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Review

Preparation, Properties and Application of Polyamide/Carbon Nanotube Nanocomposites

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Abstract: The discovery of carbon nanotubes (CNTs) has opened up exciting opportunities for the development of novel materials with desirable properties. The superior mechanical properties and excellent electrical conductivity make CNTs a good filler material for composite reinforcement. However, the dispersal of CNTs in a polymer solution or melt is difficult due to their tendency to agglomerate. Many attempts have been made to fully utilize CNTs for the reinforcement of polymeric media. Therefore, different types of polymer/CNTs nanocomposites have been synthesized and investigated. This paper reviews the current progress in the preparation, properties and application of polyamide/CNTs (nylon/CNTs) nanocomposites. The effectiveness of different processing methods has increased the dispersive properties of CNTs and the amelioration of their poor interfacial bonding. Moreover, the mechanical properties are significantly enhanced even with a small amount of CNTs. This paper also discusses how reinforcement with CNTs improves the electrical thermal and optical properties of nylon/CNTs nanocomposites.

Keywords: carbon nanotubes, polyamides, nylon, nanocomposites.

Introduction

The discovery of carbon nanotubes (CNTs) can be traced back to the origin of fullerene chemistry (buckyball, C_{60}) in 1985.¹ Fullerenes provide an exciting new insight into carbon nanostructures, particularly those constructed from sp^2 carbon units based on geometric architectures. CNTs were first discovered by Iijima in 1991. The CNTs were believed to be elongated fullerenes, where the walls of the tubes are hexagonal carbons that are often capped at each end.² There are two types of CNTs: multi-walled CNTs (MWCNTs) and single-walled CNTs (SWCNTs). MWCNTs consist of two

or more concentric cylindrical shells of graphite sheets arranged coaxially around a central hollow core with inter-layer separations as in graphite. In contrast, SWCNTs are a single graphite cylinder. SWCNTs and MWCNTs both have the physical characteristics of solids and are micro-crystals with a high aspect ratio of 1,000 or more, even though their diameter is close to molecular dimensions.^{3,4}

CNTs have unique mechanical, thermal, electrical, magnetic and optical properties. High-performance lightweight structural materials are required in some special applications, such as space exploration. Such materials can be developed by adding CNTs to polymers or other matrix materials. Moreover, although graphite is a semi-metal, CNTs can be either metallic or semiconducting by the pres-

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ence of topological defects from the fullerene-like end caps (pentagons in a hexagonal lattice). Therefore, the physico-mechanical properties of CNTs are dependent upon their dimensions, helicity or chirality. The synthesis, structures, properties and applications of CNTs have been widely discussed.⁵⁻⁷

Regarding the preparation of polymeric nanocomposites filled with CNTs, nanotubes generally need to be dispersed homogeneously and be compatible with the polymer matrix.⁸⁻¹⁰ An effective approach for these requirements is to functionalize nanotubes with polymers that are identical or structurally similar to the matrix polymers.¹¹

Polyamide (PA), which is commonly referred to as nylon, is made from condensation copolymers formed by a reaction of equal parts of a diamine and a dicarboxylic acid. In such a reaction, peptide bonds form at both ends of each monomer through a process analogous to polypeptide biopolymers. Nylon was the first commercially successful polymer and the first synthetic fiber to be made entirely from coal, water and air. It is a thermoplastic silky material, which was first used commercially nylon-bristled toothbrushes, followed more famously by women's "nylons" or stockings. Nylon was intended as a synthetic replacement for silk and was used as a substitute for silk in many different products when silk became scarce during World War II. Nylon fibers are used in a wide variety of applications, including fabrics, bridal veils, carpets, musical strings and rope.

As an important commodity polymer with a wide variety of applications, there has naturally been considerable interest in nanocomposites of nylon with CNTs.^{12,13} For an investigation of these materials, the preparation of nylon-functionalized CNTs is highly relevant and beneficial. Different mechanical tests show that the incorporation of a small amount of CNTs into a nylon matrix can improve the modulus, strength and hardness of the new nanocomposites.

This paper reviews the structure and properties of CNTs as well as the preparation and properties of polymer/CNTs composites. The current situation in terms of the preparation, properties and application of nylon/CNTs nanocomposites is also discussed. The improvement and properties of nylon/CNTs nanocomposites is also reviewed, particularly the remarkable enhancement of the mechanical properties of new nanocomposites.

Carbon Nanotubes

Structure and Properties of CNTs. CNTs are long, slender fullerenes, in which the walls of the tubes are hexagonal carbon (with a graphite-like structure) and the end caps contain pentagonal rings. Theoretically, carbon tubules can be constructed by rolling up a hexagonal graphite sheet.¹⁴ In graphite, sp^2 hybridization occurs, where each atom is connected evenly to three carbons (120°) in the xy plane, and a weak π bond is present in the z axis. The sp^2 set forms a

hexagonal (honeycomb) lattice that is typical of a sheet of graphite. The p_z orbital is responsible for the van der Waals interactions. The free electrons in the p_z orbital move within this cloud and are no longer local to a single carbon atom. This phenomenon can explain why graphite (and CNTs) conducts electricity but not diamond, which behaves as an insulator because all the electrons are localized in the bonds within the sp^3 framework. Besides being responsible for the high conductivity, the delocalized π -electrons of CNTs can be used to promote the adsorption of an assortment of moieties onto the surface of CNTs through π - π stacking interactions.

The properties of CNTs are extremely sensitive to their degree of graphitization, diameter, and whether they are in a single- or multi-walled form. SWCNTs, which were first reported in 1993,¹⁵ are seamless cylinders, made from a single graphite sheet. MWCNTs, which were discovered in 1991,² consist of two or more concentrically arranged seamless graphene cylinders. And the production method dictates the quality of the tubes generated, particularly the distribution of diameters and lengths, the degree of entanglement, and the amount of impurities.¹⁶ The literature refers to a wide variety of processing techniques: namely, evaporation,¹⁷ laser ablation¹⁸ and electrochemical methods.¹⁹ However, chemical vapor deposition appears to have the highest potential for growing large quantities of pure crystalline CNTs.

Because the carbon-carbon bond observed in graphite is one of the strongest bonds in nature, CNTs are excellent candidates for the stiffest and strongest material ever synthesized. Despite the large variations in the reported values, CNTs exhibit superior mechanical performance to that of classic advanced fibers. Regarding the electric properties, the mechanical strength of the tubes depends on the crystallinity of the material, number of defects, diameter etc. The mechanical properties of SWCNTs usually exceed those of MWCNTs but the task of measuring the mechanical properties of SWCNTs is more complex and less precise due to their smaller size and massive arrangement in ropes.²⁰

One of the unique properties of CNTs is that their metallicity can be controlled by an external magnetic field applied parallel to the tube axis.^{21,22} This means that a CNT can be either semiconducting or metallic, depending on the strength of the applied field, and its band gap is predicted to be an oscillatory function of the magnetic field. Therefore, metallic tubes can be made semiconducting by applying a magnetic field parallel to the tube axis, and semiconducting tubes can be made metallic in ultrahigh magnetic fields.

Aggregation and Poor Solubility of CNTs. The nano-scale dimensions of CNTs make dispersion a considerable challenge. The high aspect ratios of CNTs, combined with high flexibility,²³ increase the probability of their entanglement and close packing.²⁴ The range of the attractive van der Waals interparticle potentials was recently determined by the

number of microscopic versus mesoscopic dimensions.²⁵ Most polymer/CNTs composite studies carried out in a solution used sonication to disperse the CNTs. However, sonication introduces defects in the carbon structure, including buckling, bending and dislocations. Prolonged sonication increases the level of disorder, reduces the nanotube length, and ultimately leads to the formation of amorphous carbon.²⁶ In addition, high shear mixing in the presence of selected polymers has also been used to disentangle ropes, yielding a homogeneous dispersion. If sonication is carried out in the presence of a polymer, then it is also important to understand the effect of sonication on the polymer molecular weight.

