Carbon Nanotubes/Nanofibers and Carbon Fibers

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10.1

Introduction

Carbon nanotube and nanofiber reinforced polymer nanocomposites and micron-sized carbon fiber-based polymer composites look set to have significant impact on emerging advanced products ranging from aerospace, automotive and PEM (proton exchange membrane) fuel cell parts, to surgical implants and to components for nanoelectronics. The area of micron-scale carbon fiber filled composites, unlike that of the emerging field of carbon nanotube and nanofiber-based nanocomposites, is relatively mature. Although both areas are discussed in this chapter, we focus more on the rapid advances being made in the field of carbon nanotube-based nanocomposites, discuss some new developments in conventional micron-scale and sub-micron scale carbon fiber composites, and point out possible synergies.

10.1.1

Types of Carbon Nanotubes/Nanofibers and their Synthesis

There has been intense interest in carbon nanotubes (CNTs) since their discovery by Iijima in 1991 [1], in large part because they possess unique structural and electronic properties. Single-wall carbon nanotubes (SWNTs) are the fundamental form of carbon nanotubes, with unique electronic properties that emerge due to their one dimensionality; an SWNT is a single hexagonal layer of carbon atoms (a graphene sheet) that has been rolled up to form a seamless cylinder. Three types of SWNTs with differing chirality can be formed, as depicted in Fig. 10-1. The one dimensional unit cell shown has a circumference given by the chiral vector $C = na + mb$, where n and m are integers equivalent to the roll up vectors and a and b are unit vectors of the hexagonal lattice. A multiple-wall carbon nanotube (MWNT) is a stack of graphene sheets rolled up into concentric cylinders. This stacking results in a loss of the some of the unique one-dimensional

properties present in the single (SWNT) and double (DWNT) tube structures. The walls of each MWNT layer are parallel to the central axis. A stacked cone or herringbone arrangement is also formed by catalytic chemical vapor deposition (CVD), which can grow with a hollow, tubular center. These structures have relatively large diameters (typically ≥50 nm) compared with the near molecular-scale dimensions of SWNTs and the low nanoscale dimensions of most MWNTs, and are therefore referred to as carbon nanofibers (CNFs).

Insert Fig. 10-1

MWNTs were first synthesized using a non-catalytic carbon arc discharge method by Iijima [1]. SWNTs were initially synthesized in 1-2% yields in soot generated in an arc struck between graphite electrodes containing a few percent Fe, Co or Ni by Bethune et al. [2] and Iijima and Ichihashi [3]. Smalley and co-workers [4] then scaled up SWNT synthesis using a dual laser ablation technique with transition metal particles incorporated in the graphite target. This method could produce SWNTs with yields of up to 70%. The carbon nanotubes are formed catalytically in the extremely high temperature of the ablation plume with a narrow distribution of diameters around 1.3 nm and, due to van der Waals forces, generally assemble into bundles or ropes of parallel SWNTs. Soon afterwards Journet et al. [5] showed that about 50% yields of SWNT bundles, similar in size to those produced by laser ablation, can be obtained using the arc-discharge method when catalyst particles of rare-earths like Y are incorporated together with transition metals in the graphite rods. CVD methods involving the decomposition of hydrocarbon precursor gases, typically ethylene and acetylene, in the presence of transition metal (iron, cobalt or nickel) catalysts on a support material like alumina or silica, have been used to make CNFs [6,7] and MWNTs [8] at temperatures in the 550 to 1000^{o}C range. MWNTs grown by the CVD

technique, however, have high defect densities in their structures. Arc-grown MWNTs on the other hand, are largely defect-free because growth occurs at plasma-generated temperatures in excess of 2000^{o}C. Recently plasma enhanced CVD (PE-CVD) growth of MWNTs has emerged as a technique for the growth of vertically aligned MWNTs and CNFs [9,10].

Since the late 1990s, largely defect-free SWNTs have been grown at near or above 90% purity by CVD techniques involving the catalytic decomposition of methane at temperatures near 1000^{o}C [11,12], by the catalytic disproportionation of carbon monoxide (CO) under high pressures (the so-called high pressure carbon monoxide or HIPCO process) and temperatures above 1000^{o}C [13], and at 1 atmosphere and temperatures below 1000^{o}C [14-17], using catalyst supported on silica and MgO. Cheng et al. [18] produced SWNTs at 1200^{o}C and undetermined purity levels by heating flowing benzene together with ferrocene and thiophene precursors to form floating catalytic particles, whereas Maruyama et al. [19] generated SWNTs at temperatures down to 550^{o}C using ethanol under low-pressure conditions. Because of the etching effect of OH radicals produced on decomposition of alcohol, non-SWNT phases, such as amorphous and non-tubular nanocarbons and MWNTs, were not formed. Maruyama's group has also been able to grow vertically aligned SWNTs on catalyst coated quartz substrates using ethanol as precursor [20] in a thermal CVD process. Low pressure conditions using either ethylene or propylene as the carbon source were employed by Sharma and Iqbal [21] to grow and observe in real-time both SWNTs and MWNTs *in-situ* in an environmental transmission electron microscope.

As-synthesized SWNTs are typically bundled and comprise of a range of tube diameters and chiralities. A method to grow single diameter, individual SWNTs is to form them inside zeolites with selected pore sizes. Catalyst-free SWNTs with a diameter of 0.42 nm corresponding to that

of the smallest fullerene, C_{20}, were grown by Wang et al [22] by this method. Another catalyst-free method [23] that provides thin bundles of SWNTs with a narrow diameter distribution in the 1.2 to 1.6 nm range, involves horizontal templated growth of the tubes on the Si face of hexagonal silicon carbide (6H-SiC), although growth occurs only at temperatures above 1500^{o}C. More recently PE-CVD with methane as carbon source has been used for the first time to grow SWNTs in the 550 to 900^{o}C temperature range. In the first study reported, SWNTs were grown bridging the pores of a zeolite positioned on a Ni plate [24]. In the second study, largely semiconducting SWNTs were grown on ferritin (a precursor for nanoscale Fe catalyst particles) on silica [25], and in the third study SWNTs were formed on sol-gel produced bimetallic Co-Mo catalysts on MgO [26]. It remains to be seen as to whether more controlled alignment of SWNTs can be obtained by the PE-CVD technique.

