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Smart Materials and Structures Based on Carbon Nanotube Composites

Sang-ha Hwang[1], Young-Bin Park[1]*, Kwan Han Yoon[2] and Dae Suk Bang[2]
[1]*School of Mechanical and Advanced Materials Engineering*
Ulsan National Institute of Science and Technology (UNIST)
[2]*Department of Polymer Science and Engineering*
Kumoh National Institute of Technology
Korea

1. Introduction

Since the first discovery of carbon nanotubes (CNTs) in 1991, CNTs have generated enormous research activities in many areas of science and engineering due to their combined exceptional mechanical, thermal and electronic properties. These properties make nanotubes ideal, not only for a wide range of applications but also as a test-bed for fundamental scientific studies (Baughman *et al.*, 2002). They can be described as a graphite sheet rolled up into a nanoscale tube. Two structural forms of CNTs exist: single-walled (SWCNTs) and multi-walled (MWCNTs) nanotubes. CNT lengths can be as short as a few hundred nanometers or as long as several micrometers. SWCNT have diameters between 1 and 10 nm and normally capped ends. In contrast, MWCNT diameters range from 5 to a few hundred nanometers because their structure consists of many concentric cylinders held together by van der Waals forces. CNTs are synthesized in a variety of ways, such as arc discharge, laser ablation, high pressure carbon monoxide (HiPCO), and chemical vapor deposition (CVD) (Dresselhaus, 1997). CNTs exhibit excellent mechanical, electrical, thermal and magnetic properties. The exact magnitudes of these properties depend on the diameter and chirality of the nanotubes and whether their structure is single- or multi-walled. Fig. 1 shows a segment of a single graphene plane that can be transformed into a carbon nanotube by rolling up into a cylinder. To describe this structure, a chiral vector is defined as $OA = na_1 + ma_2$, where a_1 and a_2 are unit vectors for the hexagonal lattice of the graphene sheet, n and m are integers, along with a chiral angle θ, which is the angle of the chiral vector with respect to the x direction. Using this (n, m) scheme, the three types of nanotubes are characterized. If $n = m$, the nanotubes are called ''armchair". If $m = 0$, the nanotubes are called ''zigzag". Otherwise, they are called ''chiral". The chirality of nanotubes has significant impact on their transport properties, particularly the electronic properties. For a given (n, m) nanotube, if ($2n + m$) is a multiple of 3, then the nanotube is metallic, otherwise the nanotube is a semiconductor. Each MWCNT contains a multi-layer of graphene, and each layer can have different chiralities, so the prediction of its physical properties is more complicated than that of SWCNT (Jin & Yuan, 2003).

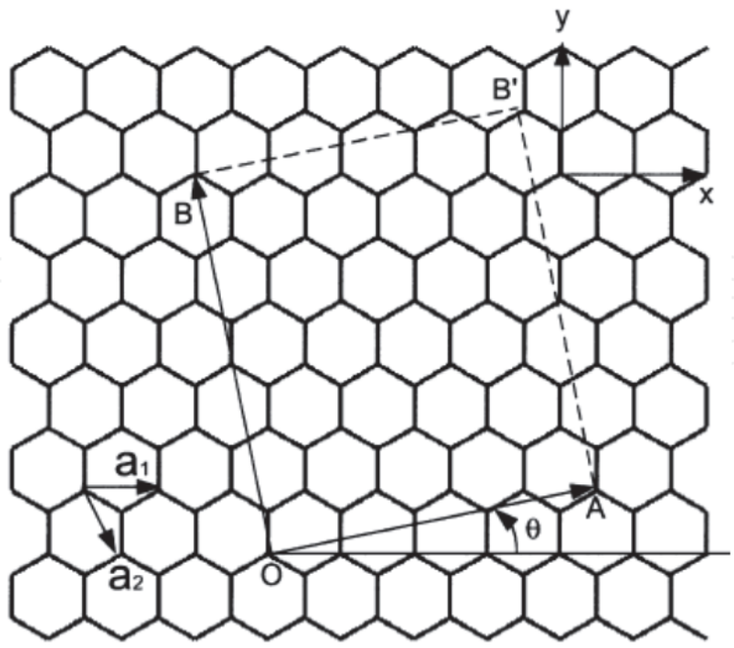


Fig. 1. The graphite plane of nanotube surface coordinates (Jin & Yuan, 2003).

The basic structure of CNTs is comprised of sp^2 carbons. This sp^2 structure provides CNTs with higher mechanical properties compared to any materials, even diamonds. It is well known that the mechanical properties of CNTs exceed those of any existing materials. Although there is no consensus on the exact mechanical properties of CNTs, theoretical and experimental results have shown exceptional mechanical properties of CNTs with Young's modulus of 1.2 TPa and tensile strength of 50–200 GPa (Coleman *et al.*, 2006).
Other excellent physical properties of CNTs have also attracted much attention. The properties are summarized and compared with other carbon allotropes in Table 1. Because of their unique properties, many promising applications and potential practical applications have been reported, such as field emission materials, catalyst support, electronic devices, nanotweezers, reinforcements in high performance composites, supercapacitors, hydrogen storage and high sensitivity sensors and actuators. These are just a few possibilities that are currently being explored. As research continues, new applications will also develop (Dresselhaus *et al.*, 2004).

Property	Graphite	Diamond	Fullerene	CNTs	
				SWCNT	MWCNT
Specific gravity (g cm^{-3})	1.9-2.3	3.5	1.7	0.8	1.8
Electrical conductivity (S cm^{-1})	4000	10^{-2}-10^{-15}	10^{-5}	10^{2}-10^{6}	10^{3}-10^{5}
Electron mobility (cm^2 V^{-1} s^{-1})	2.0	1800	0.5	~10^{5}	10^{4}-10^{5}
Thermal conductivity (W $m^{-1}K^{-1}$)	298	900-2320	0.4	6000	2000
Coefficient of thermal expansion (K^{-1})	-1×10^{6}	$(1\text{-}3) \times 10^{6}$	6.2×10^{-5}	~0	~0
Thermal stability (in air) (K)	450-650	<600	600	>600	>600

Table 1. Different physical properties of carbon allotropes (Ma *et al.*, 2010)

2. Processing of carbon nanotube composites

CNT-based polymer composite materials are being utilized in an increasing number of applications including automotive, aerospace, defence, sporting goods and infrastructure sectors. This is due to their high durability, high strength, light weight, design and process flexibility, *etc*. Thermosets such as epoxy, unsaturated polyester, gels, as well as thermoplastics have been used as the matrix. The conductivity, strength, elasticity, toughness, and durability of formed composites may all be substantially improved by the addition of nanotubes.

Especially electrically conductive CNT-polymer composites are used in anti-static packaging applications, as well as in specialized components in the electronics, automotive, and aerospace sectors. The incorporation of conductive filler particles into an insulating polymer matrix leads to bulk conductivities at least exceeding the anti-static limit of 10^{-6} S/m. Common conductive fillers are metallic or graphitic particles in any shape (spherical, platelet-like or fibrous) and size. However, the incorporation of CNTs allows lower percolation threshold compared to other conductive fillers (Fig. 2). The use of CNTs as a conductive filler in polymers is their biggest current application (Bal & Samal, 2007).

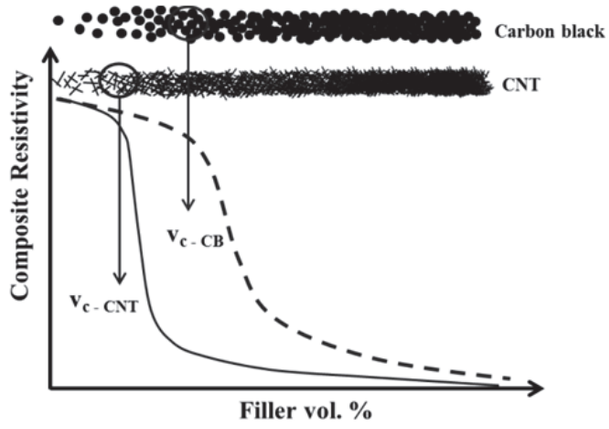


Fig. 2. Illustration of CNT network percolation (v_c) compared with carbon black

The effective utilization of CNTs in composite applications depends strongly on the ability to homogeneously disperse them throughout the matrix without destroying their integrity. Therefore, it has become clear that the issues of dispersion, alignment, and stress transfer are crucial, and often problematic at nanoscale. However, in order to be able to utilize CNTs and their properties in real-world applications, CNT-based nanocompsites provide a pathway to realize the properties of these fascinating nanostructures at macroscopic levels by bridging over a range of length scales.