The solubility of CNTs may be essential for chemical and physical examinations because it allows easy characterization and facilitates their manipulation. Extensive research has been undertaken to overcome the poor solubility of CNTs in either water or organic solvents. The solubility of SWCNTs was examined in relation to the solvent, such as dimethylformamide, chloroform, acetone, toluene, and benzene.²⁷ Highly polar solvents, such as dimethylformamide, methylpyrrolidine and hexamethylphosphoramide, were reported to properly wet SWCNTs.²⁸ The wetting properties of CNTs can be improved significantly by oxidation with strong acids, such as H₂SO₄ or HNO₃, or a mixture of acids.²⁹ As a result of this procedure, the carboxylic groups are formed preferentially on the end caps of the CNTs. Under these conditions, the end caps of the nanotubes are opened, and acidic functionalities, which may be suitable for preparing further derivatization such as esterification or amidization,^{30,31} can be formed at these defect sites as well as at the side walls. Therefore, long-chain alkylamide-functionalized nanotubes were obtained where surface-bound COOH groups were converted to thionyl chloride groups, and these nanotubes subsequently reacted with amine.³²

Preparations of Polymer/CNTs Nanocomposites

In order to obtain optimal effective reinforcements of CNTs in nanocomposites, considerable effort has been made to produce functional high property materials by imbedding nanofillers into a variety of polymeric matrices.³³⁻³⁷ However, highly aggregated CNTs are difficult to disperse in polymer solutions. There are several methods for improving the dispersion of CNTs in polymer matrices, e.g. a simply processing method for dispersing the derivatized CNTs in a polymer.³⁶ These include noncovalent attachment, covalent attachment, *in situ* polymerization or physical blending. These methods have been used to successfully prepare polymer/CNTs nanocomposites.

Noncovalent Attachment.

Polymer Wrapping: Smalley *et al.* reported that SWCNTs could be dissolved reversibly in water by non-covalently associating them with a variety of linear polymers, such as polyvinyl pyrrolidone and polystyrene (PS) sulfonate.^{37,38}

On the other hand, CNTs functionalized with biological molecules (such as protein peptides and nucleic acids) have great potential for applications in bioengineering and nanotechnology.³⁹ Peptides fold into an amphiphilic α -helix in the presence of CNTs and disperses them in an aqueous solution through noncovalent interactions with the nanotube surface.⁴⁰ An amphiphilic α -helical peptide, known as nano-1, was used to isolate individual peptide-wrapped SWCNTs, which were possibly connected end to end to form long fibrillar structures.⁴¹ DNA molecules might be encapsulated inside or wrapped around a CNT, due to the van der Waals attractions between the DNA and CNT. Recent advances in this field have been reviewed by Gao and Kong.⁴²

Polymer Adsorption: Adsorbents are generally used in the form of spherical pellets, rods, moldings or monoliths, with a hydrodynamic diameter ranging from 0.5 to 10 mm. These adsorbants must have high abrasion resistance, high thermal stability and a small micropore diameter.

MWCNTs have been solubilized in water and a variety of organic solvents through noncovalent side-wall functionalization with pyrene-containing polymers.⁴³ SWCNTs modified with the aid of a specifically adsorbed pyrene-linked ring-opening metathesis polymerization initiator were prepared for the selective ring-opening metathesis polymerization of norbornene on the surface of the SWCNTs. This process achieved a homogeneous noncovalent poly(norbornene) coating.⁴⁴

Barisci *et al.* examined a method for introducing biofunctionality to CNT fibers using biopolymers. They reported that DNA is an effective dispersant of CNTs and that fiber containing DNA can be spun using particle coagulation spinning procedures.⁴⁵

Covalent Attachment. Liu *et al.* first reported defect sites on the surface of CNTs subjected to purification in nitric acid followed by oxidation in a mixture of sulfuric and nitric acid.⁴⁶ These CNTs, which are open-ended with terminal carboxylic acid groups, allow the formation of covalent linkages with oligomers or polymers. Moreover, it is also reported that finely dispersed functionalized MWCNTs (even with a high content above 10 wt%) has been achieved by grafting a variety of end-functionalized polymers onto MWCNTs which provided the compatibility with organic solvents and polymers.⁴⁷

“Grafting to” Method: In the “grafting to” method, ready-made polymers with reactive end groups react with functional groups on the surface of nanotubes. This reaction corresponds to a reaction between the surface groups of nanotubes and readymade polymers, and may also involve physical adsorption or a covalent attachment mechanism. Polymer-grafted MWCNTs were also prepared using a “grafting to” method with an ionic mechanism. In this case, the MWCNTs were modified chemically by a ligand-exchange reaction with ferrocene.⁴⁸

Ferritin and bovine serum albumin proteins were bonded

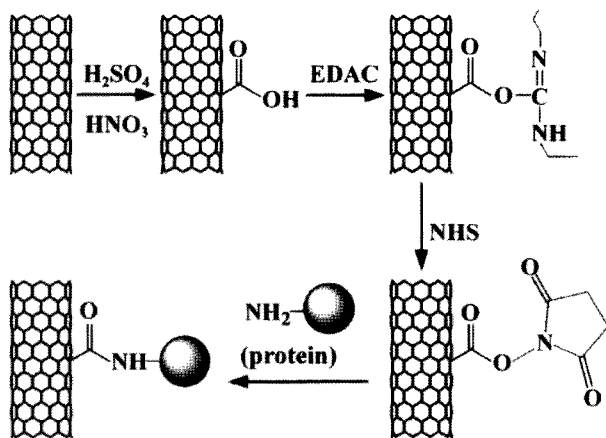


Figure 1. Schematic diagram of the two-step process for attaching proteins to CNTs (reprinted from ref. 49, Copyright 2008, with permission from The Royal Society of Chemistry, <http://dx.doi.org/10.1039/b310359e>).

chemically to nitrogen-doped MWCNTs (CN_x MWCNTs) through a two-step process of diimide-activated amidation. First, the carboxylated CN_x MWCNTs were activated by *N*-ethyl-*N*-(3-dimethylaminopropyl)-carbodiimide hydrochloride, forming a stable active ester in the presence of *N*-hydroxysuccinimide. Second, the active ester was reacted with the amine groups on the proteins of the ferritin or bovine serum albumin, forming an amide bond between the CN_x MWCNTs and proteins. This two-step process avoids the intermolecular conjugation of proteins and guarantees the uniform attachment of proteins on the CNTs (Figure 1).⁴⁹

“Grafting from” Method: In the “grafting from” method, the reactive groups were attached covalently to the nanotube surfaces and polymers were then grafted to these reactive groups. This process involves a reaction between the reactive groups on the surface of the nanotubes and monomers. Guan *et al.* reported the synthesis of an individual polyacrylamide CNTs copolymer using the *in situ* UV radiation-initiated polymerization of acrylamide in an aqueous solution in the presence of MWCNTs.⁵⁰ Oxidized MWCNTs can be grafted with PS molecules using an *in situ* radical polymerization reaction.⁵¹ In another study, Chen *et al.* obtained CNT-graft-poly(*L*-lactide) from surface-initiated ring-opening polymerization.⁵² Although covalent polymer/CNTs conjugates can now be synthesized using either of the “grafting from” or “grafting to” methods, there are still some problems. For example, the “grafting from” mechanism promises high graft densities but the tasks of attaching the initiator group to CNTs and controlling the polymer molecular weight and architecture can be difficult.^{53,54} On the other hand, the “grafting to” method allows full control of the polymer molecular weight and architecture but suffers from a low theoretical polymer loading due to steric repulsion between the grafted and reacting polymer chains.¹¹

***In Situ* Polymerization.** *In situ* polymerization has been

used to attach conjugated or conducting polymers to the surfaces of CNTs in an attempt to improve the processability, as well as the electrical, magnetic and optical properties of CNTs. Fan *et al.* synthesized conducting polypyrrole (PPY)-coated CNTs and reported that its magnetization is the sum of the two components, namely the magnetization of PPY and CNTs.⁵⁵ On the other hand, Jia *et al.* synthesized poly(methyl methacrylate)/CNTs nanocomposites by the *in situ* polymerization of methyl methacrylate with CNTs.⁵⁶ This type of nanocomposite contained 1 wt% of MWCNTs. In addition, the storage modulus at 90 °C was increased by an outstanding 1,135% and the glass transition temperature was also increased. CNTs are compromised by functionalization. There are several approaches to bringing about the covalent side-wall functionalization of the tubes. These approaches include fluorination with molecular fluorine followed by further substitution with alkyl groups and the addition of nitrenes, carbenes or radicals.