10.1.2

Types of Carbon Fibers and their Synthesis

Micron-sized carbon fibers presently used contain at least 90% carbon and are produced by heat treatment or controlled pyrolysis of different precursor fibers. The most prevalent precursors are polyacrylonitrile (PAN), cellulose fibers (such as viscose rayon and cotton), petroleum or coal tar pitch and certain phenolic fibers. Pitch is a tarlike mixture of hundreds of branched organic compounds with differing molecular weights formed by heating petroleum or coal. The so-called mesophase of pitch is in a liquid-crystalline state. The structures of the PAN, cellulose and phenolic resin are depicted in Fig. 10-2.

Insert Fig. 10-2

Micron-sized carbon fibers can be classified in terms of the precursor fiber materials as PAN-based, mesophase or isotropic pitch-based, rayon-based, and phenolic-based. The synthesis

process involves a heat treatment of the precursor fibers to remove oxygen, nitrogen, and hydrogen to form the carbon fibers. It is well established in the literature that the mechanical properties of the carbon fibers are improved by the increasing crystallinity and orientation, and by reducing defects in the fiber. The best way to achieve this is to start with a highly oriented precursor and then maintain the high orientation during the process of stabilization and carbonization through tension.

10.1.2.1 **PAN-Based Carbon Fibers**

There are three successive stages in the conversion of a PAN precursor into high-performance carbon fibers:

(a) Oxidative stabilization: The PAN precursor is first stretched and simultaneously oxidized in the 200-300^{o}C temperature range. This treatment converts thermoplastic PAN to a non-plastic cyclic or ladder compound.

(b) Carbonization: After oxidation, the fibers are carbonized at about 1000^{o}C without tension in an inert atmosphere (normally nitrogen) for a few hours. During this process the non-carbon elements are removed as volatiles to give carbon fibers with a yield of about 50% of the mass of the original PAN.

(c) Graphitization: Depending on the type of fiber required, the fibers are treated at temperatures in the range 1500-3000^{o}C; this step improves the ordering and orientation of the crystallites in the direction of the fiber axis.

10.1.2.2 **Carbon Fibers from Pitch**

Carbon fiber fabrication from pitch generally involves the following four steps:

(a) Pitch preparation: Essentially it is an adjustment in the molecular weight, viscosity, and crystallite orientation for spinning and further heating.

(b) Spinning and drawing: In this step, the pitch is converted into filaments, with some alignment in the crystallites to achieve directional characteristics.

(c) Stabilization: In this step, cross-linking is introduced to maintain the filament shape during pyrolysis. The stabilization temperature is typically between 250 and 400^{o}C.

(d) Carbonization: The carbonization temperature is typically in the range 1000 -1500^{o}C.

Carbon fibers made from the spinning of molten pitches are of interest because of the carbon yield approaching 99% and the relative low cost of the starting materials. The formation of melt-blown pitch webs is followed by stabilization in air and carbonization in nitrogen. Processes have been developed with isotropic pitches and with anisotropic mesophase pitches. The mesophase pitch-based and melt-blown discontinuous carbon fibers have a structure comprised of a large number of small domains, each domain having an average equivalent diameter from 0.03 mm to 1 mm, and a nearly unidirectional orientation of folded carbon layers assemble to form a mosaic structure on the cross-section of the carbon fibers. The folded carbon layers of each domain are oriented at an angle to the direction of the folded carbon layers of the neighboring domains on the boundary.

Carbon fibers from isotropic pitch

Isotropic pitch or a pitch-like material, such as molten polyvinyl chloride, is melt spun at high strain rates to align the molecules parallel to the fiber axis. The thermoplastic fiber is then rapidly cooled and carefully oxidized at a low temperature (<100^{o}C). The oxidation process is rather slow, so as to ensure stabilization of the fiber by cross-linking to make it infusible. However, upon carbonization, relaxation of the molecules takes place, producing fibers with no significant preferred orientation. This process is not industrially attractive due to the lengthy

oxidation step, and because only low-quality carbon fibers with no graphitization are produced. These fibers are used as fillers with various plastics to form thermal insulation materials.

Carbon fibers from anisotropic mesophase pitch

High molecular weight aromatic pitches that are mainly anisotropic in nature are referred to as mesophase pitches. The pitch precursor is thermally treated above 350^{o}C to convert it to mesophase pitch, which contains both isotropic and anisotropic phases. Due to shear stresses occurring during spinning, the mesophase molecules orient parallel to the fiber axis. After spinning, the isotropic part of the pitch is made infusible by thermosetting in air at a temperature below its softening point. The fiber is then carbonized at temperatures up to 1000^{o}C. The main advantage of this process is that tension is not required during stabilization or graphitizition, unlike in the case of rayon or PAN precursors.

10.1.2.3 **Carbon Fibers from Rayon**

The conversion of rayon fibers into carbon fibers is a three-stage process:

1. Stabilization: Stabilization is basically an oxidative process that involves different steps. In the first step, between 25 -150^{o}C, there is physical desorption of water. The next step is a dehydration of the cellulose unit between 150 -240^{o}C. Finally thermal cleavage of the cyclosidic linkage and scission of ether bonds and some C-C bonds occurs via free radical reaction (240^{o}-400^{o} C) followed by aromatization.

