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Carbon Nanotubes and Semiconducting Polymer Nanocomposites

Duong Ngoc Huyen

*Hanoi University of Science and Technology, Hanoi
Vietnam*

1. Introduction

The increasing demand for efficient machines has driven a trend towards the miniaturation of devices and instruments with smaller volume, lesser power consumption but greater performance. The progression relies upon the searching out new desirable materials and the ability of making tiny structures with high precision. However, the development is not so smooth and easy. For instance, current electronic industry based on silicon is very mature and reliable, but it is reaching an unsurmountable barrier of quantum effects as nanoscale approaching. Search for new suitable materials and fabrication methods therefore are being urgent tasks for the near coming development.

Carbon nanotubes (CNTs) and conducting polymers (CPs), newfound materials have shown exceptional characteristics. The coupling of CPs and CNTs furthermore reveals **synergistic effects** which offer an attractive route to create new multifunctional materials with greater potential in application. Envisioned applications from CPs/CNTs systems involve mechanical, thermal, electrical, electrochemical features such as supercapacitors, sensors, organic light emitting diodes (OLEDs), solar cells, electromagnetic absorbers, and, last but not the least, advanced electronic devices.

Conducting polymers commonly are classified as conjugated polymers which consist of alternating single and double bonds along its linear chains (sp^2 hybridized structure). The conductivity of the CPs relies on these double bonds which are sensitive to physical or chemical interactions [1-3]. Similarly, CNTs also have sp^2 hybridized bonds over the structure. CNTs possess unique structures and exhibit extraordinary electrical, optical, chemical, and mechanical properties, which are somewhat complementary to those of CPs [4-6]. For instance, CNTs have a very long mean free path, ultrahigh carrier mobility, and can be either very good conductors or narrow bandgap semiconductors depending on the chirality and diameter. Mixing up together, both materials show a strong interfacial coupling via dono-acceptor binding and pi-pi interaction [7, 8]. The coupling of CNTs and CPs in a composite has been found to affect their chemical and electronic structure. Beyond a simple combination of their properties, some synergistic effects and new features appear and can develop into applications [9-14]. From a chemical viewpoint of consideration, two possible impacts may take place in a CPs/CNTs system: either the CNTs are functionalized by the CPs or the CPs are modified (doped) with the CNTs. Therefore, either the morphological modifications, electronic interactions, charge transfers or a combination of these effects may occur between the two constituents in the system [15-18]. Due to the

nanoscale confinement in the system, the interaction via interfacial bonding is considered to play an essential role in the impacts [19-23]. Morphologically, the interfacial interaction sites on CNTs surface are: (a) defect sites at the tube ends and side walls (b) covalent side wall bindings (c) non-covalent exohedral side wall bindings and (d) endohedral filling (Fig. 1). Three routes have been commonly used for preparation of CPs/CNTs composite: (i) direct mixing (ii) chemical polymerization and (iii) electrochemical synthesis.

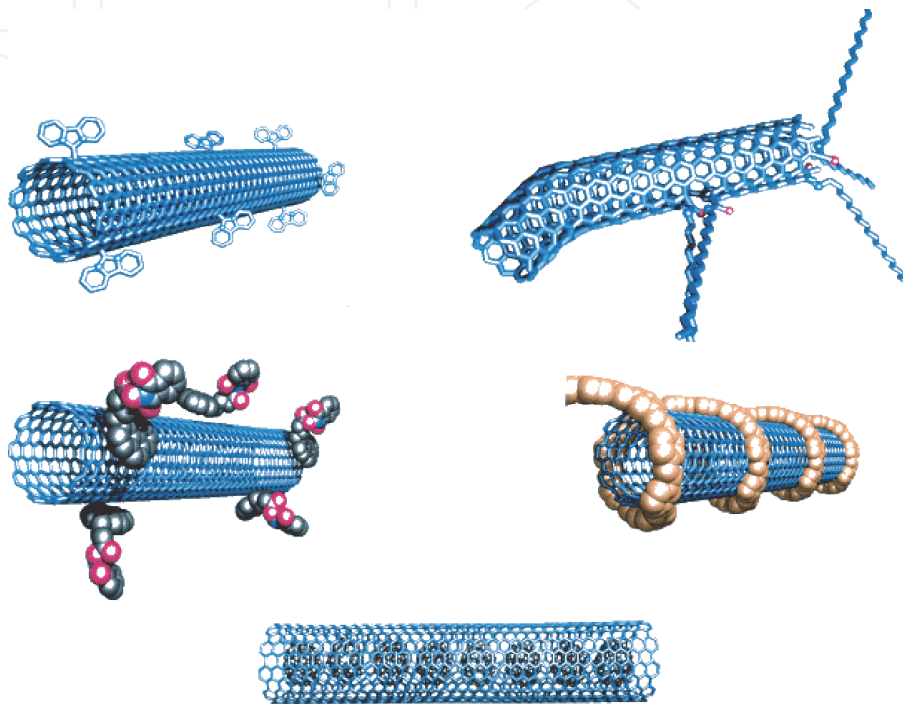


Fig. 1. Possible functional sites CNTs: (a) defect sites at the tube ends and side walls (b) covalent side wall bindings (c) non-covalent exohedral side wall bindings (d), endohedral filling [23].