Physical Blending. In order to obtain high-performance polymeric composites, nano-sized fillers could be used for compounding instead of conventional micron-sized fillers. However, agglomeration is also an encumbrance for the dispersion of nanofillers in a polymer matrix. For polymer/CNTs nanocomposites, high power dispersion methods, such as ultrasound and high-speed shearing, are the simplest and most convenient way of improving the dispersion of CNTs in a polymer matrix. For example, Qian *et al.*, employed a simple solution-evaporation method to prepare PS/MWCNTs nanocomposite films involving high energy sonication, in which the MWCNTs were dispersed homogeneously in the PS matrix.²⁸ Surfactants can be used as dispersing agents to improve the dispersion of CNTs during the processing of polymer/CNTs nanocomposites. Gong *et al.* used a non-ionic surfactant, polyoxyethylene-8-lauryl, as a processing aid for epoxy/CNTs nanocomposites. The homogeneous dispersion of CNTs in epoxy improves the thermomechanical properties of the nanocomposites. With only 1 wt% of the CNTs in the epoxy/CNTs nanocomposites, the glass transition temperature was increased by 25 °C (from 63 to 88 °C) and the elastic modulus was increased by more than 30%.⁵⁷

Properties of Polymer/CNTs Nanocomposites

In general, a significantly increased modulus and strength can be achieved by incorporating CNTs into a polymer matrix. For example, the addition of 1 wt% of MWCNTs to PS/MWCNT nanocomposite films using a solution-evaporation method results in a 36–42% and approximately 25% improvement in the tensile modulus and break stress, respectively.²⁰ Although the modulus and strength were increased as a result of reinforcement with CNTs, the impact toughness of the nanocomposites was reduced,⁵⁸ even though one study reported an observable improvement in

toughness.⁵⁹ Ruan *et al.*, reported that the toughness and ductility were improved by 150% and 104%, respectively, with the addition of 1 wt% of MWCNTs in ultrahigh molecular weight polyethylene, due to the MWCNT-induced enhancement of the chain mobility in an ultrahigh molecular weight polyethylene.⁶⁰

Improving the thermal endurance of polymeric nanocomposites is highly desirable. The addition of CNTs enables an increase in the glass transition temperature and melting and thermal decomposition temperatures of the polymer matrix, due to the constraint effect on the polymer segments and chains. Besides the addition of a surfactant, the addition of 1 wt% CNTs to epoxy increases the glass transition temperature from 63 to 88 °C.⁶¹ Choi *et al.* reported that the thermal conductivity of the epoxy was increased by up to 300% with the addition of 3 wt% of SWCNTs.²⁷

The electrically conducting component in polymer nanocomposites which also has been well studied⁶² has major commercial applications.¹⁵ Besides their use in super-capacitors,⁶³ polymer/CNTs nanocomposites have many potential applications in electrochemical actuation, electro-magnetic interference shielding, wave absorption, electronic packaging, etc.⁶⁴ Moreover, polymer/CNTs nanocomposites can also be used for optical elements, optical sensors, optical switching,⁶⁵ and organic photovoltaic devices.⁶⁴

Nylon/CNTs Nanocomposites

Nylon is an important thermoplastic material with a wide variety of applications. Reinforcement of nylon with CNTs has been investigated by several groups. Some researchers employed the chemical functionalization of CNTs with surface -COOH or -CONH₂ groups to surface-graft the nylon chains. There are many ways of synthesizing nylon/CNTs nanocomposites. These include melt-compounding, *in situ* polymerization and “grafting to” methods. In addition, melt spinning, wet spinning, dry spinning and electrospinning have been used to synthesize nylon fibers.

Nylon 6/CNTs Composites. Nylon 6, which is one of the most widely used commercial polymer fibers with a wide range of applications, is used for the synthesis of aligned MWCNTs-based nanofibrous nanocomposites through electrospinning. Several techniques have been used to synthesize nylon 6 fibers, including melt spinning, wet spinning, dry spinning and electrospinning.

MWCNTs-reinforced nylon 6 nanocomposites with excellent mechanical properties have been prepared successfully using a variety of methods, particularly the simple melt-compounding method reported by Liu *et al.*⁶⁵ Different mechanical tests, such as the tensile and nanoindentation methods, showed that the incorporation of a small amount of MWCNTs (< 2 wt%) into the nylon 6 matrix can significantly improve the modulus, strength, and hardness. Microscopy observations confirmed the successful achievement of

a uniform and fine dispersion of MWCNTs throughout the nylon 6 matrixes as well as strong interfacial adhesion between the CNTs and the matrix. Furthermore, these traits are responsible for the remarkable increase in the overall mechanical properties of the nanocomposites prepared.

Chen *et al.* reported the functionalization of MWCNTs with amine groups using a “grafting to” method. The oxidized MWCNTs (MWCNT-COOH) were converted to acyl chloride functionalized MWCNTs (MWCNT-COCl) by a treatment with thionyl chloride (SOCl₂). The MWCNT-COCl then reacts with hexamethylenediamine to yield MWCNT-NH₂. Nylon 6/MWCNT-NH₂ nanocomposites with a different MWCNTs loading were prepared using a simple melt compounding approach. A fine dispersion of MWCNTs throughout the nylon 6 matrixes was observed. The incorporation of MWCNTs improved the mechanical properties significantly. In addition, higher thermal stability was obtained for nanocomposites with better dispersed MWCNTs.⁶⁶

Kim *et al.* synthesized electrically conducting nylon 6 non-woven membranes consisting of nanofibers with MWCNTs adsorbed on their surface.⁶⁷ Triton X-100 was used as the surfactant to generate a dispersion of MWCNTs in aqueous media. A scanning electron microscopy (SEM) image shows that the MWCNTs adhered well to the surface of the highly porous nylon 6 nanofibrous membranes (Figure 2). Due to the presence of a small amount of MWCNTs (approximately 1.5 wt%) on the surface of the nanofibers, the membranes exhibited good conductivity ($2.2 \times 10^{-2} \text{ S} \cdot \text{cm}^{-1}$), highlighting their potential use in the development of new materials,

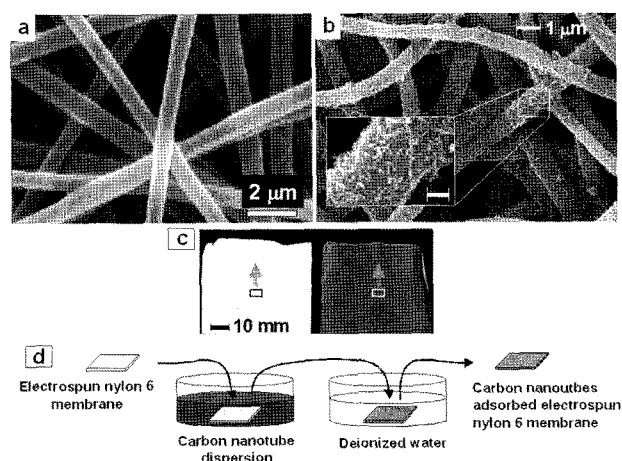


Figure 2. High-resolution SEM images of the non-woven fibrous nylon 6 membranes (a) before and (b) after dip-coating in a dispersion of MWCNTs in water (0.05 wt%) containing the Triton X-100 surfactant (0.3 wt%). (c) Images of non-woven fibrous nylon 6 and the MWCNT-adsorbed non-woven fibrous nylon 6. (d) Schematic diagram of the simple processing technique used to produce the MWCNT-adsorbed non-woven fibrous nylon 6 membranes (reprinted from ref. 67, Copyright 2008, with permission from Wiley-VCH Verlag GmbH & Co. KGaA).

such as electronic textiles.

