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REVIEW

Polymer/Carbon Nanotube Nanocomposites: A Novel Material

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Polymer/carbon nanotubes (CNTs) nanocomposites have been fabricated for its good processability characteristics of the polymer and excellent functional properties of the CNTs. It is a problem how to enhance dispersion of CNTs in the polymer matrix. Present review deals with recent trends and advances that have been made. The dispersion of CNTs in a polymer matrix can be achieved including optimum blending, *in situ* polymerization and chemical functionalization. The alignment of CNTs in the matrix can possible to enhance by *in situ* techniques, force and magnetic fields, electro spinning and liquid crystalline phase-induced methods. Further, it is discussed on mechanical, thermal, electrical, electrochemical, optical and super-hydrophobic properties and applications of polymer/CNT composites. The enhancement in dispersion and alignment of CNTs in the polymer matrix will promote and extend the applications for developments of polymer/CNT nanocomposites. An improvement of the physical properties of polymer nanocomposites, based on CNTs, is passionated to a good dispersion and strong interactions between the matrix and the filler.

Key Words: Polymer/Carbon Nanotubes, Nanocomposites.

INTRODUCTION

Fullerenes[1] have provided an exciting new insight into carbon nanostructures built from sp^2 carbon units based on geometric architectures. Iijima *et al.*[2] discovered carbon nanotubes (CNTs) that are elongated fullerenes where the walls of the tubes are hexagonal carbon and often capped at each end. There are two types of CNTs: multi-walled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs). The former consists of two or more concentric cylindrical shells of graphene sheets coaxially arranged around a central hollow core with interlayer separations as in graphite. In contrast, SWCNT comprises a single graphene cylinder. Both SWCNTs and MWCNTs have physical characteristics of solids and are micro-crystals with high aspect ratios of 1000 or more, although their diameter is close to molecular dimensions. The comparative properties of CNT and graphite are summarized in Table-1.

Carbon nanotube is well known novel materials with respect to following applications *i.e.*, CNTs have extraordinary electrical conductivity, heat conductivity and

TABLE-1
COMPARATIVE PROPERTIES OF CARBON NANOTUBE (CNT) WITH GRAPHITE

Property	Carbon nanotubes	Graphite
Specific gravity	0.8 g/cm^3 for SWCNT; 0.8 g/cm^3 for MWCNT	2.26 g/cm^3
Elastic modulus	*ca.* 1 TPa for SWCNT; *ca.* 0.3-1 TPa for MWCNT	1 TPa
Strength	50-500 GPa for SWCNT; 10-60 GPa for MWCNT	
Resistivity	5-50 μΩ cm	50 μΩ cm
Thermal conductivity	3000 $W m^{-1} K^{-1}$	3000 $Wm^{-1} K^{-1}$
Magnetic susceptibility	22×10^6 EMU/g	
Thermal expansion	Negligible	
Thermal stability	> 700 ºC (in air); 2800 ºC	$-1 \times 10^{-6} K^{-1}$
Specific surface area	10-20 m^2/g	450-650 ºC (in air)