Back to the development, the study made on the composites of CPs and CNTs relatives started in early 90s of the last century. Since 1992, Heerger *at al.* [24] observed the photovoltaic effects arising from the photoinduced charge transfer at the interface between CPs as donors and a C_{60} film as acceptor although the conversion efficiency was too low (less than 1%). However, the conversion efficiency of CPs based solar cell have been significantly improved ($\sim 6\%$) by further use of CNTs derivatives acting as the electron acceptors in the CP/CNTs matrices [25]. The conversion efficiency is still moderate in comparison to that of inorganic systems but the simple in processing and low cost enable CPs/CNTs systems to be promising choice for photovoltaic future. On the other hands, the introduction of CNTs into a polymer matrix improves the electric conductivity, while possibly providing an additional active materials for capacitive energy storage and secondary batteries [26]. Gas sensors fabricated with the PPy/SWNTs nanocomposite has shown sensitivity higher than that of PPy. The improvement is explained as the effect of the increase of specific surface area and anion doping in PPy matrix. The gas sensing improvement in PANi/SWNTs is also shown the same manner [27]. For biosensor applications, it has been demonstrated that the CPs/CNTs nanocomposites are very attractive as transducers because they provide the best electron transfer and assure a faster

ion mass transfer [28]. In some host polymers, the CNTs additive has found to act as a hole-blocking causing a shift of the recombination emission [29, 63]. The interaction between host polymer and CNTs additive is considered to be the main reason accounting for all of these modifications.

Studies on CPs/CNTs systems will further contribute to the fundamental understanding of the nucleating capability of CNTs, epitaxial interaction, and templated crystallization of the polymer at the CNT-polymer interface, and may ultimately lead to more efficient production of bulk nanocomposites. The combination of strong polymer-CNT interaction, nucleation ability of CNTs, CNTs templating of polymer orientation and crystallinity are all features that one can build on to develop high performance composites. With that goal, this chapter tries to provide a look on the development and trend in future research of CPs/CNTs systems.

2. Composite preparation

Generally, the composite properties are governed by variety of factors such as the preparation conditions, quantity, contents as well as the nature of its components. With respect to those of CPs/CNTs composite, the **purity** of carbon nanotubes, the **dispersion** and the **interfacial interaction** strength between components are considered to be the essential factors [10, 13]. Carbon nanotubes are created and recombined from carbon sublimation, then naturally accompany with variety of contaminants such as residual catalysts and amorphous carbon phases. In order to obtain purer CNTs, many purification procedures have been proposed to remove these inherent contaminants. Most techniques have been based on chemical and thermal treatment. In the first stage,, strong chemical oxidants, surfactants or burning the unpurified carbon nanotubes were commonly used. However, these techniques have shown some disadvantages such as adding some defects on CNTs surface and poor yield. Later, Davey *et al.* developed a non-destructive and more efficient purification method for that a coiled polymer was used to extract nanotubes from carbonaceous soot [30]. With respect to the mechanical, thermal, electrical, and optical properties, a better dispersion and an increase in interfacial interaction between the CNTs and polymer matrix would lead to even greater improvement. Depending on use purpose, either uniform dispersion or alignment of CNTs in polymer matrix is required. However, due to the Van der Waals attraction, CNTs are held together as bundles and ropes and remain as entangled agglomerates. In order to facilitate a better dispersion of CNTs in polymer matrix, direct mixing, in-situ chemical polymerization or electrochemical polymerizations have been proposed. Direct mixing is actually mechanical/physical means involving solid-state, high shear, solution mixing or melt blending, agitated in a solvent by magnetic stirring, reflux or ultrasonication. Sometimes, additive surfactant or chemical modifications are used to enhance the dispersion of CNTs in the solution. On the other hand, the alignment of nanotube in the polymer matrix is an additive essential factor because it is the only way to optimize the preferred anisotropic behavior of a CNTs composite. The approaches to achieve the alignment of CNTs depend on how nanotubes are introduced into polymer matrices. Carbon arc discharge, composite slicing, film rubbing, chemical vapor deposition, mechanical stretching of CNT-polymer composites and magnetic orientations have been the techniques used for aligning nanotube in composites.

For thermoplastic polymers, melt processing is a common technique. As the dispersion of CNTs in polymer melt is much more difficult than in solution, additive techniques such as mechanical stirring, ultrasonic vibration, melt blending, extrusion and melt spinning are used to enhance the dispersion. For insoluble and thermally unstable polymers, chemical processing is often chosen, which involves *in-situ* polymerization or covalent functionalization of CNTs with polymer molecules. In these methods, CNTs is mixed with monomers and then is chemically polymerized with added oxidant.. Depending on the nature of polymer and the preparation condition, CNTs have been found to play the role of the nucleation sites for polymer growth and crystallized. As a result, the crystallinity and polymerization rate increases when the CNTs are introduced.. The interaction between two entities is a physical factor affecting the polymer orientation and crystallization. This interaction change the morphology and then strongly modify the physical properties of the polymer. The combination of mechanical mixing and *in-situ* polymerization also gives a good dispersion of CNTs in the polymer matrix.

Electrochemical polymerization is another way for the preparation of polymer CNTs composites. A direct electrochemical deposition of monomer on CNTs layers acting as an electrode or an electropolymerization from an aqueous dispersion of monomer and CNTs are common approaches to realize the composites.

3. Characterization

Normally, the composites have been characterized by microscopic, spectral, conductivity, mechanical and thermal measurement. Scanning electron microscope (SEM), scanning tunneling microscope (STM), atomic force microscope (AFM), and transmission electron microscope (TEM) are the main techniques used for morphological characterization of the composite. For example, the morphology of the composites could reveal the wrapping of CNTs by conducting polymers in core-shell structure with several modes. UV-Vis, photoluminescence spectra, Raman and FTIR are complementary means used to investigate the chemical structure of the composites. X-ray diffraction, X-ray photoelectron spectral studies made on the composites show the crystallinity, intrinsic oxidation states.