2.1 Carbon nanotube dispersion

The potential of using nanotubes as a constituent of polymer composites has not been presently realized mainly because of the difficulties associated with dispersion and processing. High aspect ratio, combined with high flexibility, increase the possibility of nanotube entanglement and close packing. The low dispersity comes from the tendency of pristine nanotubes to assemble into bundles or ropes like shown in Fig. 3 (Thess *et al.*, 1996). Thus, a significant challenge in developing high-performance CNT-polymer composites is to

introduce the individual CNTs in a polymer matrix in order to achieve better dispersion and alignment and strong interfacial interactions, to improve the load and electron transfer across the CNT-polymer matrix interfaces.

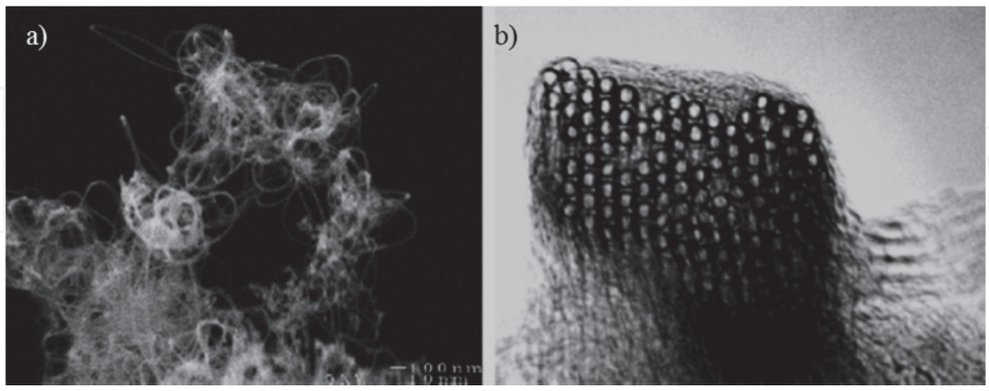


Fig. 3. (a) SEM image of entangled SWCNT agglomerates and (b) TEM image of a SWCNT bundle (Thess *et al*., 1996).

2.1.1 Mechanical dispersion of carbon nanotubes

Ultrasonication

Although in most cases, it is very difficult to get a homogeneous dispersion of the CNTs in the polymeric matrix, ultrasonication is a very effective method of dispersion and de-agglomeration of CNTs, as ultrasonic waves of high-intensity ultrasound generates cavitation in liquids. There are two major methods for delivering ultrasonic energy into liquids, the ultrasonic bath (Fig. 4. (a)) and the ultrasonic horn (Fig. 4(b)). Ultrasonication disperses solids primarily through a microbubble nucleation and collapse sequence. The ultrasonication bath has a higher frequency (40–50 kHz) than cell dismembrator horns (25 kHz). Ultrasonication of fluids leads to three physical mechanisms: cavitation of the fluid, localized heating, and the formation of free radicals. Cavitation, the formation and implosion of bubbles, can cause dispersion (Lu *et al.*, 1996).

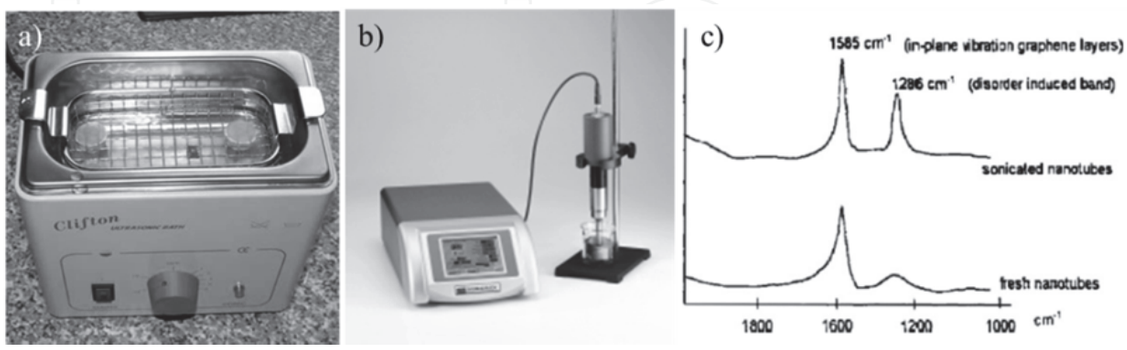


Fig. 4. (a) Bath type, (b) horn type sonicator and (c) Raman spectra of CNTs before and after sonication

However, ultrasonication affects not only CNT dispersion but also its length and diameter (Fig. 4 (c)). After reducing their lengths during ultrasonication, SWCNTs rearrange into

superropes. These superropes have diameters more than 20 times the initial bundle diameter (Shelimova *et al.*, 1998). In MWCNTS, ultrasonication creates expansion and peeling or fractionation of MWCNT graphene layers. The destruction of MWCNTs seems to initiate on the external layers and travel towards the center. It has been reported that the nanotube layers seem quite independent, so MWCNTs would not only get shorter, but actually thinner with time (Lu et al., 1996). There have been attempts to develop less destructive ultrasonication methods. One example is ultrasonication with diamond crystals, a method that reportedly destroys the SWCNT bundles but not the tubes. Raman spectra showed typical SWCNT peaks even after 10 hours of treatment with this method (Haluska *et al.*, 2001).

Ball Milling

Ball milling is a method that is usually used to grind bulk materials into fine powder. During milling, a high pressure is generated locally due to the collision between the rigid balls in a sealed container (Fig. 5). Cascading effect of balls reduces the size of material to fine powder. Balls are usually made by ceramic, flint pebbles and stainless steel.

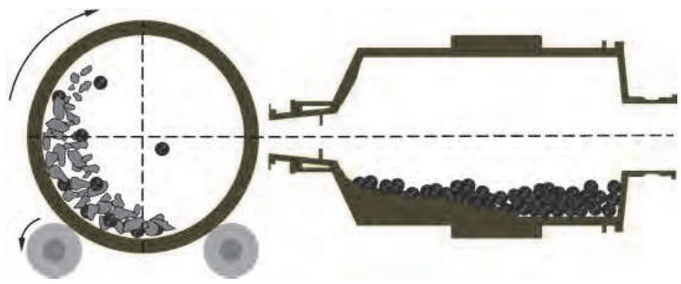


Fig. 5. Schematics of ball milling technique

Ball milling has been successfully applied to CNT dispersion into polymer matrices. To obtain narrow length and diameter distributions of CNTs and to open the nanotubes for improved sorption capacity for gases, ball-milling is a very useful method (Awasthi *et al.*, 2002). However, it has also been observed that a large amount of amorphous carbon is created which clearly indicates that the tubes are damaged in different ways and that ball-milling is a destructive method (Jia *et al.*, 1999).

Calendering (Three-Roll mill)

Calendering, also commonly known as three-roll-milling (Fig. 5 (a)) is a dispersion technique that employs both shear flow and extensional flow created by rotating rolls of different speed to mix and disperse CNTs or other nanoscale fillers into polymers or other viscous matrixes. The first and third rollers (usually called the feed and apron rolls, respectively) in Fig. 5 (b) rotate in the same direction while the center roller rotates in the opposite direction. In order to create high shear rates, angular velocity of the center roll must be higher than that of feed roll ($\omega 2 > \omega 1$). As the resin suspension is fed into the narrow gap (δ) between feed and center rolls, the liquid mixture flows down covering (essentially coating) the adjacent rolls through its surface tension under intensive shear forces. At the end of each subsequent intended dwell time, the processed resin suspension is collected by using a scraper blade in contact with the apron roll. This milling cycle can be repeated several times to maximize dispersion.