2. Carbonization: Heat-treatment between 400 and 700^{o}C converts the carbonaceous residue into graphite-like layers.

3. Graphitization: Graphitization is carried out under strain at 700 -2700^{o}C to obtain high modulus fibers through a longitudinal orientation of the planes.

10.1.2.4 **Carbon Fibers from Phenolic Resins**

Micron-sized carbon fibers are synthesized from phenolic resin fibers such as Kynol [27] The carbon fibers prepared are typically in an activated form, which produces well developed mesopores for use in applications as high surface area adsorbents.

10.1.2.5 **Vapor-Grown Carbon Fibers**

Vapor grown carbon fibers (VGCFs) comprise of a large family of filamentous nanocarbons. They can be distinguished in terms of the arrangement of the graphene layers in their molecular scale structure: they can be “plate-like”, with near-parallel graphene layers that are approximately perpendicular to the fiber axis, or they can have the “fish-bone” microstructure with stacked cones of graphene planes. Sub-micron (50 to 200 nm diameter) VGCFs of the “fish-bone” structure approach the dimensions of MWNTs and are referred to as CNFs (see above) in this review. VGCFs and CNFs are generally grown by depositing carbon by the high temperature (typically in the 900 to 1200^{o}C range) decomposition of a hydrocarbon (usually methane) catalyzed by finely divided transition metal catalyst particles. Depending on the catalyst, different growth forms are found: one-directional growth (the fiber grows with the catalyst at the tip: "tip-mode" or at the rear "rear-mode"), bi-directional growth (simultaneous growth in two opposite directions with the catalyst particle in the middle), multi-directional growth (more than two fibers grow out of one catalyst particle: "octopus fiber") as well as branched growth (a larger catalyst particle explodes during the growth resulting in a branched growth of a number of smaller fibers).

10.1.3

Chemical Modification/Derivatization Methods

The development of carbon nanotube-based nanocomposites was initially impeded by the inability to uniformly disperse the nanotubes in the polymer matrix due to a lack of compatibility

between the chemical structures of the two components. Compatibility has now been achieved in many cases by chemical modification or derivatization of the nanotube sidewalls. Some degree of derivatization or functionalization is achieved following nanotube chemical vapor deposition synthesis by the adsorption of electron-withdrawing oxygen on the tube walls and the net formation of acidic –COOH groups as a result of acid purification procedures to remove the catalyst and support as well as amorphous/microcrystalline carbon produced as impurity during synthesis. Derivatization also allows for solubility of the nanotubes in specific organic solvents and in water, and enables covalent interaction between the nanotube sidewalls and the polymer side groups, leading to better adhesion at the nanotube-polymer interface and the formation of nanocomposites with exceptionally high mechanical strength.

Two approaches have been utilized to achieve derivatization. The first has involved chemical modification of the nanotube surface, while the second has involved chemical interaction with various defects on the graphitic walls of the tubes and at the tube ends. The surface modifications reported in the literature for nanotubes have been somewhat similar to that achieved on the C_{60} fullerene, although closer examination has revealed sizable differences in reaction type, location and symmetry of the chemistry involved. On the other hand, defect site functionalization involves chemistry that is not applicable to the fullerenes because they are free from similar defects.

A large amount of literature exists on the chemical modification of carbon nanotubes, but detailed understanding is still lacking because of the paucity of theoretical calculations and simulations. Several research groups have reported the successful functionalization of both SWNTs and MWNTs [28-33]. These modifications have involved the direct attachment of functional groups like fluorine or hydrogen to the graphitic walls, reactions with nitrenes and

carbenes, or the use of carboxylic acid groups bonded to the nanotube walls produced on oxidation of shortened and unbundled tubes. Chen et al. [28] first reported the use of the acid groups for attaching long alkyl chains to SWNTs via amide linkages. There is now ample evidence that nanotube-bound carboxylic acid groups are the sites at which a variety of functional groups for the solubilization of both shortened and full length carbon nanotubes are attached. For example, it has been shown that esterification of the carboxylic groups can be used to functionalize and solubilize nanotubes of any length [34-36]**.** Mono-, di- and tri-nitroanilines have been recently attached to SWNTs via carboxylic groups and reaction with thionyl chloride [37]. Multiple sulfonate, $-OSO_3H$, groups have been chemically introduced on MWNTs [38] and compounded with emeraldine–base polyaniline to form composites with enhanced electrical conductivity and thermal properties due to concomitant doping of the polymer by the sulfonated nanotubes in the course of composite fabrication. Solubilization in water has been achieved by wrapping with polymers like polyvinyl pyrollidone (PVP) [39] and polyethylene imine (PEI) [40,41]**,** and by reaction with glucosamine [42]. SWNTs have also been effectively dispersed/solubilized in water by their sonication in the presence of the single-stranded version of the central polymeric molecule in biology, DNA [43] and enzymes suitable for use in biosensing and biofuel cells [44,45]. In the case of DNA, molecular modeling suggests that single stranded DNA binds to SWNTs through π-stacking interactions that result in helical wrapping to the nanotube sidewalls [43].