Qu *et al.* examined the functionalization of SWCNTs with nylon 6 using the “grafting from” method in a two-step process. In this process, the covalent attachment of ϵ -caprolactam molecules to the nanotubes was followed by anionic ring-opening polymerization of these bound ϵ -caprolactam species with the same monomers in bulk form.⁶⁸

Another study on the synthesis of nylon 6/MWCNTs nanocomposites reported that the existence of grafted nylon 6 chains on the surface of MWCNTs can improve the nylon/MWCNTs interfacial interaction.⁶⁹ Gao *et al.* reported that the grafting yields of nylon 6 chains on the SWCNTs are affected by the -COOH concentration, which can affect the nylon/SWCNTs interfacial interaction, as manifested in the mechanical performance. Gao *et al.* also synthesized nanocomposites from SWCNTs bearing amide functional groups (SWCNT-CONH₂), and reported an increase in the length of the grafted nylon 6 chains. The mechanical properties of the nanocomposite fibers reinforced with 0.5 wt% SWCNT-CONH₂ had a higher tensile strength and break strain but a lower Young's modulus.⁷⁰

A variety of techniques have been used to synthesize nylon 6/CNTs fibers. Haddon *et al.*⁷¹ obtained nylon 6/CNTs nanocomposite fibers using a chemical processing technology that facilitated the continuous spinning of nanocomposites produced from the *in situ* polymerization of caprolactam in the presence of CNTs. CNT-filled nanofibrous membranes were produced by electrospinning to improve their performance characteristics. Although nanofibrous membranes produced in this manner show significant enhancement of their mechanical properties,⁷² their electrical properties are inferior to those of typical semiconductors or conductors. Their conductivities are even lower than those of nanocomposite films with the same concentration of CNTs due to the high porosity of the membranes and the excellent wrapping of the polymers around the CNTs, as reported in a previous study.⁷³

For diamine-modified SWCNTs, the nylon 6 chain is grafted onto SWCNTs by a reaction between the carboxylic acid groups of nylon 6 and the amide group of the diamine-modified SWCNTs. The grafted nylon 6 chains contain amine-terminal groups through which the grafted PA6 chains can continue to propagate (Figure 3). Therefore, the grafted nylon 6 chain of diamine-modified SWCNTs is expected to have a higher molecular weight than the polymer chain of acid-modified SWCNTs because acid-modified SWCNTs and diamine-modified SWCNTs both contain the same concentration of functional groups (4.2%). Therefore, the number of grafted polymer chains is similar but the longer chain length of the grafted nylon 6 chains can explain the higher grafting yield of diamine-modified SWCNTs. The long chemically bonded nylon 6 chains of diamine-modified SWCNTs are expected to increase the plasticity of the composite and are probably responsible for the higher

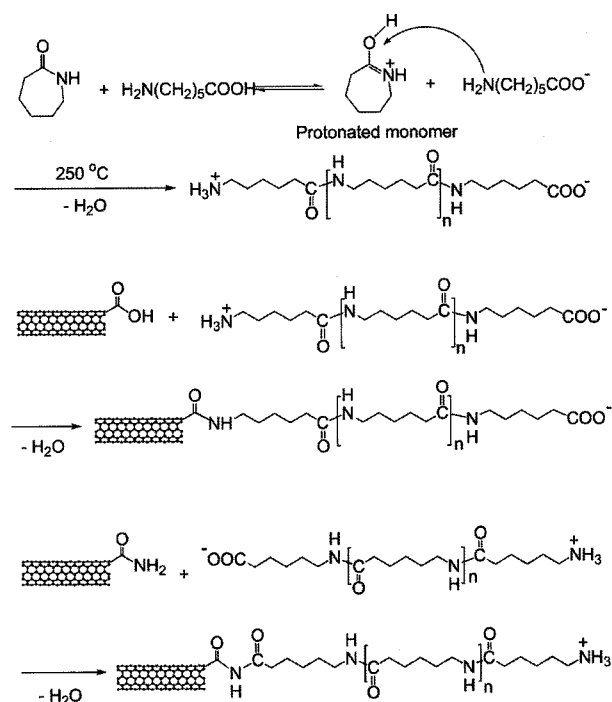


Figure 3. Schematic diagram of the synthesis of a nylon/SWCNTs composite made with acid-modified SWCNT and diamine-modified SWCNT (reprinted from ref. 70, Copyright 2008, with permission from American Chemical Society).

break strain and toughness of the composite.⁷⁰

The electrospinning of nanocomposite solutions is a useful method for producing fibers with well-embedded CNTs. During the electrospinning process, the nanotubes are well oriented by the charged fluid jet. The effect of the nylon fiber alignment and the enhanced orientation of CNTs are also manifested in the mechanical properties, i.e. they improve with increasing take-up speed and nanotube concentration. During the electrospinning process, the nanotubes are oriented by a charged fluid jet, and serve as oriented nuclei for the polymer chains (Figure 4). The effect of the nylon fiber alignment and enhanced CNTs orientation is also manifested in the mechanical properties. The storage modulus of the fibers increases significantly, even though the concentration of MWCNTs is relatively low (0.1 and 1.0 wt%).⁷⁴

The thermal degradation behavior of composites embedded with CNTs was also examined. Li *et al.* used thermogravimetric analysis to examine the thermal degradation behavior of nylon 6/MWCNTs composites in air and nitrogen atmosphere.⁷⁵ The presence of MWCNTs clearly improves the thermal stability of nylon 6 in air but has little effect on the thermal degradation behavior of nylon 6 in a nitrogen atmosphere. Amino-functionalized MWCNTs, which have a less integrated structure, have a smaller effect on the second degradation of nylon 6 in a nitrogen atmosphere than

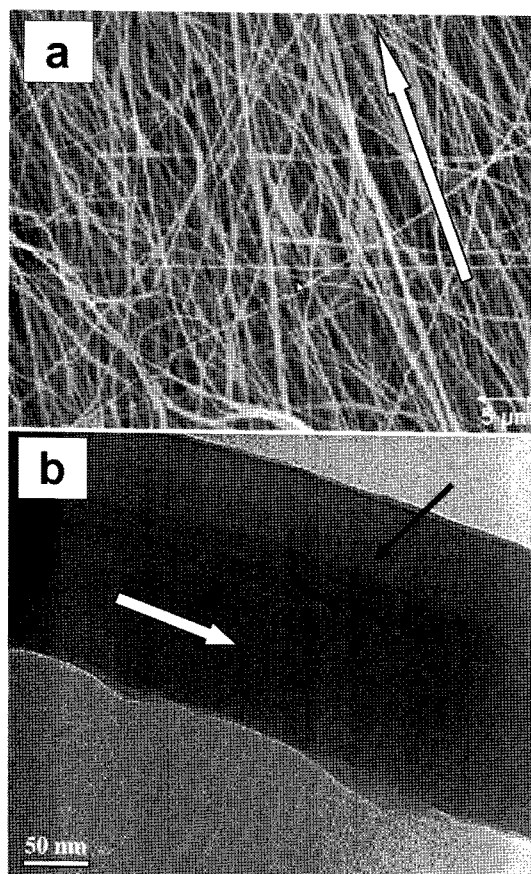


Figure 4. SEM image of nylon 6/MWCNTs (0.1 wt%) nanocomposite nanofibers collected at 4,500 rpm (the arrows denote the alignment direction) and a TEM image of 1.0 wt% of CNTs in nylon 6 (the black arrows denote the nanotubes and the white arrow denotes the fiber axis) (reprinted from ref. 74, Copyright 2008, with permission from Elsevier).

purified MWCNTs.