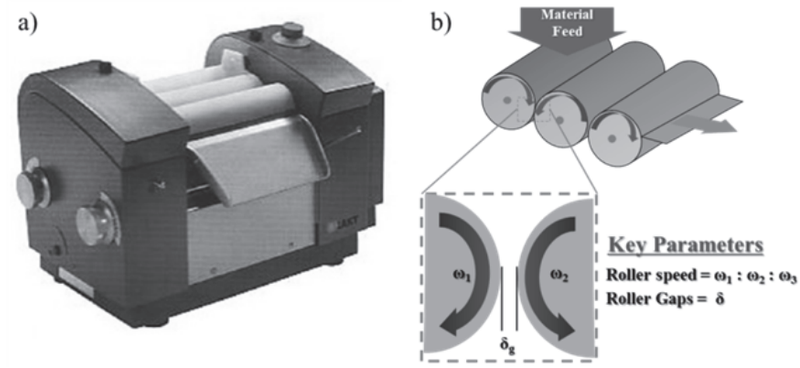


Fig. 6. (a) Calendering machine (three-roll mill) used for CNT dispersion into a polymer matrix and (b) general schematic diagram of its mechanism.

One of the unique advantages of this technique is that the gap width between the rollers can be mechanically or hydraulically adjusted and maintained, thus it is easy to obtain a controllable and narrow size distribution of particles in viscous materials. In some operations, the width of gaps can be decreased gradually to achieve the desired level of particle dispersion (Viswanathan *et al.*, 2006). A typical calendering machine and its principle are shown schematically in Fig. 5. The employment of a calender to disperse CNTs in a polymer matrix has become a very promising approach to achieve relatively good CNT dispersion according to some recent reports (Thostenson & Chou, 2006a).
However, the fed material should be in a viscous state when mixed with CNTs, thus this tool may not be applied to disperse CNTs into thermoplastic matrices, such as polyethylene, polypropylene and polystyrene. In contrast, CNTs can be conveniently dispersed into the liquid monomer or oligomer of thermosetting matrices, and nanocomposites can be obtained via *in situ* polymerization.

Extrusion (Melt Compounding)

Extrusion is a popular technique used to disperse CNTs into solid polymers, including most thermoplastics, where thermoplastic pellets mixed with CNTs are fed into the extruder hopper. In particular, twin-screw extruders (Fig. 7. (a)) are used extensively for CNT-polymer mixing and compounding. The modular design of twin-screw extruder allows this operation to be designed specifically for the formulation being processed (Fig 7. (b)) (Bauhofer & Kovacs, 2009). For example, the two screws may be co-rotating or counter-rotating, intermeshing or non-intermeshing. In addition, the configurations of twin-screw extruders themselves may be varied using forward conveying elements, reverse conveying elements, kneading blocks, and other designs in order to achieve each CNT-polymer mixing characteristics. This technique is particularly useful in producing CNT-polymer composites with high filler contents. However, care must be taken to prevent CNT damages due to excessive shear stresses imposed during the extrusion process.
Polymer melt compounding is useful, especially in industry because it does not demand additional processes. However, the melt compounding studied and optimized so far has been mostly focused on micro-compounders at lab-scale. Scale-up of these techniques are not just a matter of size but also a matter of different rheological and thermodynamical issues (Oh & Hong, 2010).

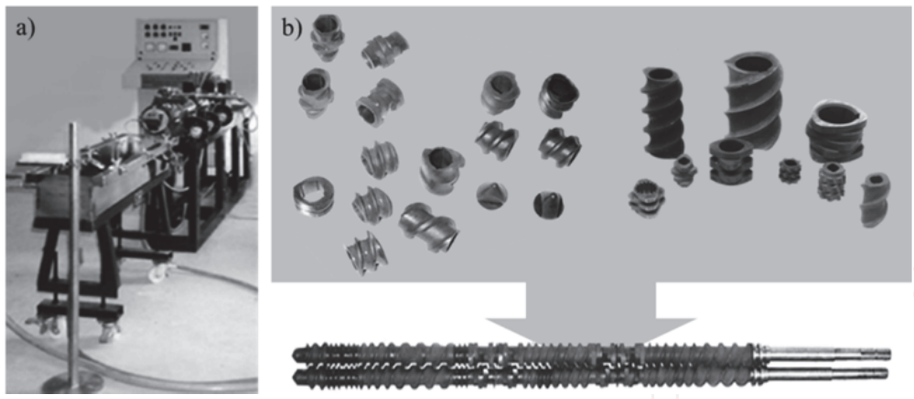


Fig. 7. (a) Lab scale twin screw extruder and (b) screw modular design.

2.1.2 Dispersion of carbon nanotube based on functionalization

Covalent Functionalization

Functionalization of CNTs is an effective way to minimize nanotube interaction, which helps to better disperse and stabilize the CNTs within a solvent or polymer matrix. There are several approaches for functionalization of CNTs, including covalent and non-covalent functionalizations.

In the case of covalent functionalization, the structure of CNTs is disrupted by changing sp^2 carbon atoms to sp^3 carbon atoms, and the physical properties of CNTs, such as electrical and thermal conductivities, are influenced. However, functionalization of CNTs with covalent bonding can improve dispersity in solvents and polymers. Generally, surface modification starts from acid treatment, which create –COOH and –OH functional groups on the CNT during oxidation by oxygen, reactive gas, sulfuric acid, nitric acid and other concentrated acids or their mixtures. The quantitative amounts of –COOH and –OH functional groups depend on oxidation conditions and oxidizing agent. Nanotube ends can be opened and residual catalyst and amorphous carbons are removed during the oxidation process (Spitalskya *et al.*, 2010).

Carboxylic functionalized CNT surfaces can be further used to chemically attach other small molecules or macromolecules through the reaction of the oxidation-induced functional groups. One of the common chemical reactions with acid functionalized CNT is the amidization, in which amide bond between amine group moieties is formed. One example is the use of amino-functionalized MWCNTs in epoxy systems to yield improved mechanical properties (Stevens *et al.*, 2003). The improved mechanical performance in these functionalized systems may reflect both the enhanced dispersion and an improved surface interaction between CNT and polymer matrix. Further improvements in solubility can be achieved by fluorination, again leading to improvements in both the stiffness and strength, with the addition of 1 wt.% of oxidized and fluorinated SWCNTs. Also, it has been established that the electrical properties of MWCNTs change after fluorination, leading to a wide range of electrical structures, from insulating over to semiconducting and metallic-like behavior (Seifert *et al.*, 2000).

The chemically functionalized CNTs can produce strong interfacial bonds with many polymers, allowing CNT-based nanocomposites to possess high mechanical and functional properties.

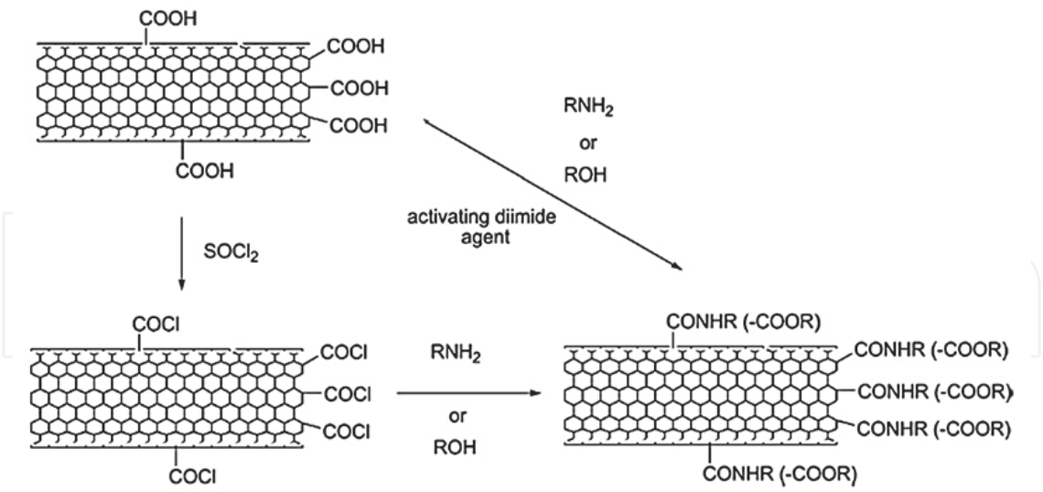


Fig. 8. Schematic representation of amidization process which starts from oxidized CNTs (Spitalsky *et al.*, 2010).