For carbon nanofibers and conventional micro-fibers, the key to the formation of high strength polymer composites is the adhesion of the fibers to the polymeric matrices. The adhesion forces are still not fully understood, primarily because the surfaces of the carbon fibers are complex with respect to their structure and chemistry. The forces result from different

interactions across the interface, which include dispersive interactions of the van der Waals type involving London forces, non-dispersive interactions involving acid-base processes, and covalent chemical bonds. Typical surface treatment involves oxidation treatment in air or ozone to form oxygen containing functional groups. Alternative approaches involve the use of plasma-induced surface modification [46] or electrochemical anodization in an acidic electrolyte such as phosphoric acid [47]. Surface groups produced consist of basic pyrone-like structures, neutral quinines, and acidic carboxylic groups. The strength of the composites formed has been correlated with the surface roughness observed by means of detailed scanning electron and tunneling microscopies [48]. Recently, microwave and ultraviolet irradiation techniques have been used to functionalize SWNT sidewalls with acid ($-SO_3^-$ H^+) and hydroxyl (OH^-) groups [49,50], respectively. Interestingly, hydroxyl group functionalization of SWNTs dispersed with surfactants in water using 254 nm uv-radiation is diameter and nanotube-type sensitive, and can, therefore, provide a method for the separation of metallic from semiconducting SWNTs.

10.1.4

Polymer Matrices

As discussed in section 10.1.3, PVP and DNA have been used to wrap and water-solublize SWNTs. For specific actuator, electrical and electro-optic applications, SWNTs have been wrapped by piezoelectric polyvinylidene fluoride and trifluoroethylene co-polymer [51] or with conjugated polymers [52,53]. The conjugated polymer used to form a composite with MWNTs and an electron-transport layer in light emitting diodes is poly(m-phenylene-vinylene-co-2,5-dioctyloxy-p-phenylene-vinylene) (PmPV) [54]. Wrapping coupled with electron doping has been achieved with polyethylene imine (PEI) to form p-n junction devices [40, 41].

Thermosetting epoxy resins are widely used in the fabrication of carbon fiber-based composites for aerospace applications. High temperature amorphous thermoplastics with high impact strength, which include polycarbonate, polysulphones, polyetherimide, polyethersulphones and partially crystalline polyetheretherketone, are alternative polymers bearing functional groups that can undergo selective interactions with the functional groups formed on the carbon fiber surface. For the fabrication of electrically conductive bipolar plates for proton exchange membrane fuel cells, chemically passive polymers such as polypropylene are preferred [55], whereas poly(acrylonitrile-butadiene-styrene) (ABS), polystyrene (PS), and high impact polystyrene (HIPS) are used in the fabrication of composites for applications where high impact strength is required.

10.2 Polymer Matrix Composites

10.2.1 Fabrication

In contrast to short carbon fiber reinforced thermoplastics, which are processed by conventional melt processing techniques, the limited availability, high cost, and the difficulties encountered in achieving a high degree of dispersion continue to present challenges in the manufacture of carbon nanotube composites. Currently, most carbon nanotube-reinforced composites are prepared in the laboratory using the so-called solution-evaporation method [56-59]. The solution and curing agent may vary with different polymer matrices. The general procedure involves dissolving the polymer to form a first solution, dispersing/dissolving SWNTs or MWNTs to form a second solution, mixing the two solutions with the aid of ultrasonication, and finally casting films or solid parts from the mixed solution and subjecting them to a curing process.

In order to achieve more uniform nanotube dispersion in composites, Haggenmueller et al. [60] developed an alternative melt mixing method consisting of a combined solution-evaporation technique to prepare a thin SWNT-polymer film followed by repeated compression molding of the latter. The resulting product was reported to yield compositionally uniform films. Using a small batch mixer, adequately dispersed nanotube composites from polypropylene (PP), poly(acrylonitrile-butadiene-styrene) (ABS), polystyrene (PS), and high impact polystyrene (HIPS) have been prepared [61].

Another technique, known as the dry powder mixing method, has been employed by Cooper et al. to produce nanotube-reinforced polymethyl methacrylate (PMMA) composites [62]. Like most of the currently used fabrication methods for nanotube-based polymer composites, this technique is a combination of several protocols including solution-evaporation, sonication, kneading, and extrusion. More specifically, these workers used ultrasonic techniques to blend carbon nanotubes with PMMA particles, and the blend was later extruded to orient the nanotubes. Yang et al. [63] prepared small-scale batches of ABS nanocomposites without the use of solvents or ultrasonic techniques with good dispersion of the nanotubes.

Another method used known as Extrusion Free-form Fabrication (EFF) belongs to a family of manufacturing processes in which different parts are built in layers. It is a solid freeform fabrication (SFF) technique, where the feed is in the form of a solid. A 3-D computer model is generated and transferred to a computer supported by the SFF software. The model is sliced into layers and the geometrical information is fed for each layer of the part, which is then built layer by layer. Carbon nanotubes and carbon fibers are very suitable for this technique because they do not clog the nozzles. In EFF, the solid feed material is placed in a heated head and is forced through a nozzle by a piston into a specified shape. Once a layer is complete, the

support base is lowered in the z-direction. The EFF process helps in tailoring the alignment of fibers in composites since the extrusion path can be changed in different parts. A study of SWNTs and VGCFs mixed with ABS polymer using Banbury mixing and EFF was conducted by Shofner et al. [64]. A high degree of dispersion of the nanotubes and fibers was achieved without porosity. For both VGCF and SWNTs, sizable tensile strength and modulus improvements were observed.

A recently reported method for producing novel SWNT-polymer nanocomposites involved the use of self-assembled SWNT nanopaper films produced by vacuum-filtration of SWNTs dispersed with surfactants in aqueous solution. The free-standing nanopaper films were soaked in a polymer resin followed by drying and hot-pressing to form a composite in which the polymer is intercalated into the free volume between the SWNT bundles [65].