4. Application

4.1 Electrically conductive composite

The incorporation of CNTs in polymer matrices is made to design electrical properties suitable for variety of applications such as circuit components, electronic products or electrostatic shields. For example, to protect against electrostatic discharge a lower level of conductivity is enough whereas to prevent electromagnetic interference a higher conductivity is needed and for circuit components the level of conductivity must be comparable to those of metals. However, most of composites, although a high weight percentage of CNTs has been used, have only a moderate conductivity below the required level in electronic applications, except for a composite developed by Blanchet-Fincher *et al.* [31]. To prepare a mechanically strong and electrically conductive composite, Niu *et al.* [32] proposed an approach based on solution and melting methods based on polyvinylidene fluoride and CNTs (PVDF/CNTs). The conductivity of this composite has been claimed to be higher than other known polymer composites and can be adjusted by varying the CNTs

content as illustrated in Fig. 2. The conductivity achieves a level of CNTs mats with a composite having about 13 wt% of CNTs. Their results shown that the composite prepared by the solution method were better electrical conductors than that by the melting method. Based on Niu route, Charati *et al.* [33] developed a method for manufacturing conductive composites for material-handling, electronic devices (computers, printers etc.) and automotive components that require electrostatic dissipation and electromagnetic shielding. The composite was prepared by blending an organic polymer precursor with SWNTs and polymerizing the polymer precursor to form an organic polymer using an ultrasonicator and shear, elongational forces. They claimed that in this way, at least a portion of the CNTs could be functionalized either at the side wall or hemispherical ends.

In principle, the conductivity of a conducting polymer can be largely tuned by “doping”, however highly conductive polymers have been limited in practical applications as they are chemically unstable in use and unsuited for solution or melt processing. Among the conductive polymers, polyaniline (PANi) is known to be chemically stable and readily soluble in environmentally friendly solvents. Protonic acid doped PANi emeraldine is the most highly conductive form with conductivity about 5 S/cm, which is well below the 10^2 S/cm threshold conductivity required for widespread utility in electronics. Blanchet-Fincher *et al.* [31] disclosed a method for the preparation of a composite comprising PANi emeraldine salt and CNTs that exhibited electronic conductivities of 10^2 S/cm while retaining the desirable chemical stability of PANi with only a small wt% of CNTs. They have applied the above composite as a conductive pathway, produced by laser thermal transfer imaging, in electronic circuits. In addition, McElrath *et al.* [34] made a polymer-CNT composite comprising at least one polar polymer with electrical and/or thermal conductivity enhanced six orders higher that of polymer alone. These examples showed the evidences that CNTs acting as effective physical dopants in conducting polymers.

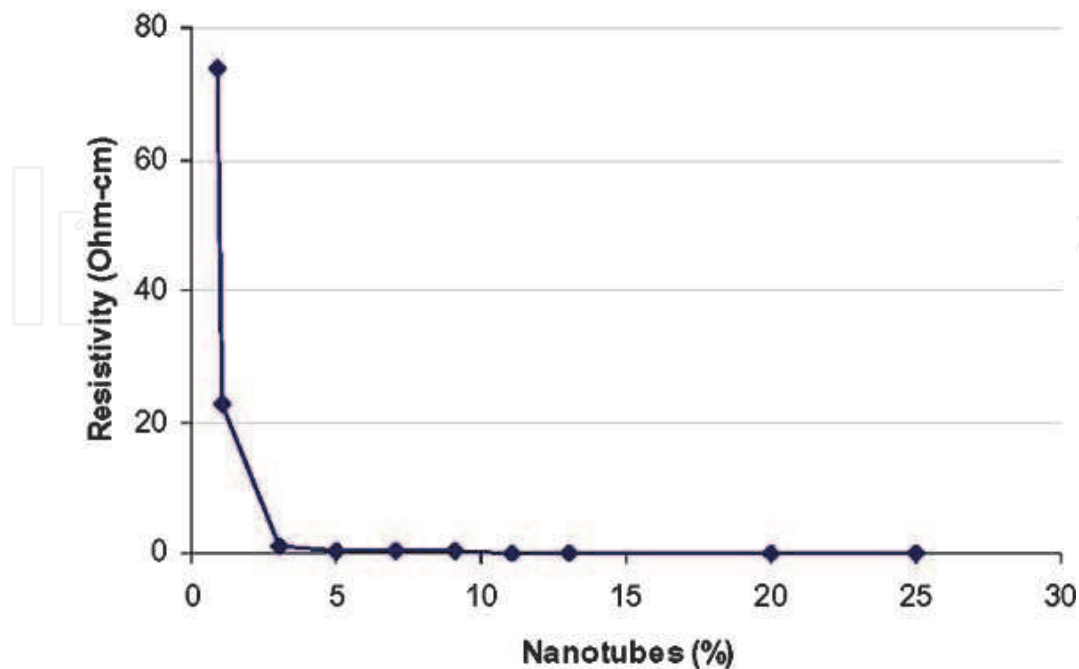


Fig. 2. Resistivity of PVDF/CNT composite as a function of CNT content [32].

4.2 Mechanically reinforced composite

With respect to mechanically effective reinforcement, basically required features for composite components are purity, aspect ratio, dispersion, alignment and interfacial stress transfer. Among these, **the interfacial stress transfer**, characterized by the applied shear stress at which the interface fails, is the most important. However, CNTs have atomically smooth non-reactive surfaces, and then lack of interfacial bonding between the CNTs and polymer. In order to increase bonding sites to the polymer chain, chemical modification and functionalization of CNTs such as solution processing, melt processing, and chemical processing were proposed. Quantum mechanics and molecular dynamics calculations supported this approach [35-38]. By chemical functionalizing and integrating CNTs into epoxy polymer, Margrave *et al* [39] found that the composite with 1wt% functionalized CNTs showed an increase of 18% and 24% in tensile strength and modulus respectively over the epoxy composites with unfunctionalized CNTs and a 30% increase in tensile modulus over pure epoxy resin. The enhancement was due to the strong interaction between epoxide rings on the epoxy resin and the functionized groups on CNT walls which were confirmed by infra-red and Raman spectroscopy.