Non-covalent Functionalization

A non-covalent method used to modify CNT surface is popular functionalization method since it does not compromise the physical properties of CNTs. The electrostatic repulsion provided by adsorbed surfactants stabilizes the nanotubes against the strong van der Waals interactions between the nanotubes, hence preventing agglomeration. This repulsive and attractive force balance creates a thermodynamically stable dispersion, which results in separation of CNTs from the bundles into individual nanotubes. Anionic surfactants, such as sodium dodecylsulfate (SDS) and sodium dodecylbenzene sulfonate (NaDDBS), are commonly used to disperse CNT aggregation in polar media. The interaction between the surfactants and the CNTs depends on the nature of the surfactants, such as its alkyl chain length, headgroup size, and charge (Fig. 9) (Ma *et al.*, 2010).

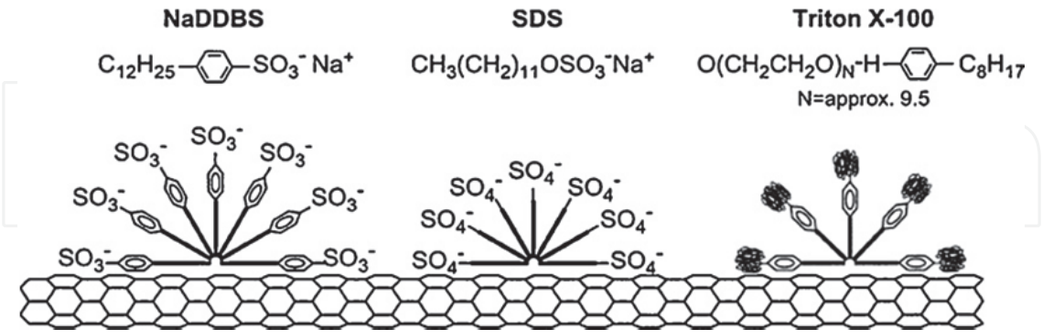


Fig. 9. Schematic diagram of surfactants adsorbed nanotube (Sahoo *et al.*, 2010).

The physical interaction of polymers with CNTs to make specific formation can be explained by the 'wrapping' mechanism which is π-stacking interactions between the polymer and the nanotube surface. Usually, wrapping polymer consists of aromatic groups on main chain or substitutional groups. For example, polyvinyl pyrrolidone (PVP) or polystyrene sulfonate (PSS) wrapped CNT shows improved dispersity and electrical properties compared to those of the individual components (Cheng *et al.*, 2008).

Small angle neutron scattering studies demonstrated a non-wrapping conformation of polymers in CNT dispersions. In these cases, different structures and compositions of copolymers efficiently act as stabilizers. The suggested mechanism of non-wrapping is that one of the blocks in block copolymers adsorbed to the nanotubes surfaces and another solvophilic blocks act as a steric barrier that leads to the formation of stable dispersions of individual CNTs above a threshold concentration of the polymer. A study of the stabilization effect produced by different diblock or multiblock copolymers led to the conclusion that selective interaction of the different blocks with solvent is essential in order to obtain stable colloidal dispersions of CNTs (Nativ-Roth *et al.*, 2007).

2.2 Control of carbon nanotube orientation

Similar to conventional fiber-reinforced composites, both mechanical properties and functional properties, such as electrical, thermal and optical properties of CNT-polymer composites are directly related to the alignment direction of CNTs in the matrix. Recently, this topic has drawn much attention due to the advance in nanocomposite processing techniques and the limitaions of randomly oriented, discontinuous nanotube composites.

2.2.1 Orientation of carbon nanotube by yarn formation

Recent advances in fabrication of CNTs allow to grow up to several millimeters in length, and these CNTs are possibly aligned to continuous macroscopic SWCNT fibers (Fig. 10). This provides an opportunity for fabricating continuous nanotube reinforced composites.

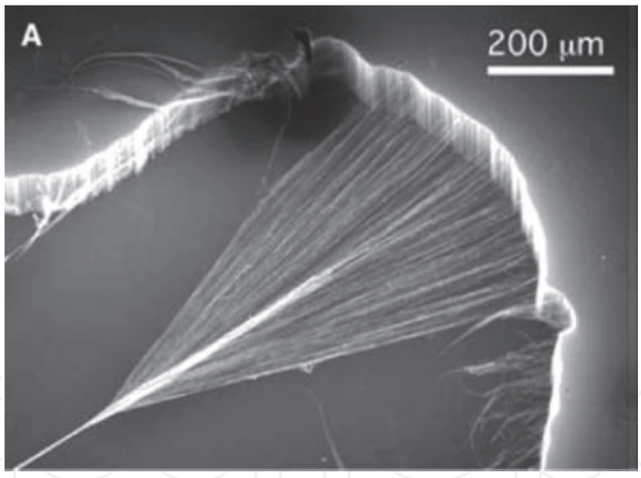


Fig. 10. SEM image of direct yarn formation from MWCNT forest (Zhang et al., 2004).

It has been reported that free-standing arrays of millimeter long, vertically aligned multiwalled nanotubes exhibit supercompressibility, outstanding fatigue resistance, and viscoelastic characteristics. Continuously aligned nanotube reinforced polydimethylsiloxane (PDMS) composite shows remarkably enhanced compressive modulus and strength, anisotropic characteristics, and damping capability (Ci *et al.*, 2008).

2.2.2 Force field orientation

The first method developed to fabricate aligned CNTs in polymer matrix was by ''cutting'' an CNT-epoxy nanocomposite. This process is simply explained by the nature of rheology in

composite media on nanometer scales and flow-induced anisotropy produced by the ''cutting'' process. The fact that CNTs do not break and are aligned after cutting also suggests that they have excellent mechanical properties along the nanotube direction. However, the orientation of CNTs in CNT-epoxy composite is affected by the cut slice thickness, since the alignment effect is only effective near the slice surface (Ajayan *et al.*, 1994).

A solution approach involved a SWCNT-dispersed surfactant solution (sodium dodecyl sulfate, SDS) injected through a syringe needle into a polyvinyl alcohol (PVA) solution. Because the PVA solution is more viscous than the SWCNT suspension, there is a shear contribution in the flow at the tip of the syringe needle, the flow-induced alignment is maintained by the PVA solution, and SWCNTs are rapidly stuck together as they are injected out from the syringe. By pumping the polymer solution from the bottom, meter-long ribbons are easily drawn, and well-oriented PVA-CNT composite fibers and ribbons are formed by a simple process. It offers a method to align CNTs by a flow field (Vigolo *et al.*, 2000).

The more effective and convinient method in CNT orientation is uniaxially stretching of polymer-CNT composite films. CNT-polymer composite films and fibers produced by any process can be drawn uniaxially showing higher conductivity along the stretched direction than the direction perpendicular to it. Also, the mechanical properties such as elastic modulus and yield strength of composite fibers increased with draw ratio, and CNTs in the composite fibers were better aligned. It is also possible to prepare aligned CNT composite films by extruding the composite melt through a rectangular die and drawing the film prior to cooling. For example, as compared to the drawn polystyrene (PS) film, the tensile strength and modulus of the PS-MWCNT composite films were greater (Thostenson & Chou, 2002).