Meng *et al.* examined the effects of acid-modified MWCNTs and diamine-modified MWCNTs on the mechanical properties and crystallization behavior of nylon 6.⁷⁶ Because the diamine modification of acid-modified MWCNTs grafts diamine molecules onto the surface of MWCNTs, the interactions between MWCNTs are weakened resulting in a less compact stacking morphology than that of acid-modified MWCNTs. A better dispersion and a stronger interfacial adhesion of MWCNTs in the nylon 6 matrix can be obtained using diamine-modified MWCNTs. The storage modulus,

glass transition temperature, yield strength, Young's modulus and crystallization temperature of nylon 6 were improved significantly through the incorporation of diamine-modified MWCNTs. Moreover, compared with the acid-modified nylon 6/MWCNTs nanocomposites, diamine-modified nylon 6/MWCNTs nanocomposites had a higher crystallization temperature due to the superior dispersion of diamine-modified MWCNTs and lower degree of crystallinity as a result of the stronger interaction between the diamine-modified MWCNTs and nylon 6.

Nylon 6,10/CNTs Composites. Kang *et al.* prepared nylon 6,10/MWCNTs nanocomposites by dispersing MWCNTs by the *in situ* interfacial polymerization of two liquid phases, one containing hexamethylenediamine and the other containing sebacyl chloride in the presence of MWCNTs with Triton X-100. As shown in Table I, the interfacial polymerization process was useful for dispersing MWCNTs in the nylon 6,10 matrix, and was efficient in enhancing the mechanical properties (such as a 170% increase in Young's modulus) of the matrix polymer containing a small amount of MWCNTs (1.5 wt%). The incorporation of MWCNTs into the nylon 6,10 matrixes also increases the thermal stability of the nanocomposite.⁷⁷

Another study was carried out by Kim *et al.* which was similar to that reported by Kang *et al.*⁷⁸ Acyl chloride-functionalized MWCNTs (MWCNT-COCl) and sebacyl chloride in carbon tetrachloride were mixed with hexamethylenediamine and NaOH in distilled water (Figure 5). Interfacial polymerization was carried out with ultrasonication to maintain the dispersion of MWCNTs. The resulting nylon 6,10/MWCNT nanocomposite was obtained after washing and drying. Furthermore, Table I shows that the Young's modulus and tensile strength of the nanocomposites increased significantly after the incorporation of MWCNTs into pure nylon 6,10.

Interfacial copolymerization occurs at the interface between two immiscible, low molecular weight fluids, each containing a different reactant. The dissolved monomers were diffused in the interface, where they undergo a copolymerization reaction. The resulting copolymer is usually incompatible with the liquid phases and a polymer film grows at the interface.⁷⁹

Nylon 6,10 nanocomposites with functionalized SWCNTs were synthesized by interfacial *in situ* polycondensation (Figure 6).⁸⁰ The SWCNTs were functionalized with alkyl acid chloride groups for the nanoscale manipulation of the

Table I. Mechanical Properties of Nylon 6,10/MWCNTs Composites (reprinted from ref. 77, Copyright 2008, with permission from Elsevier)

Samples	Tensile Modulus, E^a (GPa)	Tensile Strength, $\sigma_y^{a,b}$ (MPa)	Elongation ^a (%)	η_{inh} (dL/g)
Nylon 6,10	0.9±0.1	35.9±0.5	10.2±0.3	1.06
Nylon 6,10/MWCNTs	2.4±0.3	51.4±1.7	12.7±0.7	1.40

^a $N=5$, average ± standard deviation. ^bStrength at yield.

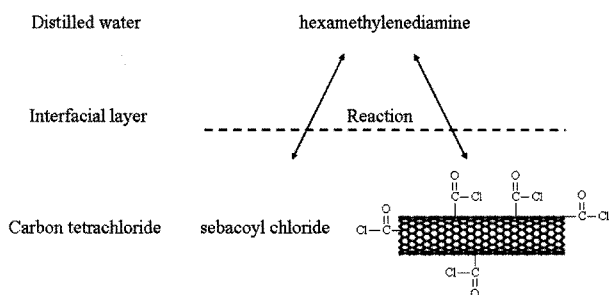


Figure 5. Schematic diagram of interfacial polymerization (reprinted from ref. 78, Copyright 2008, with permission from Elsevier).

nylon 6,10/CNTs interface. In the composites, CNTs exhibit a good dispersion. As a result, the nylon 6,10/SWCNTs composites showed significant improvements in the tensile modulus, strength and toughness. With 1 wt% SWCNTs in nylon 6,10, the composite fibers exhibited the highest Young's modulus of 2,309 MPa, which is 162% higher than that of nylon 6,10 fibers. In addition, the tensile strength and toughness was increased by 149% and 106%, respectively. Furthermore, Jeong *et al.*⁸¹ prepared 4-chlorobenzoyl-functionalized MWCNTs (F-MWCNTs) via "direct" Friedel-Crafts acylation for chemical affinity. F-MWCNTs were homogeneously dispersed in carbon tetrachloride that was used as an organic solvent for interfacial polymerization.⁸¹ A large scale of nylon 6,10/F-MWCNTs composite could be conveniently prepared by *in situ* interfacial polymerization of 1,6-hexamethylenediamine in an aqueous phase, and sebacoyl chloride with F-MWCNTs in an organic phase.⁸¹

Nylon 6,6/CNTs Composites. Nylon 6,6 is a commer-

cially important thermoplastic that cannot be solvent processed with nanotubes because it is soluble in only a few solvents that either do not suspend nanotubes, (for example, formic acid) or might even damage the nanotubes (for example, sulfuric acid). Melt compounding can be used. However, the melt viscosity of nylon 6,6 is rather low, and small shear forces as well as the poor dispersion of SWCNTs are observed when dry nanotubes are added. However, the noncovalent functionalization of MWCNTs with nylon 6,6 single crystals can be accomplished through controlled solution crystallization.⁸² A morphological study reported that the structure of the functionalized MWCNTs is similar to the classical shish-kebab structure. Figure 7 shows a hybrid with the so-called nano-hybrid shish-kebab (NHSK) structure.⁸³ These nylon 6,6/functionalized MWCNTs were used as precursors to prepare polymer/MWCNT nanocomposites. Nitric acid etching of the nanocomposites in nylon 6,6 showed that the MWCNTs had formed a robust network. Moreover, the crystallization rate initially increased and then decreased with increasing MWCNT content.

Haggenmueller *et al.* reported an interfacial *in situ* polymerization method for the synthesis of nylon 6,6/SWCNTs nanocomposites.⁸⁴ The quality of the nanofiller suspension prior to *in situ* polymerization has a significant effect on the nanofiller dispersion in the resulting nanocomposite. The functionalization of SWCNTs with alkyl chains promotes their suspension and subsequently improves their dispersion in nanocomposites. Furthermore, the use of surfactants to disperse the nanotubes is less reliable in two-phase *in situ* polymerization.