10.2.2

Mechanical and Electrical Property Modification

Carbon fibers have been used in both thermosetting and thermoplastic polymer composites for a long time, imparting higher modulus and strength and lighter weight than glass fibers (see comparison of properties in Table 2-1), electrical and thermal conductivity, chemical resistance, and reduced wear. Specific examples of their effects on thermoplastics and thermosets may be found in the handbooks and general references listed in Chapters 1 and 2. However, with the discovery of the near-molecular scale carbon nanotubes and advances in understanding their mechanical and electrical properties over the past decade, new nanocomposites based on these novel materials are now possible. Experimental estimates of SWNT strength are in the range of 13-52 GPa and tensile modulus is of the order of 1TPa [66-68], values that are much higher than those for carbon fibers (also see Table 2-1). Electrical resistivity and thermal conductivity

measurements along the length of a bundle of SWNTs indicate values of approximately 10^{-4} Ω cm and 200 W/m/K, respectively [69]. Two main issues to be addressed for effective use of nanotubes in composites are alignment and uniform dispersion in the polymer matrix. This is because SWNTs form in bundles and tend to agglomerate with weak van der Waals forces. A great deal of work has been done aimed at overcoming this and several surfactant-based and organic solutions have been identified to disperse and chemically functionalize carbon nanotubes [70-75]. Another issue being addressed is that of interfacial bonding between the nanotubes and the polymer matrix, which affects the efficiency of load transfer across the nanotube–polymer interface.

Several studies on the characterization and fabrication of carbon nanotube-polymer nanocomposites have highlighted the important roles of the parameters discussed in Chapter 2 (such as, orientation, dispersion, and interfacial adhesion) in determining the properties of the composites. Jia et al. [76] used an *in situ* process for the fabrication of a PMMA/MWNT composite. An initiator was used to open up the π bonds of the MWNTs in order to increase the linkage with the PMMA. The formation of C-C bonds results in a strong interface between the nanotubes and the PMMA. For samples mixed with carbon nanotubes, smaller amounts of initiator are required and improved mechanical properties are obtained. In another example, simple sonication of SWNTs in solvents such as DMF was found not to yield good dispersion according to the method of Haggenmueller et al. [60] introduced above; therefore repetitive film forming with sonication and drying followed by mixing at higher temperatures and pressure was required to obtain a uniform dispersion (Figure 10-3). The melt could be formed as a film or spun into fibers. With the introduction of SWNTs, the draw ratio is reduced and a roughened surface results for the fiber, as viewed under an optical microscope. Mechanical and electrical

properties are improved with increasing SWNT concentration. Melt processing, therefore, appears to be a very effective method for realizing targeted mechanical and electrical properties in the bulk composites.

Insert Fig. 10-3

Nanotubes were found to be oriented in the extrusion flow direction, increasing the impact strength of the PMMA nanocomposites formed by the method of Cooper et al. [62]. Jin et al. [73] proposed a method of casting a suspension of carbon nanotubes in a solution of thermoplastic polymer polyhydroxyaminoether (PHAE) in chloroform. In this study, it was found that the resulting nanocomposites could be stretched up to five times their original length without breaking under varying mechanical loads at a temperature range of 90 - 100^{o} C. The nanotubes were aligned inside the polymer matrix, as indicated by x-ray diffraction and transmission electron microscopy (Fig.10-4). Highly aligned SWNTs in polystyrene and polyethylene have been obtained by Haggenmueller et al. [77] using a twin-screw extruder. Composite fibers obtained with 20% nanotube loading showed a 450% increase in elastic modulus relative to polyethylene fibers.

Insert Fig. 10-4

Carbon nanotube-polystyrene nanoporous membranes with aligned MWNTs traversing the membrane thickness have recently been fabricated by Hinds et al.[78]. The structures formed are depicted in Fig. 10-5. These nanoporous membranes have the ability to gate molecular

transport through the cores of the nanotubes, offering potential applications in chemical separations and sensing.

Insert Fig. 10-5

Carbon nanotubes have been introduced into conducting polymers, such as poly(m-phenylene-vinylene-co-2,5-dioctyloxy-p-phenylene-vinylene) (PmPV), as an electron transport layer in organic light emitting diodes. Their introduction led to a significant increase in efficiency and an increase in electrical conductivity by four orders of magnitude [52]. The normalized photoluminescence intensity and electrical conductivity as a function of MWNT loading for these composites are shown in Fig. 10-6. Helical wrapping of the conducting polymer around the nanotubes has been modeled Lordi and Yao [79]; such a model is depicted in Fig. 10-7.

Insert Figs. 10-6 and 10-7.

10.3

Cost/Availability

Tables 10.1 and Table 10.2 list U.S. and international companies that supply nanotubes, related nanocarbon materials, and carbon fibers. The prices at the time of writing are also given where available. Note that the cost of pure SWNTs still remain very high.

Insert Table 10.1

10.4

Environmental/Toxicity Considerations

Fullerene soot with a high SWNT content was tested to assess its biochemical activity [80]. The dermatological trial results did not show any signs of health hazards related to skin irritation and allergic risks. To determine whether carbon nanotubes and in particular SWNTs

can induce any significant health hazards, Huczko et al. [81] performed tests routinely used in the patho-physiological testing of asbestos-induced disease. No abnormalities of pulmonary function or measureable inflammation were detected in guinea pigs. However, more recent studies by Poland et al. [82] showed that on exposure of the mesothelial lining of the chest cavity of mice to long multiwalled carbon nanotubes resulted in asbestos-like pathogenic behavior, but the study does not reveal whether the nanotubes are able to persist long enough to reach the lung tissue after inhalation. In another recent experiment, mice breathed air containing 40 μm long multiwall carbon nanotubes with very little inflamatory or fibrogenic effects [83], most likely because they do not persist in the body as long as asbestos fibers do. Therefore, as also discussed in Chapter 1, care should be exercised with the use of nanofillers like the carbon nanotubes since their toxicology has not yet been fully explored.