However, PS-MWCNT composites prepared by spin casting at high speed showed that MWCNTs were aligned in specific angles relative to the radial direction: 45^{o} and 135 ^{o} on average. The presence of 2.5 vol.% MWCNTs doubles the tensile modulus and transforms the film from insulating to conducting. It is also noted that the CNTs have higher orientation than the polymer matrix during melt-drawing of the polymer-CNT composites (Bhattachacharyya *et al.*, 2003).

2.2.3 Electric or magnetic field induced orientation

Studies of SWCNT alignment using electric or magnetic fields have usually involved epoxies or polyesters as matrices because of their low viscosity before cure. Under the electric field, it was shown that both AC and DC electric fields can be used to induce the formation of aligned CNT networks spanning the gap between electrodes in contact with the dispersion. With increasing field strength, the quality of these networks and the resulting bulk conductivity of the composite material can be enhanced(Martin *et al.*, 2004). However, at high CNT content, thus high viscosity of molten resin system, the magnetic field-induced alignment of polymeric materials is more effective in CNT alignment. This technique has been the focus of several research efforts, initiated by the first use of high magnetic field to align MWCNTs in a polyester matrix to produce electrically conductive and mechanically anisotropic composites. A high magnetic field is an efficient and direct means to align CNTs. For example, to align MWCNT dispersed in methanol suspension, a magnetic field greater than 7 T is demanded. For the CNT alignment in a polymer, even higher magnetic field would be demanded because of high viscosity. Under a high magnetic

field of 10 T, it has been shown that MWCNTs were aligned in the monomer solution during their polymerization and MWCNTs were aligned parallel to the magnetic field inside the polymer matrix (Camponeschi *et al.*, 2007). Recently, magnetic field aligned polycarbonate (PC) and CNT-epoxy composites hae been reported and they suggested that aligning CNTs in polymer matrices can improve mass transport property as well as electrical conduction. It is also viewed that CNTs are better aligned in a PC matrix using magnetic field as compared to an electric field (Abdalla *et al.*, 2010).

2.2.4 Electrospinning induced orientation of carbon nanotube in polymeric nanofiber

Among several approaches to align nanotubes, the electrospinning technique has recently ben used to incorporate CNTs in a polymeric matrix to form composite nanofibers, combining the benefits of nanofibers with the merits of CNTs. Due to the sink flow and the high extension of the electrospun jet, it is expected to align the nanotubes during the electrospinning process, as was also predicted by a mathematical model. However, the distribution and alignment of the nanotubes in the nanofibers are strongly associated with the quality of the nanotube dispersion prepared before addition of the spinnable polymer solution. Generally, well-dispersed MWCNTs were incorporated as individual elements mostly aligned along the nanofiber axis. Conversely, irregular nanotubes were poorly aligned and appeared curled, twisted, and entangled. It is also suggested that the nanofiber diameter, the interaction between the spun polymer and the nanotubes and wetting ability are important factors affecting the alignment and distribution of the nanotubes. This was demonstrated by the difference in the alignment of SWCNTs in polyacrylonitrile (PAN) and polylactic acid (PLA) nanofibers (Ko *et al.*, 2003). More recent work to incorporate SWCNTs into PEO nanofibers by the electrospinning process showed SWCNTs were embedded in PEO in a more regular form since SWCNTs are much smaller and uniform in shape and size, as compared to MWCNTs. On the other hand, their stronger tendency to bundle up into coiled aggregates introduces a pronounced difficulty. Therefore, special attention is given to the dispersion process, which is essential for successful alignment of the nanotubes by the electrospinning process. Structural analysis of the composite nanofibers in terms of the distribution and orientation of both the nanotubes and the polymer matrix has been studied (Salalha *et al.*, 2004).

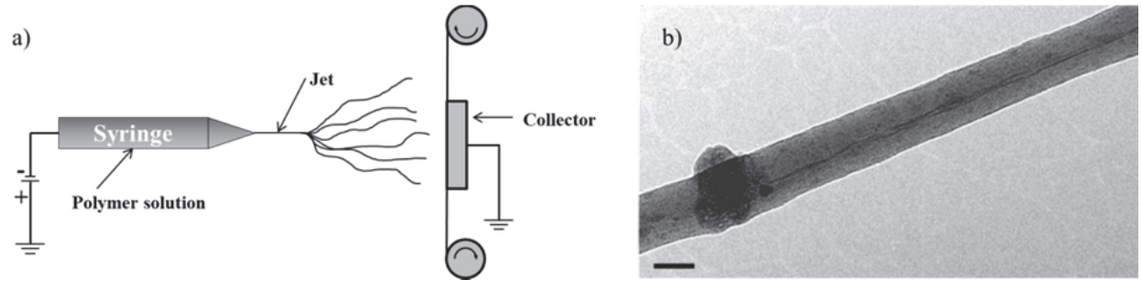


Fig. 11. (a) Simple schematic presentation of electrospinning and (b) TEM image of SWCNT aligned PEO nanofiber. Scale bar = 50 nm (Salalha *et al.*, 2004)

3. Electrical properties of carbon nanotube composites

CNTs have clearly demonstrated their capability as fillers in conductive polymer composites. Percolation theory predicts that there is a critical concentration at which

composites of insulating polymers become electrically conductive. According to the percolation theory, conductivity of composite (σ_c) can be estimated from the following equation.

$$\sigma_c = \mathrm{A}(\mathrm{V} - \mathrm{V}_c)^{\beta} \quad (1)$$

Where V is the CNT volume fraction, V_c is the CNT volume fraction at the percolation threshold, and A and β are fitted constant. The percolation threshold has been reported to ranging from 0.0025 wt.% to several wt.%. The percolation threshold for the electrical conductivity in CNT-polymer composites depends on degree of surface modification dispersion, alignment, CNTs aspect ratio, polymer types and processing methods. The electrical conductivity and percolation threshold of CNT-polymer composites are summarized in Table 2.

Polymer matrix	CNT type	Maximum filler content (wt.%)	Processing or dispersion method	Maximum electrical Conductivity (S/m)	Percolation threshold (wt/%)	Reference
PS	SWCNTs	2	Solution mixing	10^{-3}	0.27	Chang et al., 2006
PS	Aligned CNT array		Drop Casting	1330		Peng et al., 2009
HDPE	Acid-SWCNTs	6	Extrusion	10^{-1}	~4	Zhang et. al., 2006
LDPE	Acid - MWCNTs	10	Ball mill	~2	~1-3	Gorrasi et al., 2007
PP	MWCNTs	10.7	Melt mixing	4.6	1.1	Miˇcuˇsík et al., 2009
PMMA	SWCNTs	25	Coagulation	10^{-1}	~1	Narayan et al., 2009
PMMA	MWCNTs	0.4	Solution mixing	3×10^{3}	0.003	Kim et al., 2004
PMMA	Aligned CNT	-	Drop casting	1250	-	Peng et al., 2009
PC	MWCNT	15	Extrusion	20	1-2	Potschke et al., 2002
PC	PPE-SWCNTs	10	Solution mixing	4.8×10^{2}	0.11	Ramasubramaniam et al., 2003
Nylon 6	MWCNTs	10	Melt mixing	0.1	2-2.5	Krause et al., 2009
Nylon 6,6	MWCNTs	10	Melt mixing	0.1	0.5-1	Krause et al., 2009
PDMS	MWCNTs	2.5	Ultrasonica-tion	0.02	1.5	Khosla A & Gray BL, 2009