A composite formed by *in-situ* polymerization from the polycondensation of diamine and diacid monomers comprising with dispersed CNTs aligned with rigid-rod polymers [40] showed that the tensile modulus, tensile strength and elongation to break of composite having 10 wt% CNT increased by 20, 60 and 40% respectively. In this composite there was no claim of covalent bond formation at the interfaces of components. The alignment of CNTs could be the reason of the enhancement.

By combining the uniformly dispersed nanotube with polypropylene matrix/solvent mixture and then heating the nanotube/matrix mixture to a temperature above the melting point of the matrix materials, Shambaugh *et al.* [41] recently disclosed a method for producing SWNT-polypropylene composite. The fiber made from composite with 1 wt% of CNTs showed more than 50% increase in tensile strength compared to fiber drawn from matrix materials alone. This substantial increase in strength was believed to be due to a uniform dispersion of CNTs in the matrix materials. In addition, mechanical reinforcements of polymer/CNTs composites have found to be significantly enhanced when high purity nanotubes were exfoliated and well dispersed in the polymer matrix. The above results show that not only the interfacial bonding but also the type of polymer and the conditions used in making the composite are important factors to produce a strong composite.

On the other hand, in some composites, CNTs act as a nucleating agent for polymer crystallization [9, 42-44] and reorientation. For example, SWNTs induced oriented crystallization is observed in PET/SWNTs composites [42]. Two samples, PET and PET/SWNTs (1wt% loading) are prepared under identical conditions by melt compounding at 270 °C. Both PET and PET/SWNTs samples were made into 0.5 mm thick, 0.4 mm wide strips and subsequently stretched to a draw ratio of four to induce PET and SWNTs orientation. As can be seen from Fig.3, wide-angle X-ray diffraction (WAXD) of both materials shows that PET is oriented in the samples (Fig. 3A and Fig. 3C). However, when the train PET and PET/SWNTs were heated and were recrystallized by cooling down, only PET/SWNTs shows the orientation but not the neat PET (Fig. 3B and Fig. 3D). Individual CNTs also have found to promote polypropylene (PP) crystallization, as a result, thick PP interfacial layer is formed on the nanotube surface [43]. Polypropylene transcrystals were observed on the carbon nanotube surface (Figure 2E), when polymer melt was isothermally crystallized in the temperature range of 118 to 132 °C. In PP/CNTs fiber samples melted and

recrystallized spherulite growth is influenced by the presence of CNTs, where the presence of CNTs increase the number of nucleation sites for the polymer and smaller spherulites are observed (Figure 2F to I) even a low CNTs loading (0.1 wt %) [44]. PP/CNTs fibers heated at above polypropylene melting temperature and then cooled down shows that PP/CNTs fibers retain polymer orientation and the average degree of crystallinity is about 80 %. Such a high level of crystallinity is attributed to more complete PP crystallization in dilute solution and PP-CNTs interaction.