Carbon micro-fibers easily form dust during handling and get dispersed in the atmosphere. The fibers also tend to stick to the human skin or mucous membranes causing pain and itching. Protective gear for skin, eyes and throat therefore need to be worn to prevent these hazards. Local air exhausts and ventilators can help in removing the dust. Protective cream or gloves need to be used during handling of the fibers. Since the fibers are electrically conductive, care should be taken around exposed electrical circuits and outlets. Some general purpose grades of carbon fiber may ignite at temperatures lower than 150^{o}C in the presence of air or fuel. If heated to higher than 400^{o}C in the presence of air or fuel, the fibers burn slowly burns but stops burning as soon as the burning fuel is removed.

Carbon fiber waste should be treated as industrial rather than household waste. Local governments may have their own local codes for disposing carbon fiber wastes. On the positive side, carbon is thought to have good compatibility with human tissue. Carbon fibers and fiber

composites have therefore been used extensively as components for artificial body parts and devices.

10.5

Applications

Carbon fiber composites are widely used in the aerospace industry, and with the decreasing price of the fibers they are increasingly being used in automobile, marine, sports and construction industries. In aerospace, epoxy/carbon composites are used in the Space Shuttle payload door, its manipulator arm, and its booster tail and fins. There is extensive use of carbon fiber/epoxy composites in helicopter structures as well as in commercial aircraft. Carbon fiber composites have started to be used in automobiles, mainly for saving weight. Here, carbon nanotubes, in particular cost-effective MWNTs and CNFs, are being used in car bumpers and gasoline tanks. In the future, with decreasing prices, nanotubes could be used in these composites to obtain much higher strength and at much lower loading levels.

In addition to their primary function as mechanical property modifier, the high electrical conductivity of carbon fibers provides carbon-based composites with static dissipation and radio frequency shielding characteristics. This opens up a whole range of applications and with carbon nanotubes this can be achieved at enormously low loading levels. One application with future potential is the use of carbon nanotubes to fabricate bipolar interconnecting flow-field plates for fuel cells [55]. A whole range of futuristic applications in nanoelectronics is also emerging with SWNTs and MWNTs. The high thermal conductivity of carbon fibers and the diamond-like thermal conductivity of SWNTs make their composites highly attractive for heat sinks in electronics. The low density of the composites compared to copper makes them even more attractive for aerospace electronics.

Tab. 10.1: List of carbon nanotube and related material suppliers.

Company	Products	Price*	Location
Applied Science Inc.	MWNTs and CNFs (Nanofibers)	CNFs $65/lb	Cedarville, OH, U.S.A.
Bucky USA	Fullerenes, MWNTs and SWNTs	MWNT:$60-150/g SWNT: $150/g	Houston, TX, USA
Carbolex	SWNTs	$100/g	Broomall, PA, USA
Carbon Solutions	SWNTs	$50-400/g	Riverside, CA, USA
Catalytic Materials Ltd	Suppliers of Nanofibers and MWNTs	MWNT: $ 55-40/g	Pittsboro, NC, USA.
Hyperion Catalysis International	MWNTs	N/A	Cambridge, MA,USA
Hanwha Chemical Corp.	MWNTs & SWNTs	N/A	Jung-Ku, Seoul, Korea
MER Corporation	Various (from fullerenes to SWNTs)	MWNT: $10-25/g SWNT: $60/g	Tucson, AZ,USA
Mitsui XNRI	MWNTs	N/A	Tokyo, Japan
NanoCarbLab	SWNTs	$60-380/g	Moscow, Russia
Nanocs International	MWNTs	MWNT: $80/g SWNT:$ 350/g	New York, USA
Nanocyl	MWNTs and SWNTs	N/A	Namur, Belgium
Nanolab	MWNTs	MWNT $125-165/g	Newton, MA, USA.
NanoMaterials	Inorganic nanotubes and nanospheres	N/A	Longmont, CO, U.S.A.
Nanomirae	Nanofibers – Herringbone and spiral MWNTs	N/A	Guro-gu, Seoul Korea
Rosseter Holdings Ltd	MWNT, SWNTs and	$ 20/g MWNT	Limassol, Cyprus

	Nanohorns		
SouthWest Nano Technologies, Inc.	SWNTs	$ 500/g SWNT	Norman, OK, USA.
Sun Nanotech	MWNTs	N/A	Jiangxi, P.R. China
Tsinghua-Nafine Nano-Powder	MWNTs	N/A	Beijing, P.R.China
Unidym	HIPCO SWNTs		Menlo Park, CA USA.
Xintek Inc	Nanotube Materials (MWNTs/SWNTs)	N/A	Chapel Hill, NC, USA

* Prices when available are given at the time of writing. Price ranges reflect purity and quantities.

Table 10-2: List of carbon fiber suppliers.

Company	**Products**	**Trademark**	**Location**
Amoco Fabrics and Fibers	pitch-type fibers	THORNEL	USA
Asahi Kasei Corporation		HI CARBOLON	USA
Toho Rayon Co.	PAN-type fibers	BESFIGHT	Japan
Toray	PAN-type fibers	TORACA	Japan
Mitsubishi Rayon	pitch-type fibers	Dialead	Japan
NGF	pitch-type fibers	N/A	
BASF	PAN-type fibers	CELION	USA
Hercules	PAN-type fibers	MAGNAMITE	USA

SGL Carbon	SIGARTEX	Germany/USA
Zoltex	PANEX	USA
RK Carbon Fibers Ltd	CURLON	UK
Courtauld Ltd	COURTELLE	UK
Ashland	CARBOFLEX	USA

Figure Captions

Fig. 10-1: Armchair (*n,m*=5,5) –top– , zig-zag (9,0) –middle– , and chiral (10,5) single wall nanotubes. All armchair tubes are metallic, whereas only 1/3 of the chiral tubes has metallic character. (*n,m*), the roll up vectors are proportional to the tube diameter. The dangling bonds at the tube ends are saturated by hemispherical fullerene caps.