PI	MWCNTs	1.5		3.83×10^{-4}	-	Xiaowen et al., 2005
PI	Acid-MWCNTs	7	Solution mixing	3.8×10^{-6}	-	Yuen et al., 2007
PU	MWCNTs	27	Solution casting	2×10^{3}	0.009	Koerner et al., 2005
PET	SWCNTs	5	Melt mixing	~1	0.024	Hernandez et al., 2009
Epoxy	Aligned SWCNT	5	Solution casting	$\sim10^{-5}$	0.5	Qing et al., 2008
Epoxy	Silane-MWCNT	1	Solution mixing	1.67×10^{-2}	-	Lee et al., 2011
Epoxy	MWCNT	8	3-roll mill	2.3×10^{4}	0.0117	Iosif et al., 2009
Epoxy	SDS-MWCNTs	0.5	Bulk mixing	2.5×10^{-7}	-	Santos et al., 2008
Nafion	SWCNTs	18	Solution mixing	3.2×10^{3}	-	Landi et al., 2002

Table 2. Electrical properties of CNT-polymer composites

4. Smart, multifunctional applications of carbon nanotube composites

CNT-based polymer composites have found numerous multifunctional applications owing to their capability to serve as reinforcing, lightweighting agents and a material platform for electrostatic discharging, electromagnetic interference shielding, radar absorbing, mechanical/chemical sensing, energy harvesting, and flame retardation. Smart applications can be categorized into sensing and actuation, and this chapter will primary focus on the review of research on electromechanical sensing using CNT-based polymer composites. The studies on sensors and actuators based on CNTs and their composites up to 2007 are well summarized by Li *et al.* (Li *et al.*, 2008), and this chapter primarily presents more recent studies.

4.1 CNT Nanocomposites for electromechanical sensing

Electromechanical sensing and structural health monitoring typically utilize the piezoresistive behavior of the electrically conductive network formed by CNTs in polymer matrices, that is, the behavior characterized by a change in resistivity with respect to the structural deformation incurred by an external load. For example, when a CNT nanocomposite is subjected to a tensile load, the percolated CNT network is disrupted, resulting in an increase in resistivity. The variation in resistivity under a load is attributed to the variation in contact configurations and tunnelling distances among the contacting CNTs upon nanocomposite deformation.

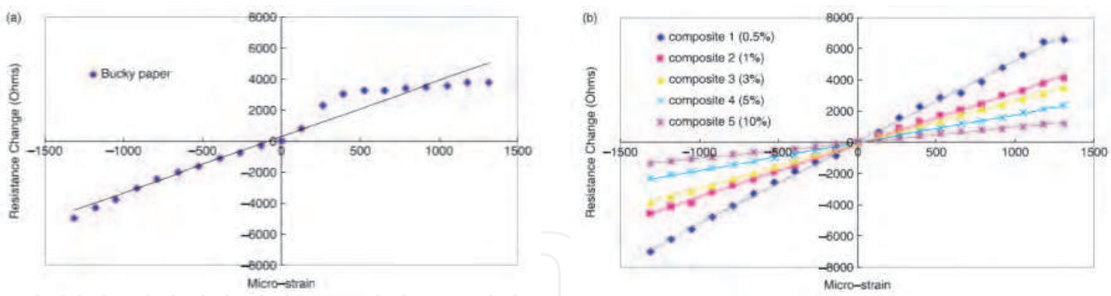
Initial studies on piezoresistivity of conductive CNT network involved free-standing CNT films or sheets, also known as "buckypapers." CNT buckypapers are typically made by filtration, similar to the papermaking process, where the CNTs are uniformly dispersed in a solvent, usually with the aid of surfactants, and subsequently passed through a filtering paper on which the CNTs are eventually deposited, dried, and detached. The CNT sheets

were bonded to the surfaces of various substrates, including brass (Li *et al.*, 2004; Vemuru et al., 2009), aluminium (Li *et al.*, 2004), and fiberglass (Kang *et al.*, 2006). While these substrates were loaded under tension or flexure, the resistance between two electrodes attached to the CNT sheet was measured *in situ*. Most of these studies employed isotropic, randomly oriented CNT networks, and showed that the resistance increase linearly under tension and decreased linearly under compression. The isotropy allows multi-directional, multi-location strain measurements.

It has been reported that CNTs can be added to various materials, including general-purpose thermoplastics and thermosets, specialty polymers, such as polyvinylidene fluoride (PVDF) and shape memory polymers, elastomers, and concrete, and utilize the piezoresistivity of the nanocomposites for strain or pressure sensing.

4.1.1 Thermoplastic-based nanocomposites

The research group at the University of Cincinnati (Kang *et al.*, 2006) reported comprehensive research work on strain sensing using buckypapers and SWCNT-polymethylmethacrylate(PMMA) composites. Fig. 12(a) shows the strain response of a SWCNT buckypaper sensor, which shows higher sensitivity in the linear bending range. However, it shows saturated strain behavior above 500 microstrains, which is probably attributed to the slippage among CNT bundles due to the weak van der Waals interactions at nanotube interfaces. When the sensor is compressed, the individual CNTs do not slip as much as compared to the tension case, resulting in the lack of saturation. Fig. 12(b) shows the strain response of composite sensor at varying CNT loadings. Although the composite strain sensors show lower sensitivities than buckypaper, they show linear symmetric strain response trends in both compression and tension. The interfacial bonding between CNTs and the polymer reduces slip and effectively increases the strain in the sensor.



(a) Buckypaper (b) SWCNT-PMMA composite

Fig. 12. Piezoresistive response of: (a) buckypaper sensor and (b) SWCNT-PMMA composite sensor (Kang *et al.*, 2006a, 2006b)

Pham et al. (Pham *et al.*, 2008) reported the development of conductive, MWCNT-filled, polymer composite films that can be used as strain sensors with tailored sensitivity. The electrical resistance of MWCNT-PMMA composite films subjected to tensile strains was measured, and the potential applications of the films as strain sensors with a broad range of tunable sensitivity were investigated. The surface resistivity of the films was observed to increase with increasing tensile strain, which is due to the reduction in conductive network density and increase in inter-tube distances induced by applied strains. The highest sensitivity achieved in this study was almost an order of magnitude greater than

conventional resistance strain gages (Fig. 13). A semi-empirical model, based on the percolation theory, was developed to identify the relationship between applied strain and sensitivity factor (Fig. 14). Not only can the sensitivity be tailored over a broad, but also it can be increased significantly be having the conductive filler content approach the percolation threshold.

Zhang et al. (Zhang *et al.*, 2006) presented a study on MWCNT-polycarbonate(PC) composites as multifunctional strain sensors, where a 5 wt.% composite showed instantaneous electrical resistance response to linear and sinusoidal dynamic strain inputs and a sensitivity of ~3.5 times that of a typical strain gage. Billoti *et al*. (Billoti *et al.*, 2010) presented a study on thermoplastic polyurethane (TPU) fibers containing MWCNTs, fabricated via an extrusion process, which demonstrated a tuneable level of electrical conductivity. The observation of Arrhenius dependence of zero-shear viscosity and the assumption of simple inverse proportionality between the variation of conductivity, due to network formation, and viscosity allow a universal plot of time variation of conductivity to be composed, which is able to predict the conductivity of the extruded fibers. The same nanocomposite fibers also demonstrated good strain sensing abilities, which were shown to be tunable by controlling the extrusion temperature.