A study of the properties of the various nylon 6,6/SWCNTs

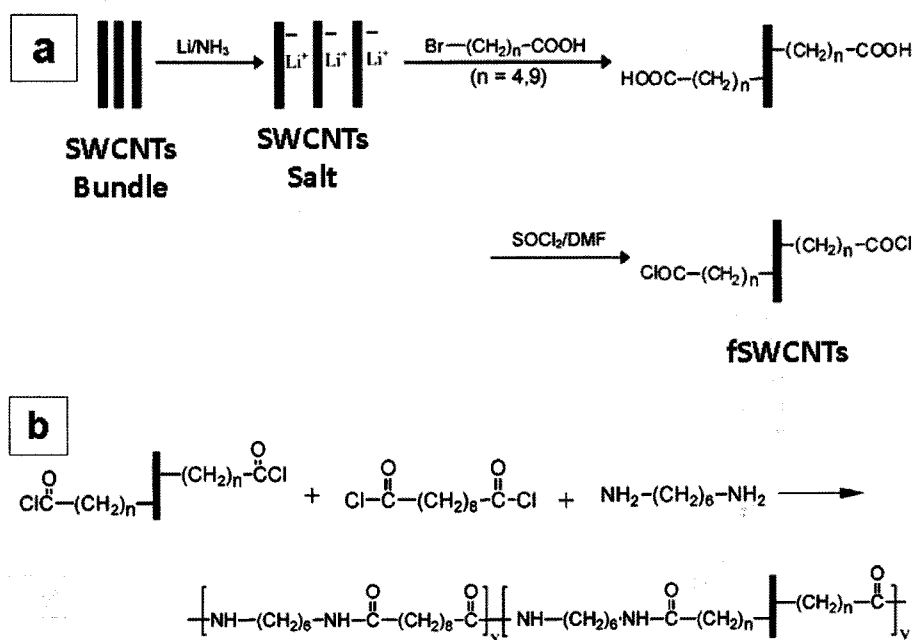


Figure 6. Schematic diagram of (a) functionalization of SWCNTs with the alkyl acid chloride group and (b) synthesis of nylon 6,10-f-SWCNTs composites (reprinted from ref. 80, Copyright 2008, with permission from American Chemical Society).

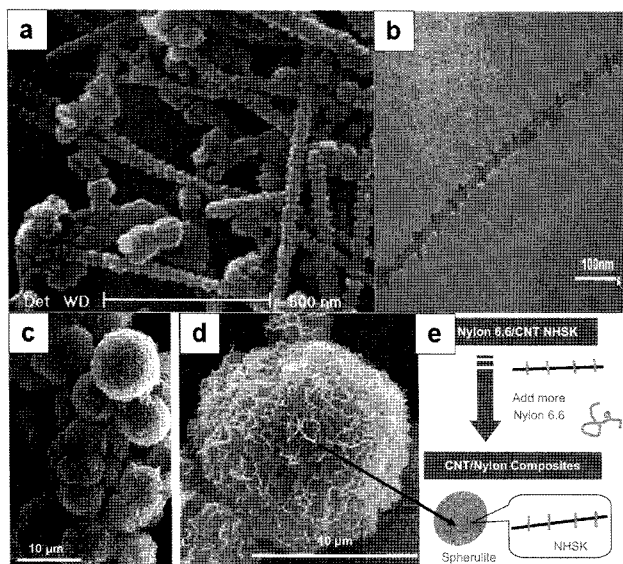


Figure 7. Nylon 6,6/CNTs nano-hybrid shish-kebab (NHSK) structure produced by the crystallization of nylon 6,6 on CNTs at 185 °C in ρ -xylene for 0.5 h. (a) A SEM image showing that CNTs are decorated by nylon 6,6 single crystals. (b) A TEM image of nylon 6,6/CNTs NHSK structures: the inset shows an enlarged section. TEM micrograph of the NHSK structure obtained by crystallizing a nylon 6,6-CNT-glycerin solution at 172 °C for 0.5 h. (c) SEM micrograph of nylon 6,6 spherulites formed using the NHSK structure (d) as a seed to further crystallize pure nylon 6,6 at 185 °C. (e) The formation process of CNTs-containing nylon 6,6 spherulites (reprinted from ref. 83, Copyright 2008 with permission from Elsevier).

nanocomposites showed that the low shear forces in these nanocomposites can cause nanotube agglomeration. Therefore, these forces must be considered during nanocomposite processing.

Another interesting morphological transition was observed by Zou *et al.*⁸⁵ By adding a small amount of acid-treated MWCNTs to poly(*p*-phenylene sulfide)(PPS)-PA66(60/40 w/w) blends, they found that the morphology changes from a sea-island structure to a co-continuous structure (Figure 8). It should be noted that MWCNTs are located selectively in the PA 6,6 phase, and that their assembly determines the final morphology of PPS/PA 6,6 blends. For a low load, the well-dispersed CNTs form a dendritic edge-touched network structure, resulting in a co-continuous structure. For a high load, the MWCNTs agglomerate to produce island morphology. This work can be a new way of creating a rich diversity of new structures and useful nanocomposites.

Nylon 10,10/CNTs Composites. Nylon 10,10 is an important engineering plastic on account of its high intensity, elasticity, toughness and abrasion resistance (albeit with a poor modulus).⁸⁶ Accordingly, nylon 10,10/CNTs nanocomposites were prepared using an *in situ* polymerization method.⁸⁷ Initially, the MWCNTs were functionalized by an

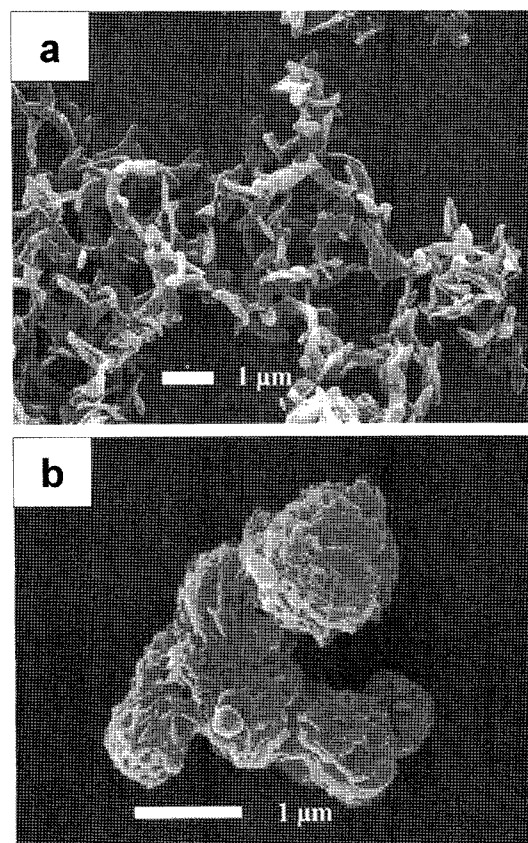


Figure 8. SEM images of the extracted products from the nano-composites: (a) with 0.01 phr MWCNTs; (b) with 1 phr MWCNTs ('phr'='part per hundred of resin', means the weight percent of filler to 100 units weight polymer matrix) (reprinted from ref. 85, Copyright 2008, with permission from Elsevier).

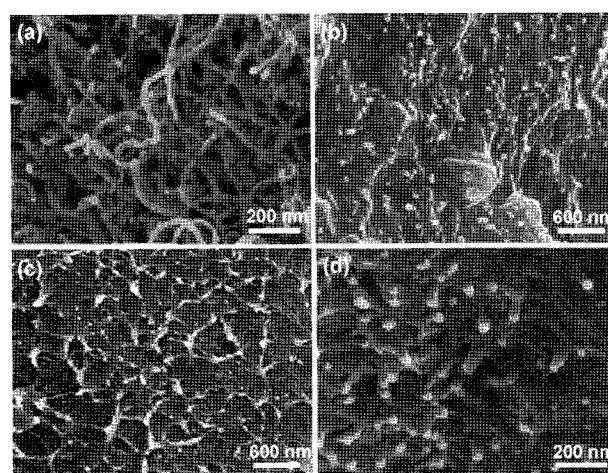


Figure 9. SEM images of (a) crude CNTs and (b) the failure surfaces of nylon 10,10/ MWCNTs nanocomposites with an MWCNTs content of 5 wt%. Figures (c) and (d) show the failure surfaces of the nylon 10,10/MWCNTs nanocomposites with an MWCNTs content of 30 wt% (reprinted from ref. 87, Copyright 2008, with permission from Elsevier).

acid treatment in order to introduce carboxylic acid groups onto the tube surfaces. The nylon 10,10/MWCNTs nanocomposites were then prepared using a polymerization compounding method. SEM (Figure 9) showed that the MWCNTs on the fractured surfaces of the nanocomposites were dispersed uniformly exhibiting strong interfacial adhesion with the polymer matrix. MWCNT-reinforced nylon 10,10 nanocomposites with excellent mechanical properties were prepared successfully using an *in situ* polymerization method.⁴⁹ The Young's modulus of nylon 10,10 could be improved by 87.3% at an MWCNT content of 30.0 wt%. The elongation at the break, which is an indicator of the toughness of a material, decreased to approximately 110% when MWCNTs are incorporated into the nylon 10,10 matrix.