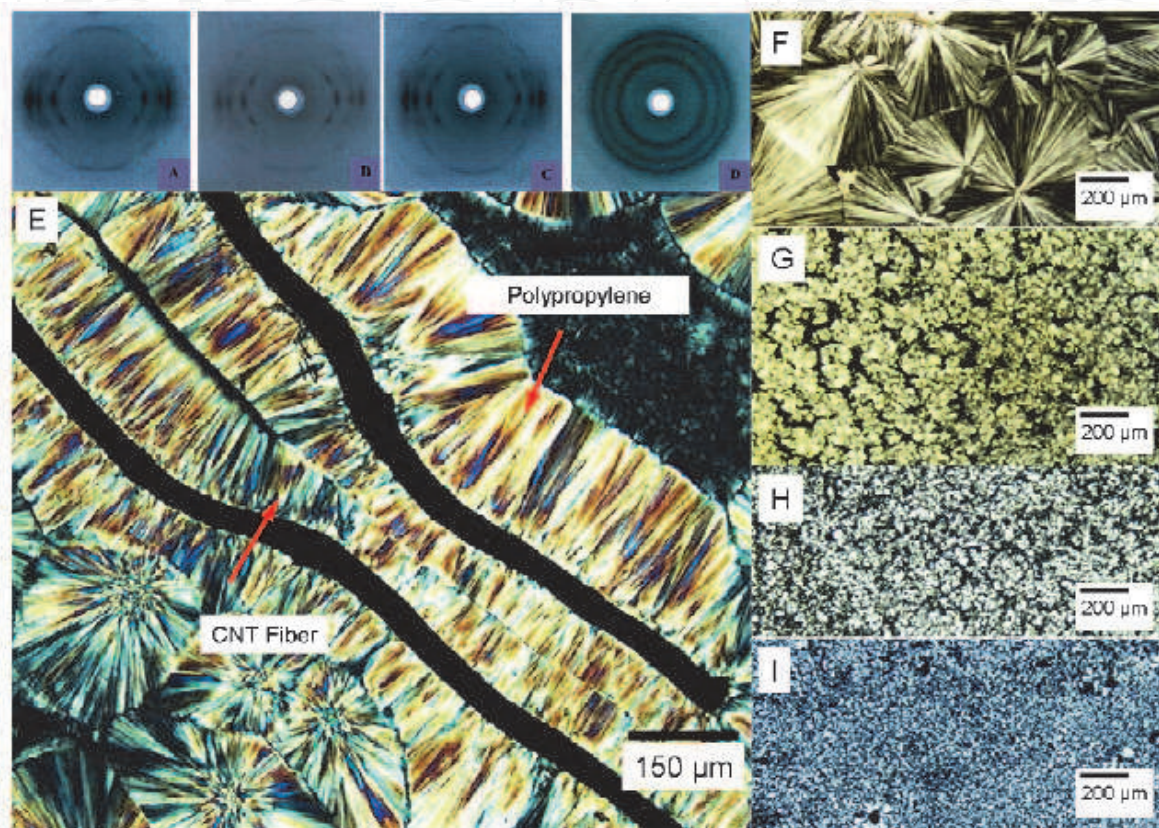


Fig. 3. Wide-angle X-ray diffraction patterns of (A) drawn PET/SWNTs (1.0 wt%) nanocomposite film, (B) PET/SWNTs 1 wt% nanocomposite film after melting to 300 °C and subsequently slowly cooled down to room temperature, (C) drawn neat PET film, (D) drawn neat PET film after melting to 300 °C and subsequently slowly cooled to room temperature [42]. (E) PP transcrystalline interfacial layer on CNTs fibers [43]. The development of transcrystallinity provides the evidence of interaction between PP and CNTs. Optical micrographs with cross-polarizers of spherulite formation in (F) PP, (G) PP/SWNTs (0.1 wt% SWNTs), (H) PP/SWNTs (1 wt% SWNT), and (I) PP/MWNTs (1 wt% MWNTs) bulk samples [44].

In addition, some proteins have been shown to crystallize in an ordered helical fashion on the surfaces of MWNTs. The MWNTs that induce protein crystallization are of a specific size, and protein crystallization occurred consistently throughout the system. The SWNTs have also been shown to induce crystallization and orientation in the sheared polymer melt, and polymer melt containing aligned SWNTs. These observations are important evidences indicating that CNTs can be used as nucleating agents in polymer processing to promote polymer crystallization and orientation.

4.3 Electrochemical capacitors

The requirement for energy store and conversion systems has drawn much attention on development of effective energy store devices. Electrochemical capacitor (EC) (or so called supercapacitor) is device which can store the electric field energy in high density by using an electrochemical double-layer with high specific surface-area. With respect to classification, supercapacitors may be distinguished by criteria such as the electrode materials, the electrolyte, or the cell design. Traditionally, the electrode materials are divided into three main groups: carbon based, metal oxides (mainly ruthenium dioxide) and polymeric materials such as PPy, PANi and PTh [45-49]. Polymer-based electrochemical capacitors in particular have attracted much attention due to the polymeric materials possess high capacitive energy density and low cost. However, these kinds of capacitors have shown some disadvantages, namely, lower cycle-life and slow ion transport kinetics because the redox sites in the polymer backbone are not sufficiently stable. As an alternation, the composites of CPs and CNTs (both SWNTs and MWNTs) have been investigated as an electrode materials for supercapacitors [50-52]. The combination of CNTs into a polymer matrix provides an additional active materials for capacitive energy storage. For example, using MWNTs coated with PPy as the active electrode for a supercapacitor assembly, Frackowiak *et al.* report a specific capacitance increase from ca. 50 to 180 F/g demonstrating a synergy between the two components in this composite [53]. The excellent charge storage and transfer capabilities accounted for the improvement are due to the homogeneous coating on the nanotubular materials, high surface area, conductivity, and electrolytic accessibility of the nanoporous structure.

4.4 Solar cell

Solarcells are specific devices which transform light into electricity. Depending on the materials and techniques, solarcell may be classified into inorganic or organic (including conducting polymer) based devices. Currently, most solarcells in the market are based on inorganic materials such as Si or CuInGaS(Se) or CdTe. However, due to the production cost and shortage of rare materials organic based solarcell emerges as potential alternative. In principle, photon absorption in the organic-based materials produces primarily bound-state excitons. Some of these charge pairs eventually are dissociated generating free carriers (electrons and holes) which give rise to a current in the materials. The dissociation is facilitated by the potential difference across a polymer-metal junction, provided by agglomeration of excitons near the interface. The dissociation can be further accomplished via electron acceptor impurities [54]. Under illumination, a transfer of electrons to the acceptors will take place and the holes will be preferentially transported through the CPs. This process is known as photo-induced charge transfer. Since the discovery of photo-induced charge transfer, a variety of acceptor materials have been introduced into CPs to produce photovoltaic devices. Amongst of these materials, CNTs have shown to be one of the most effective acceptor materials [24, 25, 55, 56]. Since the efficiency of photo-induced charge generation is dependent on the interface between the two components, the extremely high surface area of CNTs (for purified SWNTs, $\sim 1600 \text{ m}^2/\text{g}$), offers a tremendous opportunity for exciton dissociation. The primary step in these polymer photovoltaic devices is an ultrafast photo-induced electron transfer reaction at the donor-acceptor interface, which results in a metastable charge-separated state. In the case of the oligo(phenylenevinylene)/C60 composite, the quantum efficiency of this step is assumed to

be close to one [57, 58]. However, the overall conversion efficiency of these solar cells is limited by the carrier collection efficiency, which is greatly influenced by the morphology of the active film.

SWNT/poly(3-octylthiophene) (P3OT) composites have been used for the fabrication of new photovoltaic devices [25, 26]. P3OT, acting as the photoexcited electron donor, is blended with SWNTs which act as the electron acceptors. In such devices the transferred electrons are transported by percolation paths provided by the addition of SWNTs. It was shown that the internal polymer/nanotube junctions act as dissociation centers, which are able to split up the excitons and also create a continuous pathway for the electrons to be efficiently transported to the negative electrode. This results in an increase of electron mobility, and hence, balances the charge carrier transport to the electrodes. The CP/SWNTs composite represents an alternative class of hybrid organic semiconducting materials that is promising for organic photovoltaic cells with improved performance. Other beneficial properties of SWNTs relevant to polymeric photovoltaic development include composite reinforcement and thermal management. The high Young's modulus and strength/weight ratio of SWNTs could help provide much-needed mechanical stability to large-area thin-film arrays. SWNTs, on the other hand, may provide assistance in thermal management for such arrays, too. Polymer composites doped with as little as 1% wt SWNTs have shown a 70% increase in the thermal conductivity at 40 K [59].