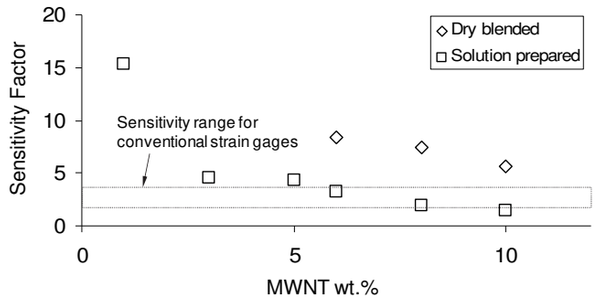


Fig. 13. Comparison of sensitivity factors between MWCNT-PMMA films and conventional resistance strain gages

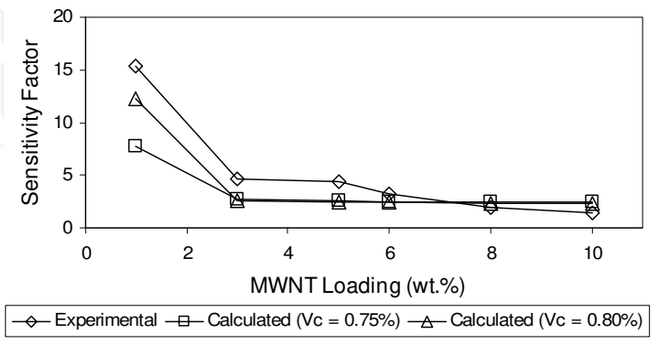


Fig. 14. Calculated and experimental sensitivity factors of MWCNT-PMMA films

Abraham et al. (Abraham *et al.*, 2008) reported the development and characterization of a CNT-PMMA nanocomposite flexible strain sensor for wearable health monitoring applications. These strain sensors can be used to measure the respiration rhythm which is a

vital signal required in health monitoring. A number of strain sensor prototypes with different CNT compositions have been fabricated and their characteristics for both static as well as dynamic strain have been measured. Bautista-Quijanoa *et al.* (Bautista-Quijanoa *et al.*, 2010) reported the electrical and piezoresistive responses of thin polymer films made of polysulfone (PSF) modified with 0.05–1% w/w MWCNTs. Gage factors were measured for films with 0.2–1% CNT weight loadings. The films were then bonded to macroscopic aluminum specimens and evaluated as strain sensing elements during quasi-static and cycling tensile loading. Excellent piezoresistive capabilities were found for films with MWCNT loadings as low as 0.5% w/w.

CNTs were added to a piezoelectric polymer, PVDF, to for various smart applications, including strain sensing. Deshmukh *et al.* (Deshmukh *et al.*, 2009) presented an experimental evidence of the creation of an electrostrictive response in PVDF by addition of small quantities of CNTs. It was demonstrated that the piezoelectric response of nanocomposites can be dramatically enhanced through addition of conductive nanoparticles such as CNTs without additional weight penalties. Most importantly, these improvements were achieved at much lower actuation voltages and were accompanied by an increase in both mechanical and dielectric properties. In the work by Kim *et al.* (Kim *et al.*, 2008), CNTs were included in a PVDF matrix to enhance the properties of PVDF. The CNT-PVDF composite was fabricated by solvent evaporation and melt pressing. The inclusion of CNT allowed the dielectric properties of PVDF to be adjusted such that lower poling voltages can be used to induce a permanent piezoelectric effect in the composite. The CNT-PVDF composites were mounted on the surface of a cantilever beam to compare the voltage generation of the composite against homogeneous PVDF thin films.

4.1.2 Thermoset-based nanocomposites

The primary types of thermosets used as the matrices for strain sensing nanocomposites include epoxy, vinyl ester, and polyimide, among which epoxies are most popular. In the work by Wichmann *et al.* (Wichmann *et al.*, 2009), electrically conductive epoxy based nanocomposites based on MWCNTs and carbon black were investigated concerning their potential for strain sensing applications with electrical conductivity methods. It was found that the nanocomposites exhibited a distinct resistance vs. strain behavior in the regime of elastic deformation, which is in good agreement with prevalent theories about charge carrier transport mechanisms in isolator/conductor composites. Applying an analytical model, it was shown that the piezoresistivity of nanocomposites may contribute valuable information about the conductive network structure and charge carrier transport mechanisms occurring in the nanocomposites. The authors also developed a direction-sensitive bending strain sensor consisting of a single block of MWCNT-epoxy composite by generating a gradient in electrical conductivity throughout the material (Wichmann *et al.*, 2008).

Zhang *et al.* (Zhang *et al.*, 2007) demonstrated a simple, effective and real-time diagnostic, and repair technique featuring MWCNTs that are infiltrated into epoxy. It was shown that by monitoring volume and through-thickness resistances, one can determine the extent and propagation of fatigue-induced damage such as crack and delamination growth in the vicinity of stress concentrations (Fig. 15). The conductive nanotube network also provides opportunities to repair damage by enabling fast heating of the crack interfaces; the authors show up to 70% recovery of the strength of the undamaged composite.

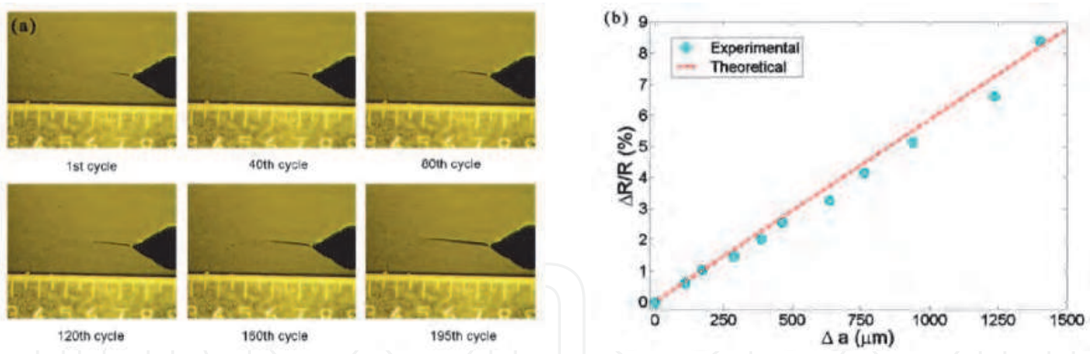


Fig. 15. Detection of real-time fatigue crack growth: (a) snapshots of fatigue crack growth; (b) the change in electrical resistance across the crack interface

Quasi-static and dynamic strain sensing of CNT-epoxy composites was studied by Anand and Mahapatra (Anand & Mahapatra, 2009), and de la Vega, *et al.* (de la Vega *et al.*, 2011) characterized the local and global stress response of SWCNT–epoxy composites by simultaneous Raman spectroscopic and electrical measurements on nanocomposite specimens subjected to various levels of surface strain. Both the Raman G-band resonance frequency and the electrical resistance of the composite are found to change monotonically with strain until an inflection point is reached at 1.5% strain.

Thostenson *et al.* (Thostenson *et al.*, 2009) synthesized vinyl ester monomer from the epoxy resin to overcome processing challenges associated with volatility of the styrene monomer in vinyl ester resin. Calendering was employed for MWCNT dispersion in vinyl ester monomer and the subsequent processing of nanotube/vinyl ester composites. The high aspect ratios of the carbon nanotubes were preserved during processing, and an electrical percolation threshold below 0.1 wt.% carbon nanotubes in vinyl ester was observed. A systematic study of the effect of SWCNTs on the enhanced piezoresistive sensitivity of polyimide nanocomposites from below to above percolation was reported by Kang *et al.* (Kang *et al.*, 2009). The maximum piezoresistive stress coefficient obtained just above the percolation threshold concentration (0.05 wt.%) exceeded those of metallic piezoresistive materials by two orders of magnitude.

4.1.3 Elastomer-based nanocomposites

Hwang *et al.* (Hwang *et al.*, 2011) fabricated a piezoresistive composite using MWCNTs as a conductive filler and polydimethylsiloxane (PDMS) as a polymer matrix, which operated in the extremely small pressure range required for finger-sensing. To achieve a homogeneous dispersion of MWCNTs in PDMS, the MWCNTs were modified by a polymer wrapping method using poly(3-hexylthiophene) (P3HT). The percolation threshold of the composites was significantly lowered by the presence of P3HT. The electrical conductivity and piezoresistive sensitivity of the composite were found to strongly depend on the P3HT concentration. The well-dispersed P3HT-MWCNT/PDMS composite showed good piezoresistive characteristics in the 0–0.12 MPa pressure range.