Conclusions

The wide range of applications of CNTs was realized long ago. For the successful utilization of their properties, it is important that the problems with the aggregation and poor dispersion of CNTs in a variety media be solved. Several approaches have been suggested to decrease the level of nanotube agglomeration, such as ultrasonication, high shear mixing, chemical treatment of CNTs (covalent and non-covalent) and *in situ* polymerization. This review focuses on the improvement and application of nylon/CNTs nanocomposites. A key conclusion is the significant progress made in the preparation, properties and application of nylon/CNTs nanocomposites. Remarkable enhancement of the Young's modulus, strength and toughness has been observed, all of which points to a bright future. Overall, it is believed that nano-scale fillers with a higher aspect ratio, such as nanorods and nanowires, might be the next fillers for polymers.

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References

- (1) H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, *Nature*, **318**, 162 (1985).
- (2) S. Iijima, *Nature*, **354**, 56 (1991).
- (3) P. M. Ajayan, L. S. Schadler, and P. V. Braun, *Nanocomposite Science and Technology*, Wiley-VCH, Verlag GmbH & Co. KGaA, Weinheim, Germany, 2003.
- (4) H. S. Nalwa, *Handbook of Nanostructured Materials and Nanotechnology*, Academic Press, San Diego, USA, 2000, vol. 5.
- (5) M. S. Dresselhaus, G. Dresselhaus, and P. Avouris, *Carbon Nanotubes: Synthesis, Structure, Properties and Application*, Springer, Berlin, Germany, 2001.
- (6) X. L. Xie, Y. W. Mai, and X. P. Zhuo, *Mater. Sci. Eng. R*, **49**, 89 (2005).
- (7) M. Moniruzzaman and K. I. Winey, *Macromolecules*, **39**, 5194 (2006).
- (8) Y. P. Sun, K. Fu, Y. Lin, and W. Huang, *Acc. Chem. Res.*, **35**, 1096 (2002).
- (9) C. A. Mitchell, J. L. Bahr, S. Arepalli, J. M. Tour, and R. Krishnamoorti, *Macromolecules*, **35**, 8825 (2002).
- (10) B. S. Kim, S. H. Bae, Y. H. Park, and J. H. Kim, *Macromol. Res.*, **15**, 357 (2007).
- (11) Y. Lin, B. Zhou, K. A. S. Fernando, P. Liu, L. F. Allard, and Y. P. Sun, *Macromolecules*, **36**, 7199 (2003).
- (12) J. K. W. Sandler, S. Pegel, M. Cadek, F. Gojny, M. van Es, J. Lohmar, W. J. Blau, K. Schulte, A. H. Windle, and M. S. P. Shaffer, *Polymer*, **45**, 2001 (2004).
- (13) M. Endo, S. Koyama, Y. Matsuda, T. Hayashi, and Y. A. Kim, *Nano Lett.*, **5**, 101 (2005).
- (14) M. S. Dresselhaus, G. Dresselhaus, and R. Saito, *Carbon*, **33**, 883 (1995).
- (15) S. Iijima and T. Ichihashi, *Nature*, **363**, 603 (1993).
- (16) R. H. Baughman, A. A. Zakhidov, and W. A. De Heer, *Science*, **297**, 787 (2002).
- (17) T. W. Ebbesen, *Ann. Rev. Mater. Sci.*, **24**, 235 (1994).
- (18) T. Guo, P. Nikolaev, A. G. Rinzler, D. Tomanek, D. T. Colbert, and R. E. Smalley, *J. Phys. Chem.*, **99**, 10694 (1995).
- (19) W. K. Hsu, M. Terrones, J. P. Hare, H. Terrones, H. W. Kroto, and D. R. M. Walton, *Chem. Phys. Lett.*, **262**, 161 (1996).
- (20) E. T. Thostenson, Z. Ren, and T.-W. Chou, *Compos. Sci. Technol.*, **61**, 1899 (2001).
- (21) J. P. Lu, *Phys. Rev. Lett.*, **74**, 1123 (1995).
- (22) J. Jiang, J. Dong, and D. Y. Xing, *Phys. Rev. B*, **62**, 13209 (2000).
- (23) S. Cui, R. Canet, A. Derre, M. Couzi, and P. Delhaes, *Carbon*, **41**, 797 (2003).
- (24) O. Lourie, D. E. Cox, and H. D. Wagner, *Phys. Rev. Lett.*, **81**, 1638 (1998).
- (25) R. Shvartzman-Cohen, E. Nativ-Roth, E. Baskaran, Y. Levi-Kalishman, I. Szleifer, and R. Yerushalmi, *J. Am. Chem. Soc.*, **126**, 14850 (2004).
- (26) L. A. Girifalco, M. Hodak, and R. S. Lee, *Phys. Rev. B*, **62**, 13104 (2000).
- (27) H. T. Ham, Y. S. Choi, and I. J. Chung, *J. Colloid Interf. Sci.*, **286**, 216 (2005).
- (28) D. Qian, E. C. Dickey, R. Andrews, and T. Rantell, *Appl. Phys. Lett.*, **76**, 2868 (2000).
- (29) J. Liu, A. G. Rinzler, H. Dai, J. H. Hafner, R. K. Bradley, P. J. Boul, A. Lu, T. Iverson, K. Shelimov, C. B. Huffman, F. Rodriguez-Macias, Y. S. Shon, T. R. Lee, D. T. Colbert, and R. E. Smalley, *Science*, **280**, 1253 (1998).
- (30) Y. Qin, L. Liu, J. Shi, W. Wu, J. Zhang, Z. X. Guo, Y. Li, and D. Zhu, *Chem. Mater.*, **15**, 3256 (2003).
- (31) J. Chen, M. A. Hamon, H. Hu, Y. Chen, A. M. Rao, P. C. Eklund, and R. C. Haddon, *Science*, **282**, 95 (1998).
- (32) D. Tasis, N. Tagmatarchis, V. Georgakilas, and M. Prato, *Chem. Eur. J.*, **9**, 4000 (2003).
- (33) J. N. Coleman, S. Curran, A. B. Dalton, A. P. Davey, B. McCarthy, W. Blau, and R. C. Barklie, *Synth. Met.*, **102**, 1174 (1999).
- (34) F. Ko, Y. Gogotsi, A. Ali, N. Naguib, H. Ye, G. Yang, C. Li, and P. Willis, *Adv. Mater.*, **15**, 1161 (2003).
- (35) T. M. Wu and Y. W. Lin, *Polymer*, **47**, 3576 (2006).
- (36) J. M. Tour, J. L. Bahr, and J. Yang, US 7,304,103 B2.
- (37) R. E. Smalley, D. T. Colbert, K. A. Smith, and M. O'Connell,