Optical and photovoltaic properties of a composite based on MWNTs and PPV was studied by Curran *et al.* [60]. These authors claim that the helical structure of the polymer chain helps the MWNTs disperse in the polymer solution, and that LEDs made with this composite are five times more stable in air compared with devices without the MWNTs. However, a drastic reduction of the PL efficiency and a change in the vibration structure of the PL spectrum were affected by MWNTs. The reduction of the PL efficiency was understood as an inter-system energy transfer (singlet-triplet), a partial hole transfer from PPV chains to MWNTs and both superposing on an intense scattering and absorption of the exciting light by MWNTs.

4.5 Optical limiting devices

Organic light emitting diodes (OLEDs) are one of most interest in recent years for their potential applications in electronic informatic, lighting, display technology. The simplest version of OLED consists of an electroluminescent organic material layer sandwiched between two electrodes. The luminescent emission of OLEDs is due to the radiative recombination of excitons, a process is somewhat opposite to that of solar cell. Fabrication of high efficient OLEDs depends not only on the electronic and the optical properties of the pure organic materials but also on the control of charge transport, holes or electrons through the electroluminescent layers and on the enhancement of charges migration by doping the emissive materials [61, 62]. A proper layer combination in OLEDs can also balance the injected charges in an emissive layer thus increasing the external efficiency. The buffer layer leads to a reduction of the charge injection barrier and an even charge distribution with a large contact area at the electrodes/organics interface. A recent work shows that the dispersion of SWNTs in a host polymer (PmPV, hole conducting) traps the holes in a double emitting organic light emitting diode (DE-OLED) [63]. The device fabricated without SWNTs dispersed in the PmPV has shown a dominant emission near red at 600 nm, which is in the range of the characteristic emission of Nile Red-doped Alq₃, while the addition of a

small amount of SWNTs enhances a green emission, In addition, the devices fabricated with the polymer/SWNTs composite have shown an increase in the oscillator strength of the green emission with a dominant emission peak near 500 nm, the characteristic emission of PmPV. The shift in the emission indicates that the SWNTs in the PmPV matrix act as a hole-blocking materials that causes a shifting of the recombination region from the Nile Red-doped Alq3 layer to the PmPV composite layer. The addition of CNTs in conducting polymer also has found to modify the electronics properties of polymer composite. For example, OLEDs fabricated with a hole conducting polymers composite dispersed with SWNTs such as PEDOT, poly-carbazole (PVK),... show a change in EL, PL and I-V data. The modification in electronic structure of the composite originates from the hole trapping nature of SWNTs and SWNT-CP interaction.

4.6 Sensors and actuators

Both CPs and CNTs inherit a delocalized π -electron system over the structure with an "intrinsic" wide band gap. Owing to the interaction with various analytes, the π -electron system is modulated resulting in physicochemical modifications such as resistance, current, or electrochemical potential/work function. Based on that feature, CPs and CNTs have been the materials widely studied for application in chemical, gas sensors and biosensors, and there are excellent reviews on this topic [2, 3]. With respect to conductivity, the major charge carriers in CPs are polarons and bipolarons arising from variety of chemical and physical doping, charge injection or electronic defects within their pi-orbital backbone. Consequently, through surface interaction the conductivity of a CPs layer is affected by surrounding environment. The feature enables CPs a promising candidate for sensing materials that are superior to the metal oxides counterparts. CNTs also show a similar feature. Kong *et al.* [64] demonstrated chemical sensors based on individual SWNTs. They found that the electrical resistance of a semi-conducting SWNT changed dramatically upon exposure to gas molecules such as NO₂ or NH₃. From physical view of consideration, the change in conductivity involves the extraction or addition of electrons from valence band of semiconducting CPs and SWNTs (*p*-type) as a result of gas molecule interaction (physical adsorption). As the O₂, NO₂ (oxidizing agent) concentration in the environment increases, more electrons are extracted, the conductivity of the materials is increased and vice versa. On the other hand, upon exposure to a reducing agent such as NH₃, the conductivity of the materials is decreased. The NH₃ gas impact is equivalent to an injection of electron to valence band of *p*-type semiconducting CPs and SWNTs and then reduces the conductivity of the materials. With expectation of achieving synergetic effect, the CP/CNTs composites has been the attractive subject drawn much of attention to develop tiny but ultrasensitive sensor. Some promising. Some works have demonstrated the use of CNT-polymer composite as sensors. Ajayan *et al.* [65] developed a controlled method of producing free-standing nanotube-polymer composite films that can be used to form nanosensor. The nanosensor contains at least one conductive channel comprising an array of substantially aligned carbon nanotubes embedded in a matrix materials (e.g. poly (dimethylsiloxane)). This sensor can be used to determine a real time physical condition of a materials, such as monitoring the physical condition of an airplane wing or chassis while the airplane is in flight. A gas sensor based on poly(*o*-anisidine)-CNTs composite offers a sensitivity of about 28 % compared to a mere 4 % by CNTs alone for the detection of inorganic vapor, HCl [66, 67]. Sensors for the detection of carbon monoxide in

the concentration range of 0.01–1000 ppm have been developed [68, 69]. A biosensor based on the composite of pyrene sulfonic acid-functionalized SWNT embedded in PANi has shown two- to sixfold enhancement depending on applied potential, compared to polystyrene sulfonate-doped PANi in the detection of glucose [70]. Another sensor for NADH has been developed with poly(1,2-diaminobenzene)–MWCNT composite in a range from 2 μ M to 4 mM [71]. A CNTs composite of poly(anilineboronic acid) functionalized with single-strand DNA (ss-DNA) shows great promise for the detection of dopamine of concentration as low as 40 pM without any interference from ascorbic acid. A biosensor for the detection of chlorine without any interference due to ascorbic acid and uric acid has been developed [72].