Wang *et al.* (Wang *et al.*, 2010) studied the piezoresistivity of a multi-walled carbon nanotube filled silicone rubber composite under uniaxial pressure. The experimental results showed that the active carboxyl radical on multi-walled carbon nanotubes can effectively improve

the homogeneous distribution and alignment of conductive paths in the composite. As a result, the composite presented positive piezoresistivity with improved sensitivity and sensing linearity for pressure, both of which are key parameters for sensor applications. Elastomeric composites based on ethylene-propylene-diene-monomer (EPDM) filled with MWCNTs showed improved mechanical properties as compared to the pure EPDM matrix (Ciselli *et al.*, 2010). A linear relation was found between conductivity and deformations up to 10% strain, which means that such materials could be used for applications such as strain or pressure sensors. Cyclic experiments were conducted to establish whether the linear relation was reversible, which is an important requirement for sensor materials.
High-elasticity CNT-methylvinyl silicone rubber (VMQ) nanocomposites with a high sensitivity and linear piezoresistive behavior was fabricated by dispersing conductive MWCNTs with different aspect ratios, AR = 50 and 500, into rubber matrix homogeneously (Dang *et al.*, 2008). It was found that the percolation threshold of the nanocomposites containing AR = 50 MWCNTs was significantly lower than those containing AR = 500 MWCNTs. Extremely sensitive positive-pressure coefficient effect of the resistance and excellent cyclic compression under low pressure were also observed in the MWCNT-VMQ nanocomposites with AR = 50 MWCNTs at relatively low loadings.

4.2 CNT-based multiscale hybrid composite for electromechanical sensing

Multiscale hybrid composites (MHCs) are defined as composites consisting of at least three constituents having more than two different length scales. The most common type consists of the resin (macro), continuous (unidirectional or woven) fiber fabric (micro), and nanoparticles (nano) (Fig. 16). Conventional continuous fiber-reinforced plastics (FRPs) are characterized by extremely high in-plane modulus and stiffness (fiber-dominated) and poor through-thickness properties (matrix-dominated). In MHCs, high-performance nanomaterials are added to improve the through-thickness properties and, at the same time, to impart multifunctionalities to the composites.

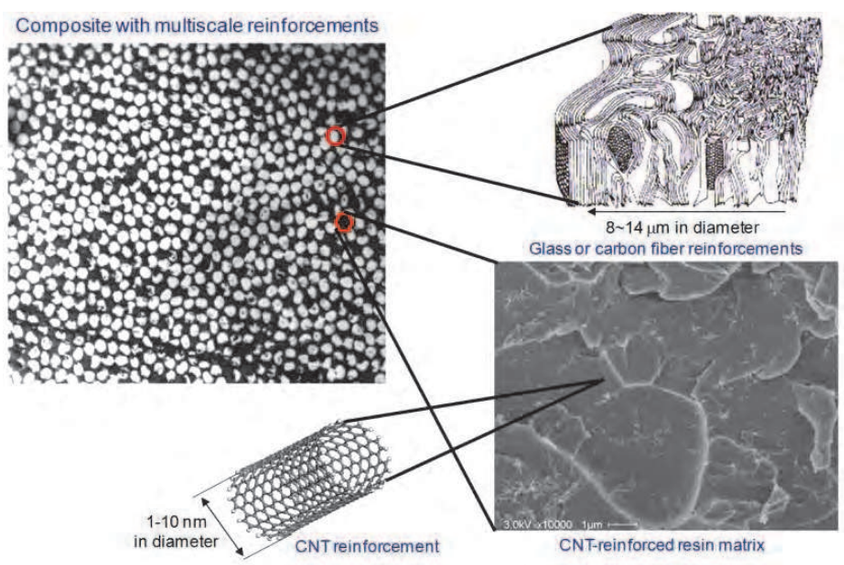


Fig. 16. Concept of multiscale hybrid composites

Research on structural health monitoring of MHCs using the piezoresistivity of the percolated network of CNTs has been pioneered by the University of Delaware. A typical MHC manufacturing process involved dispersion of CNTs in the resin using a three-roll mill, followed by composite fabrication using vacuum-assisted resin transfer molding. The MHCs thus obtained were tested under various loading conditions to *in situ* monitor and detect various failure modes, including delamination, matrix damage and fiber breakage as shown in Fig. 17 (Thostenson & Chou, 2006b), and crack growth under fatigue (Gao *et al.*, 2009). Similar research was performed in parallel by Technische Universitat Hamburg-Harburg (Boger *et al.*, 2008). Kim *et al.* (Kim *et al.*, 2010) applied 3D braided textile as reinforcement and used CNTs as the sensing components for structural health monitoring of 3D braided composites.

An alternative way to incorporate CNTs in FRPs is to surface treat or coat the fibers with CNTs, instead of dispersing them in the resin. Specific methods include dipping the fibers into a CNT solution (Gao *et al.*, 2010), aid of coupling agents (Sureeyatanapas & Young, 2009), lay-by-layer deposition (Loh *et al.*, 2009), and direct growth of CNTs on the fibers using electrophoresis (Bekyarova *et al.*, 2007). Another unique method is to embed continuous CNT fibers (Alexopoulos *et al.*, 2010) or threads (Abot *et al.*, 2010) in FRPs for large-area strain sensing.

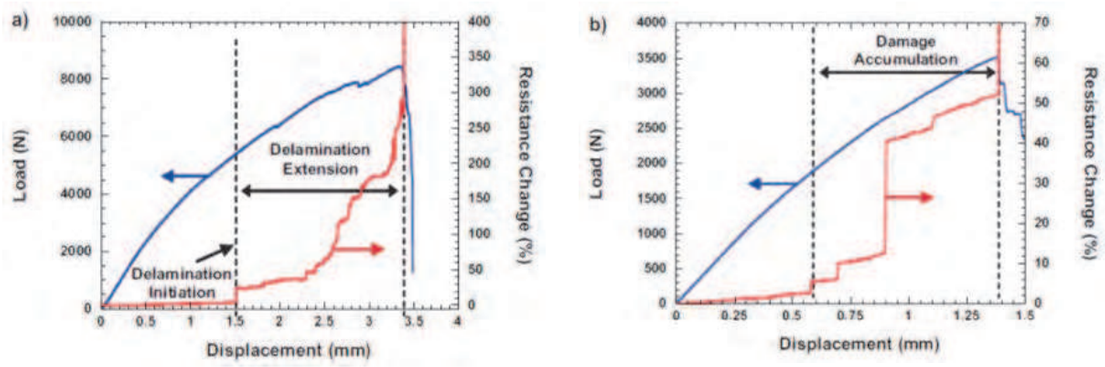


Fig. 17. Load-displacement and resistance response of: (a) a five-ply unidirectional composite with the center ply intentionally cut to initiate delamination; (b) a $(0/90)_s$ cross-ply composite showing accumulation of damage due to microcracks (Thostenson & Chou, 2006b)

5. Conclusion

CNTs have made inroads into multifunctional, smart applications, particularly strain sensing for structural health monitoring. A vast number of studies have focused on tailoring the mechanical and electrical properties of CNT-based nanocomposites by controlling CNT dispersion, orientation, and CNT-matrix interface at the nanoscale. The insights gained from the electromechanical behavior of CNT nanocomposites have open up a new field in structural health monitoring of multiscale hybrid composites. Although fundamental studies on processing-structure-property relationship in CNT nanocomposites need to be continued, allied efforts will need to be devoted to large-area strain mapping, cumulative stress/strain tracking, damage detection and life prediction algorithms, and data acquisition

and analysis to fully utilize the smart sensing and actuation capabilities of CNT nanocomposites.

6. Acknowledgment

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Carbon nanotubes are one of the most intriguing new materials with extraordinary properties being discovered in the last decade. The unique structure of carbon nanotubes provides nanotubes with extraordinary mechanical and electrical properties. The outstanding properties that these materials possess have opened new interesting researches areas in nanoscience and nanotechnology. Although nanotubes are very promising in a wide variety of fields, application of individual nanotubes for large scale production has been limited. The main roadblocks, which hinder its use, are limited understanding of its synthesis and electrical properties which lead to difficulty in structure control, existence of impurities, and poor processability. This book makes an attempt to provide indepth study and analysis of various synthesis methods, processing techniques and characterization of carbon nanotubes that will lead to the increased applications of carbon nanotubes.

InTech Europe
University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
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