [13] Margrave, J. L., Mickelson, E. T., Hauge, R., Boul, P., Huffman, C., Liu, J., Smalley, R. E., Smith, K., Colbert, D. T.: US20036645455 (2003).
- \*[14] Tour, J. M., Hudson, J. L., Krishnamoorti, R., Yurekli, K., Mitchell, C. A.: WO05030858A3 (2005).
- [15] Wang XK, Lin XW, Dravid VP, Ketterson JB, Chang RPH. Growth and characterization of buckybundles. *Appl Phys Lett* 1993; 62: 1881-1883.
- [16] Ajayan PM, Stephan O, Colliex C, Trauth D. Aligned Carbon Nanotube Arrays Formed by Cutting a Polymer Resin-Nanotube Composite. *Science* 1994; 265: 1212-1214.
- [17] deHeer WA, Bacsu WS, Châtelain A, Gerfin T, Humphrey-Baker R, Forro L, Ugarte D. Aligned Carbon Nanotube Films: Production and Optical and Electronic Properties. *Science* 1995; 268: 845-847.
- [18] Li WZ, Xie SS, Qian LX, Chang BH, Zou BS, Zhou WY, Zhao RA, Wang G. Large-Scale Synthesis of Aligned Carbon Nanotubes. *Science* 1996; 274: 1701-1703.
- [19] Fan S, Chapline MG, Franklin NR, Tomblor TW, Cassell AM, Dai H. Self-Oriented Regular Arrays of Carbon Nanotubes and Their Field Emission Properties. *Science* 1999; 283: 512-514.
- [20] Jin L, Bower C, Zhou O. Alignment of carbon nanotubes in a polymer matrix by mechanical stretching. *Appl Phys Lett* 1998; 73: 1197-1199.
- [21] Smith BW, Benes Z, Luzzi DE, Fischer JE, Walters DA, Casavant MJ, Schmidt J, Smalley RE. Structural anisotropy of magnetically aligned single wall carbon nanotube films. *Appl Phys Lett* 2000; 77: 663-665.
- \*[22] Blanchet-Fincher, Beatriz, G.: US20067033525 (2006).
- \*[23] Niu, C., Ngaw, L., Fischer, A., Hoch, R.: US20046783702 (2004).
- [24] McElrath, K. O., Smith, K. A., Tiano, T. M., Roylance, M. E.: US6936653, WO03078317 (2005).
- \*[25] Charati, S. G., Dhara, D., Elkovitch, M., Ghosh, S., Mutha, N., Rajagopalan, S., Shaikh, A. A.: US20067026432 (2006).
- [26] Frankland SJV, Caglar A, Brenner DW, Griebel M. Molecular simulation of the influence of chemical cross-links on the shear strength of carbon nanotube-polymer interfaces. *J Phys Chem B* 2002; 106: 3046-3048.
- [27] Mylvaganam K, Zhang LC. Nanotube Functionalization and Polymer Grafting: An ab Initio Study. *J Phys Chem B* 2004; 108: 15009-15012.
- [28] Mylvaganam K, Zhang LC. Deformation-promoted reactivity of single-walled carbon nanotubes. *Nanotechnology* 2006; 17: 410-414.
- [29] Mylvaganam K, Zhang LC. Chemical bonding in polyethylene-nanotube composites: a quantum mechanics prediction. *J Phys Chem B* 2004; 108: 5217-5220.
- \*[30] Margrave, J. L., Khabashesku, V. N., Zhu, J., Peng, H., Barrera, E. V.: WO05028174A3 (2005).
- [31] Kumar, S., Arnold, F. E., Dang, T. D.: US20056900264 (2005).
- [32] Alba, N. A.: WO05120823 (2005).
- \*[33] Shambaugh, R. L.: US20067001556 (2006).
- \*[34] Harmon, J. P., Clayton, L. M.: US2005245667 (2005), WO06073454C2 (2006).
- \*[35] Zhao, Y., Chen, Y., Zhang, X.-C., Ravavikar, N. R., Ajayan, P. M., Lu, T.-M., Wang, G.-C., Schadler, F., Linda, S.: US20046782154 (2004).
- [36] Woo HS, Czerw R, Webster S, Carroll DL, Ballato J, Strevens AE, O'Brien D, Blau WJ. Hole blocking in carbon nanotube-polymer composite organic light-emitting diodes based on poly (m-phenylene vinylene-co-2, 5-dioctoxy-p-phenylene vinylene). *Appl Phys Lett* 2000; 77: 1393-1395.
- [37] Courty S, Mine J, Tajbakhsh AR, Terentjev EM. *Europhys Lett* 2003; 64: 654.
- [38] Koerner H, Price G, Pearce NA, Alexander M, Vaia RA. *Nat Mater* 2004; 3: 115.
- \*[39] Ounaies, Z., Park, C., Harrison, J. S., Holloway, N. M., Draughon, G. K.: US2006084752 (2006).
- [40] Kong J, Franklin NR, Zhou C, Chapline MG, Peng S, Cho K, Dai H. Nanotube Molecular Wires as Chemical Sensors. *Science* 2000; 287: 622-625.
- \*[41] Ajayan, P., Lahiff, E., Stryjek, P., Ryu, C. Y., Curran S.: WO04053464A1 (2004).
- [42] Ito, E., Miyairi, K., Endo, M.: WO05024852 (2005).

- [43] Fabry F, Gruenberger TM, Gonzalez-Aguilar J, Okuno H, Grivei E, Probst N, Fulcheri L, Flamant G, Charlier J-C. Continuous mass production of carbon nanotubes by 3-phase ac plasma processing, In *NSTI Nanotechnology Conference and Trade Show*, (2004); Vol. 3, pp. 228-231.
- [44] Zhang G, Mann D, Zhang L, Javey A, Li Y, Yenilmez E, Wang Q, McVittie JP, Nishi Y, Gibbons J, Dai H. Ultra-high-yield growth of vertical single-walled carbon nanotubes: Hidden roles of hydrogen and oxygen. *Proc of the National Academy of Sciences* 2005; 102: 16141-16145.
- [45] Iwasaki T, Zhong G, Yoshida T, Aikawa T, Morikane R, Kawarada H, Millimeter long vertically aligned single-walled carbon nanotubes by an ultra long lifetime of catalysts, In *NSTI Nanotechnology Conference and Trade Show*, (2006); Vol. 1, pp. 94-97.
- [46] Mayya KS, Lee S, Yeo I-S, Chung U-I, Moon J-T, Diameter controlled synthesis of carbon nanotubes by CVD using steric-stabilized iron nanoparticle catalysts, In *NSTI Nanotechnology Conference and Trade Show*, (2006); Vol. 1, pp. 98-101.
- [47] Xiao KQ, Zhang LC. The stress transfer efficiency of a single-walled carbon nanotube in epoxy matrix. *J Mat Sci* 2004; 39: 4481-4486.