- US 7,264,876 B2.
- (38) M. J. O'Connell, P. Boul, L. M. Ericson, C. Huffman, Y. Wang, E. Haroz, C. Kuper, J. Tour, K. D. Ausman, and R. E. Smalley, *Chem. Phys. Lett.*, **342**, 265 (2001).
- (39) Z. Guo, P. J. Sadler, and S. C. Tsang, *Adv. Mater.*, **10**, 701 (1998).
- (40) G. R. Dieckmann, A. B. Dalton, P. A. Johnson, J. Razal, J. Chen, G. M. Giordano, E. Muñoz, I. H. Musselman, R. H. Baughman, and R. K. Draper, *J. Am. Chem. Soc.*, **125**, 1770 (2003).
- (41) V. Zorbas, A. Ortiz-Acevedo, A. B. Dalton, M. M. Yoshida, G. R. Dieckmann, R. K. Draper, R. H. Baughman, M. Jose-Yacamán, and I. H. Musselman, *J. Am. Chem. Soc.*, **126**, 7222 (2004).
- (42) H. Gao and Y. Kong, *Ann. Rev. Mater. Res.*, **34**, 123 (2004).
- (43) P. Petrov, F. Stassin, C. Pagnouille, and R. Jérôme, *Chem. Commun.*, **23**, 2904 (2003).
- (44) F. J. Gómez, R. J. Chen, D. Wang, R. M. Waymouth, and H. Dai, *Chem. Commun.*, **2**, 190 (2003).
- (45) J. N. Barisci, M. Tahhan, G. G. Wallace, S. Badaire, T. Vaugien, M. Maugéy, and P. Poulin, *Adv. Funct. Mater.*, **14**, 133 (2004).
- (46) J. Liu, A. G. Rinzler, H. Dai, J. H. Hafner, R. K. Bradley, P. J. Boul, A. Lu, T. Iverson, K. Shelimov, C. B. Huffman, F. Rodriguez-Macias, Y. S. Shon, T. R. Lee, D. T. Colbert, and R. E. Smalley, *Science*, **280**, 1253 (1998).
- (47) S. H. Lee, J. S. Park, C. M. Koo, B. K. Lim, and S. O. Kim, *Macromol. Res.*, **16**, 261 (2008).
- (48) I. C. Liu, H. M. Huang, C. Y. Chang, H. C. Tsai, C. H. Hsu, and R. C. C. Tsiang, *Macromolecules*, **37**, 283 (2004).
- (49) K. Jiang, L. S. Schadler, R. W. Siegel, X. Zhang, H. Zhang, and M. Terrones, *J. Mater. Chem.*, **14**, 37 (2004).
- (50) X. Li, W. Guan, H. Yan, and L. Huang, *Mater. Chem. Phys.*, **88**, 53 (2004).
- (51) M. S. P. Shaffer and K. Koziol, *Chem. Commun.*, **18**, 2074 (2002).
- (52) G. X. Chen, H. S. Kim, B. H. Park, and J. S. Yoon, *Macromol. Chem. Phys.*, **208**, 389 (2007).
- (53) Z. Yao, N. Braidy, G. A. Botton, and A. Adronov, *J. Am. Chem. Soc.*, **125**, 16015 (2003).
- (54) H. Kong, C. Gao, and D. Yan, *J. Am. Chem. Soc.*, **126**, 412 (2004).
- (55) J. Fan, M. Wan, D. Zhu, B. Chang, Z. Pan, and S. Xie, *J. Appl. Polym. Sci.*, **74**, 2605 (1999).
- (56) Z. Jia, Z. Wang, C. Xu, J. Liang, B. Wei, D. Wu, and S. Zhu, *Mater. Sci. Eng. A*, **271**, 395 (1999).
- (57) X. Gong, J. Liu, S. Baskaran, R. D. Voise, and J. S. Young, *Chem. Mater.*, **12**, 1049 (2000).
- (58) H. Miyagawa and L. T. Drzal, *Polymer*, **45**, 5163 (2004).
- (59) R. Andrews and M. C. Weisenberger, *Curr. Opin. Solid State Mater. Sci.*, **8**, 31 (2004).
- (60) S. L. Ruan, P. Gao, X. G. Yang, and T. X. Yu, *Polymer*, **44**, 5643 (2003).
- (61) Z. Guo, P. J. Sadler, and S. C. Tsang, *Adv. Mater.*, **10**, 701 (1998).
- (62) B. S. Kim, K. D. Suh, and B. Kim, *Macromol. Res.*, **16**, 76 (2008).
- (63) L. Stobinski, P. Tomasik, C. Y. Lii, H. H. Chan, H. M. Lin, H. L. Liu, C. T. Kao, and K. S. Lu, *Carbohydr. Polym.*, **51**, 311 (2003).
- (64) E. Kymakis and G. A. Amaratunga, *Appl. Phys. Lett.*, **80**, 112 (2002).
- (65) W. D. Zhang, L. Shen, I. Y. Phang, and T. Liu, *Macromolecules*, **37**, 256 (2004).
- (66) G. X. Chen, H. S. Kim, B. H. Park, and J. S. Yoon, *Polymer*, **47**, 4760 (2006).
- (67) H. S. Kim, H.-J. Jin, S. J. Myung, M. Kang, and I. J. Chin, *Macromol. Rapid Commun.*, **27**, 146 (2006).
- (68) L. Qu, L. M. Veca, Y. Lin, A. Kitaygorodskiy, B. Chen, A. M. McCall, J. W. Connell, and Y. P. Sun, *Macromolecules*, **38**, 10328 (2005).
- (69) H. Xia, Q. Wang, and G. Qiu, *Chem. Mater.*, **15**, 3879 (2003).
- (70) J. Gao, B. Zhao, M. E. Itkis, E. Bekyarova, H. Hu, V. Kranak, A. Yu, and R. C. Haddon, *J. Am. Chem. Soc.*, **128**, 7492 (2006).
- (71) J. Gao, M. E. Itkis, A. Yu, E. Bekyarova, B. Zhao, and R. C. Haddon, *J. Am. Chem. Soc.*, **127**, 3847 (2005).
- (72) O. Meincke, D. Kaempfer, H. Weickmann, C. Friedrich, M. Vathauer, and H. Warth, *Polymer*, **45**, 739 (2004).
- (73) S. Kumar, T. D. Dang, F. E. Arnold, A. R. Bhattacharyya, B. G. Min, X. Zhang, R. A. Vaia, C. Park, W. W. Adams, R. H. Hauge, R. E. Smalley, S. Ramesh, and P. A. Willis, *Macromolecules*, **35**, 9039 (2002).
- (74) M. V. Jose, B. W. Steinert, V. Thomas, D. R. Dean, M. A. Abdalla, G. Price, and G. M. Janowski, *Polymer*, **48**, 1096 (2007).
- (75) J. Li, L. Tong, Z. Fang, A. Gu, and Z. Xu, *Polym. Degrad. Stabil.*, **91**, 2046 (2006).
- (76) H. Meng, G. X. Sui, P. F. Fang, and R. Yang, *Polymer*, **49**, 610 (2008).
- (77) M. Kang, S. J. Myung, and H.-J. Jin, *Polymer*, **47**, 3961 (2006).
- (78) H. S. Kim, B. H. Park, J. S. Yoon, and H.-J. Jin, *Mater. Lett.*, **61**, 2251 (2007).
- (79) M. Kang and H.-J. Jin, *Key Eng. Mater.*, **321**, 934 (2006).
- (80) M. Moniruzzaman, J. Chattopadhyay, W. E. Billups, and K. I. Winey, *Nano Lett.*, **7**, 1178 (2007).
- (81) J. Y. Jeong, H. J. Lee, S. W. Kang, L. S. Tan, and J. B. Baek, *J. Polym. Sci. Part A: Polym. Chem.*, **46**, 6041 (2008).
- (82) C. Y. Li, L. Li, W. Cai, S. L. Kodjie, and K. K. Tenneti, *Adv. Mater.*, **17**, 1198 (2005).
- (83) L. Li, C. Y. Li, C. Ni, L. Rong, and B. Hsiao, *Polymer*, **48**, 3452 (2007).
- (84) R. Haggenueller, F. Du, J. E. Fischer, and K. I. Winey, *Polymer*, **47**, 2381 (2006).
- (85) H. Zou, K. Wang, Q. Zhang, and Q. Fu, *Polymer*, **47**, 7821 (2006).
- (86) Z. Mo, Q. Meng, J. Feng, H. Zhang, and D. Chen, *Polym. Inter.*, **32**, 53 (1993).
- (87) H. Zeng, C. Gao, Y. Wang, P. C. P. Watts, H. Kong, X. Cui, and D. Yan, *Polymer*, **47**, 113 (2006).