Materials such as shape-memory alloys or liquid crystal elastomers exhibit a latent ability to actuate under the right conditions whereas other systems require the blending of two or more materials to impart a new physical response leading to the actuation process. Recently, polymer nanocomposites appeared as the subject of mechanical actuation studies, but most of them concentrated on accentuating the already present features of the host matrix by adding nanotubes. In 2003, Courty *et al.* [73] reported a novel actuator response driven by an electric field due to the presence of MWNTs in nematic elastomer, polysiloxane. They produced a composite materials with embedded and aligned CNTs with an effective dielectric anisotropy, many orders of magnitude higher than in the usual liquid crystals. Koerner *et al.* [74] fabricated MWNT-polydimethyl-siloxane composite that produced a mechanical response to the infrared radiation. They reported that the sample spontaneously contracted and elongated on irradiation. They further showed that the mechanical response is due to photon absorption and not because of the trivial heating of the materials due to irradiation. However, the nature of the actuator mechanism is not known. Ounaies *et al.* [75] developed a technique for making actuating composite materials with polarizable moieties (eg. polyimide) and CNTs. With the aid of an *in-situ* polymerization under sonication and stirring, they achieved an increase of dielectric constant from 4.0 to 31 with a 0.1% volume fraction of SWNTs. The PANi/CNTs composites have received a good deal of attention as smart materials in high-strength actuators which directly convert electrical energy into mechanical energy. Dubbed as artificial muscles, these electrochemomechanical devices can find applications in robotics, optical fiber switches, optical displays, prosthetic devices, microscopic pumps, and antivibration systems. Conducting polymers like PANi and polypyrrole have been extensively investigated for applications in artificial muscles [76-79]. A dual-mode actuation has been reported for a composite containing fibers of chitosan, PANi, and SWCNTs. The activation depends on pH changes and redox polymer reactions. Such dual-mode actuators are expected to have design advantages in the construction of microelectromechanical systems (MEMS) [80]. A hybrid actuator based on cellulose–PANi–CNTs composite has been studied. The effects of the wt % of MWNTs in the composite and sonication time used in its preparation on the actuation behavior have been investigated in detail [81-82].

4.7 Thermal conductivity

Carbon based composites with high thermal conductivity have had a number of potential applications, particularly in thermal management such as heat sinking for electronics and motors. In particular, SWNTs are superior to carbon black and carbon fibers because their nano-scale diameter and larger aspect ratio facilitate the formation of extensive network at

the same weight loading. Theoretical calculation and measurement show that the thermal conductivity of CNTs is much more than that of best thermal conductive metals such as Ag, Cu [83-85]. The thermal conductivity of CP/CNTs nanocomposites although has received lesser attention, initial studies show that the presence of CNTs in some polymer matrices has improved the thermal conductivity of the polymer. For example, the thermal conductivity of epoxy/SWNTs composites with only 1 wt% SWNTs enhanced more than 120 % and 70% at room temperature and 40°C, respectively, as compared to epoxy filled with carbon fiber [60, 85]. However, the thermal conductivity of CNTs/epoxy composites seems to be unaffected by increasing CNTs loading in samples [86, 87]. The impact of CNTs on the thermal conductivity of polymer/CNTs systems has not been explored as far as the study on the other areas of the composites and needs to be further exploited.

4.8 Fuel cell

Fuel cell is an efficient way transforming chemical energy of hydrogen rich compounds to electrical energy. The research in this area has gained momentum since the 80s due to the increased awareness of energy and environmental concerns. Fuel cells are usually characterized by their electrolyte, temperature of operation, transported ion and fuel. The center of the fuel cell is the electrolyte membrane, as it determines the properties needed for the other components. Electrolyte membrane based on conducting polymer has shown some advantages over the other materials due to low operating temperature, high energy density and easy handling of the fuel other than hydrogen. The PANi/CNTs composites can be used as efficient electrocatalytic materials in fuel cell reactions like oxygen reduction and methanol oxidation. The CNTs provides higher surface area and better electronic conductivity while PANi facilitates the electron transfer through the conducting matrix. A PANi-grafted MWNTs composite has shown a 610 mV more positive current onset potential for the two-electron oxygen reduction with a 20-fold enhancement in amperometric current [88]. A poly(*o*-phenylenediamine)-MWNTs composite has exhibited a polymer redox-mediated electrocatalytic effect for oxygen reduction with a five-fold enhancement in current and a favorable potential shift of 130 mV compared to the values obtained at a pure poly(*o*-phenylenediamine) electrode [89]. The PANi/CNTs composites can serve as excellent host matrices for metal nanoparticles which can be used as electrode materials in methanol oxidation reaction [90-92]. It has been established that the size of the metal nanoparticles deposited on the composite matrix is smaller than that on PANi. This gives a higher dispersion and better utilization of the metal nanoparticle-impregnated composites, resulting in their high performance and stability. Apart from enhanced electrocatalytic activity, the PANi/CNTs composites consisting of metal nanoparticles have shown a reduced poisoning effect from adsorbed carbon monoxide [91]. A microbial fuel cell with PANi/CNTs composite as anode in 0.1 M phosphate buffer consisting of 5.5 mM of glucose, 2-hydroxy-1,4-naphthoquinone as mediator, and *Escherichia coli* bacteria as the microbial catalyst has been reported to give a cell voltage of 450 mV with a power density of 42 mW m⁻² [93]. In addition, the polymer nanocomposite membrane resulted in the enhanced thermal, ionic conductivity associated with the lower fuel drag than that of bare polymeric materials. These significant improvements are due to the synergetic combination of component properties. Although still in initial step, the effort of both industrial and academic activities could be triggered on the development of polymer nanocomposite electrolyte membranes to bring forth the commercialization of fuel cells in near future.