Fig. 10-2: Molecular structures of polymeric precursors for micron size carbon fibers.

Fig. 10-3: Optical micrographs of a SWNT–PMMA nanocomposite having 1 wt% purified soot: (a) only sonication and drying. The as-cast film is repeatedly subjected to hot pressing (180°C, 3000 lb, 3 min) and is shown here after; (b) 1 cycle; (c) 5 cycles; (d) 20 cycles. (Reproduced with permission from Elsevier [60]).

Fig. 10-4: (a) TEM image of an internal fracture surface of a composite about 90 nm in thickness after being microtomed parallel to the stretching direction. The nanotubes are aligned parallel to the stretching direction.and fiber pull-out is observed. In some areas, nanotubes bridge the microvoids (or microcracks) in the matrix and presumably enhance the strength of the composite. (b) Cross-sectional view of the same composite microtomed perpendicular to the stretching direction. Cross sections of the nanotubes and nanoparticles are observed. (Reproduced with permission from the American Institute of Physics [73]).

Fig. 10-5: A. As-grown aligned MWNTs produced by a Fe-catalyzed chemical vapor deposition process. B. Schematic of a target membrane structure. C. Scanning electron micrograph of MWNT-polystyrene composite membrane. Scale bar represents 2.5 microns. (Reproduced with permission from Science AAAS [78]).

Fig. 10-6: Normalized photoluminescence (PL) intensity and conductivity for conducting polymer-nanotube composite films as a function of nanotube to polymer mass ratio. (Reproduced with permission from the American Institute of Physics [52]).

Fig. 10-7: (a) Model of *cis*-poly(phenylacetylene) wrapped perfectly around a (10,10) SWNT. (b) Model of *trans*-poly(phenylacetylene), which has a slightly smaller diameter, distorts around the SWNT and wraps more tightly. (Reproduced with permission from Journal of Materials Research [79]).