4.9 Electromagnetic absorbers

Electromagnetic (EM) shielding by absorption rather than reflection is presently more important for many applications from electronics to military use. Even though metals or metal-coated materials exhibit very high EM shielding efficiency ranging from 40 to 100 dB, they cannot be used as an electromagnetic wave absorbent since their shallow skin depth makes them shield electromagnetic waves mainly through surface reflection. On the other hand, electrically conducting polymers are capable of not only reflecting but also absorbing the electromagnetic waves and therefore exhibit a significant advantage over the metallic materials. Currently, commercial and military applications require high performance absorbing materials with light weight and high strength over a broad frequency band [94]. This could be carried out if one could design and optimize a combination of different CPs components based on their dielectric properties and random scattering effects present due to their respective geometry. For example, EM absorbers with different dielectric properties and thickness were carried out on the base of the polyurethane composite containing carbon nanotubes, carbon fibers and microballoons along with polypyrrole fabric having different surface resistances. It has been shown that both the surface resistance of the PPy fabric and the order in which the composite layers are stacked are critical for the reflection. A PPy fabric composite gave greater than 15 dB reflection loss in the 4–18 GHz frequency range. With proper arrangement, the required bandwidth and better performance can be achieved by using a combination of PPy fabric and composite layer stacks [95, 96].

4.10 Other applications

Organic electronics have been a field of most research interests since it exhibits some advantages over inorganic including low-cost and flexible. The development relies on CPs with suitable properties in conductivity, processibility, charge mobility, etc. The addition of CNTs in CPs has shown to enhance the conductivity of the nanocomposites and furthermore improve the processing. For example, poly (p-phenylenevinylene-co-2, 5-dicotoxy-m-phenylenevinylene) (PmPV) with CNTs form a hybrid composite whose conductivity is increased by ten orders of magnitude due to the introduction of CNTs conducting path to the polymer [59, 97]. The addition of SWNTs in PANi doped with dinonylnaphtalene sulfonic acid (DNNSA) creates a highly conducting [31] and the composites show to be a high-resolution printable conductor. Transparent SWNTs film on a polyethylene terephthalate substrate can be used to replace ITO for PANi-based electrochromic devices [98]. Field effect transistors (FETs) based on P3HT using SWNT-contact exhibit three orders of magnitude higher current modulation ($I_{\max}:I_{\min}$) than the metal contacted devices over the same gate voltage V_{gs} equal to -2 to 2 V [99]. Schottky diodes fabricated using composites of high molecular weight PANi and MWNTs produce current levels of significantly higher magnitude than pure PANi devices [100]. However, double linear regions with two different slopes on semi-log I-V curves of these devices were observed. The behavior is explained by the difference in charge transport mechanism: consistent with Ohm's law at lower voltages and with Child's law at higher voltage. Localized defect states arising from PANi and CNTs interactions are considered to be the reason. For optoelectronics, organic materials show a possibility of fast signal processing owing to the greater state change rate and ease of hybridization change. However, the sensitivity to intensity, the long term stability and the thermal electrical conductivity of the materials need to be improved. Composites with CNTs have shown a promising approach

for the realization. For instance, an all-optical switch made from polyimide composites consisting about 0.1 wt% SWNTs showed high-sensitivity and an ultra-fast, switching speed exceeding 1 ps for 1.55 μm wavelength light [101]. A organic light emitting diode, fabricated from, PmPV and SWNTs ($\sim 0.1\text{wt}\%$), increased oscillator strength in green radiation by about 700% in comparison to that made from PmPV alone [62]. The reason is due to the hole transport blocking by hole traps which were formed in the polymer matrix as SWNTs introduced into the composite. This non-linear optical effect could be employed in developing new light sensitive shielding.

On the other aspect, radiation shielding materials have been developed to protect personnel and equipment from the damaging effects of radiation including galactic cosmic radiation (GCR). Polyethylene (PE) is a CP has been used in space applications for shielding GCR in the low temperature applications. However, transparent composites composed of SWNTs and poly-4-methyl-1-pentene (PMP) exhibit superior strength, optical and thermal properties, and has a melt temperature of 235°C (compared to 136°C for PE) [102]. The PMP is also transparent in the visible region of electromagnetic spectrum and can be modified by doping with an organic dye having phenyl ring. These composites can be employed in thermo-luminescent detection where high energy radiation excite pi-electrons in the phenyl rings and on relaxation to ground state emit photons which can be transported to photodetectors and counted. By this way, the radiation environment of the shielding materials can be continuously monitored.

5. Conclusions

This chapter presents a brief summary of the preparative methods, characterization data, and possible applications of conducting polymer/carbon nanotube composites. The electrical, thermal, mechanical and electrochemical properties of the composites in general are intermediate between pure polymer and CNTs but vary depending on the method of preparation, type, purity, content and the dispersion of CNTs in the polymer matrix. In particular, the composite reveals **synergistic effects** and new properties which account for the interaction between CPs and CNTs at nanoscale. The effect offers an attractive route to create new multifunctional materials with great potential in uses involving mechanical, thermal, electrical, electrochemical features. However, the nature of the CP/CNT interaction and its effect on overall properties of the system still are unclear and need to further exploit and develop into practical application.

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Carbon Nanotubes - Synthesis, Characterization, Applications

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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.

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University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

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