Figures

Fig. 10-1

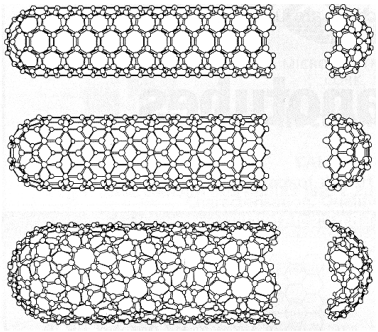


Fig. 10-2

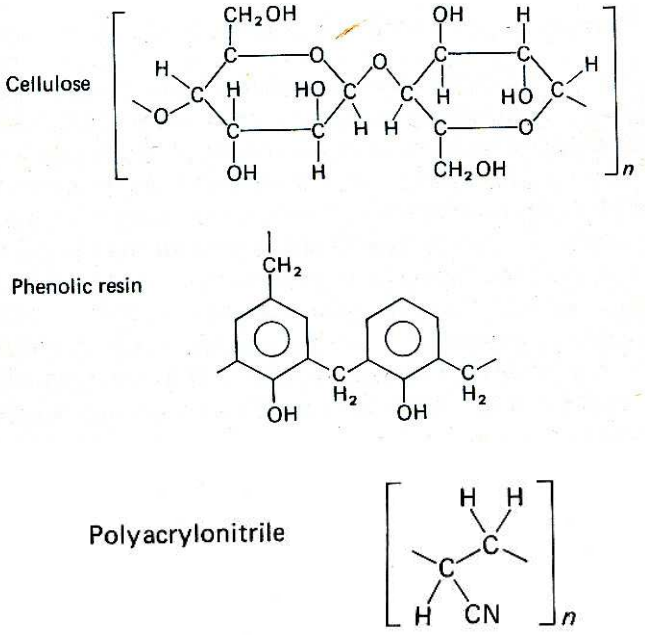


Fig. 10-3

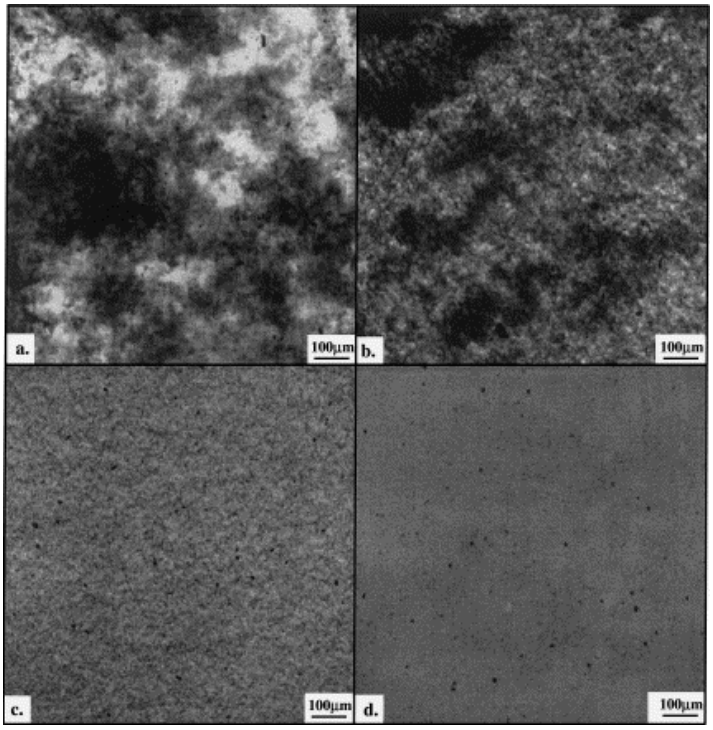


Fig. 10-4

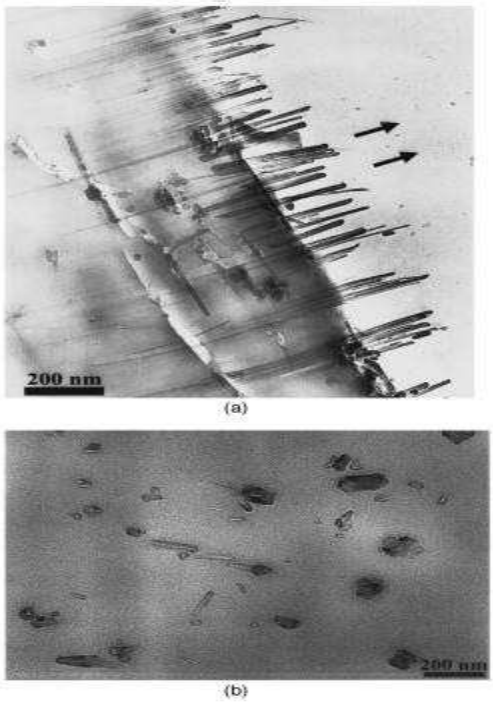


Fig. 10-5

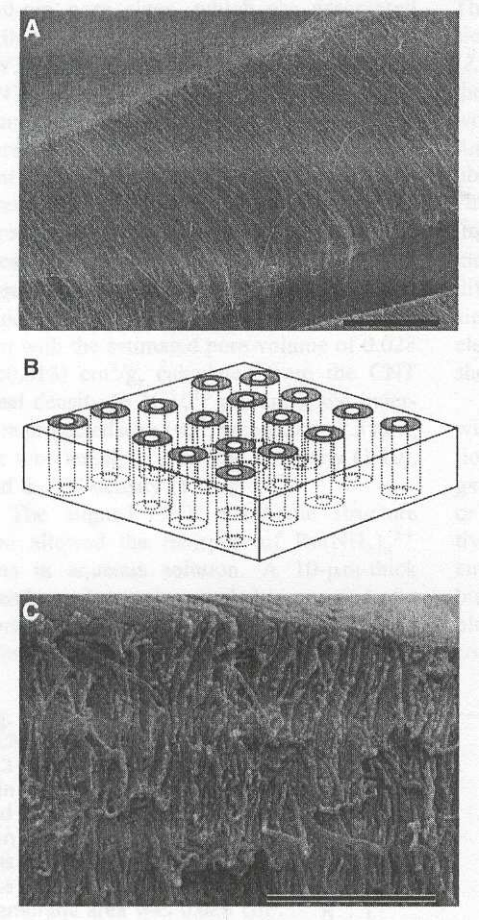


Fig. 10-6

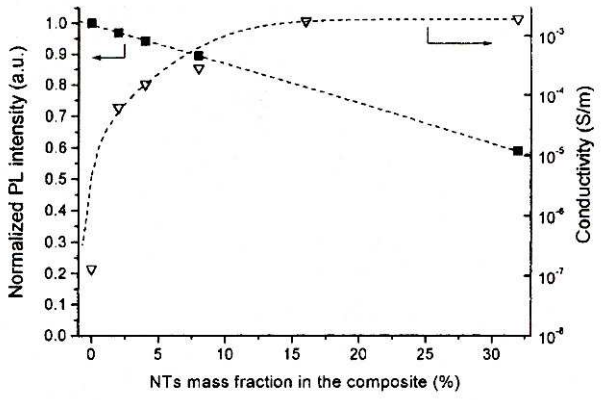
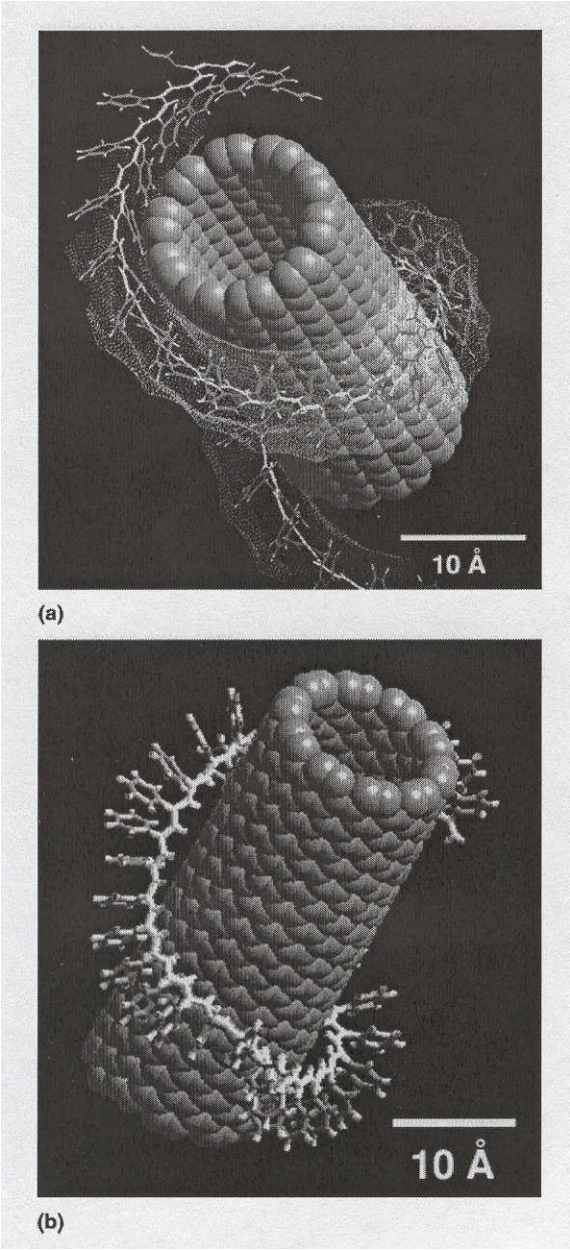


Fig. 10-7



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