mechanical properties. They are the best electron field emitter. Because of the great mechanical properties of the carbon nanotube, a variety of structures have been proposed ranging from every day items like clothes and sports gear to combat jackets and space elevators. The possibilities of cross linking CNT molecules are used in a polymer matrix to form a super high strength composite super material. Carbon nanotubes are used for making ideal components of electrical circuit. Nanotubes based transistors have been made that operate at room temperature and are capable of digital switching using a single electron. The first nanotube made integrated memory circuit was made in year 2004. Carbon nanotubes are used as composite fibers in polymers to improve the mechanical, thermal and electrical properties of the bulk product. Carbon nanotubes are used for controlling nanoscale structures due to their strength and flexibility. Thus CNTs have important role in nanotechnology. Carbon nanotubes are present in damascus steels which are used for making swords. Carbon nanotubes have enormously high surface area. They have ability to attach chemical species to their sidewalls providing an opportunity for unique catalyst supports. Cells have been shown to grow on CNTs, so they appear to have no toxic effect. The cells also do not adhere to CNTs, potentially giving rise to applications such as coatings for prosthetics as well as anti-fouling coatings for ships. The ability to functionalize the side walls of CNTs also leads to bio medical applications such as vascular stents and neuron growth and regeneration. A ceramic material reinforced with CNT is more tougher than conventional ceramic. These ceramic materials are used for coating turbine blade. With connection to above properties of carbon nanotube, it must be accepted as one of the novel material. Polymeric nanocomposites (PNCs) or polymer nanostructure materials represents radical alternative to conventional filled polymers. The reinforcement of polymers are done by fillers, which play a major role in strengthening the composite. In contrast to the conventional system where the reinforcement is of the order of microns, discrete constituents of the order of few nanometers exemplify PNCs. Uniform dispersion of these nanoscopically sized filler particles produces ultra large interracial area per volume between the nanoelement and host polymer.

The superior properties of CNTs offer exciting opportunities for new composites. NASA has invested large sums of money to develop carbon nanotube-based composites for applications[3]. Recently, polymer/CNT composites have attracted considerable attention owing to their unique mechanical, surface and multi-functional properties and strong interactions with the matrix resulting from the nano-scale microstructure and extremely large interfacial area. Wagner *et al.*[4] experimentally studied the fragmentation of MWCNTs embedded within thin polymeric films under both compressive and tensile strains. They found that the polymer/CNT interfacial shear stress is of the order of 500 MPa, which is much larger than traditional fiber composites. It suggests good bonding between CNTs and polymer matrix. However, CNTs are easy to agglomerate, bundle together and entangle, leading to many defect sites in the composites and limiting the efficiency of CNTs on polymer matrices[5]. Salvetat *et al.*[6] studied the effect of dispersion of CNTs on the mechanical properties of polymer/CNT composites and found that poor dispersion and rope-like entanglement of CNTs led to drastic weakening of the composites. Thus, alignment of CNTs in the matrix has a predominant role on the mechanical and functional properties of polymer/CNT composites[7]. To-date, the main challenges are to improve the dispersion and alignment of CNTs in a polymer matrix when processing these nanocomposites[8]. The superior mechanical properties of CNT are fascinating, if they can be incorporated compatibly into a polymer matrix. The polymer/CNT composites can be utilized as advanced structural materials that potentially replace low-strength metals such as aluminum[9]. The difficulties of current progress in the development of polymer/CNTs include the high cost of CNTs and difficulty in realization of their theoretical potential of mechanical reinforcement[10]. A full understanding of the interfacial interactions between CNTs and the polymer matrix is still lacking, which is the crucial factor for the preparation of polymer/CNT composites with the desired performance. Nevertheless, the increasing demand for CNTs will surely speedup the commercial mass production of CNTs and its cost will be lowered tremendously. Hence, an understanding of optimum fabrication conditions, such as processing, interfacial strength, crystallization behaviour and so on, is urgently needed and requires in-depth investigation. Significant enhancement of mechanical and thermal mechanical properties of the composites was achieved with addition of only 1 wt % of MWNTs[11]. In another study[12], the crystallization behaviour and morphology of PA6/MWNT composites were focused by using differential scanning calorimetry (DSC), X-ray diffraction (XRD) and polarized light microscopy (PLM). It is shown that the addition of MWNTs changes the crystallization behaviour of PA6 and more interestingly, the crystalline structures of the composites formed under different cooling rates and annealing temperatures[13].

Polymers and polymer matrix composite materials are being utilized in an increasing number of industrial applications including transportation, automotive, aerospace, defence, sporting goods, energy and infrastructure sectors. This is due to their high durability, high strength, light weight, design and process flexibility, *etc*. Polymers such as epoxy[14] thermoplastics gels as well as (poly methyl methacrylate) (PMMA)[15] have been used as the matrix. The conductivity, strength, elasticity, toughness and durability of formed composites may all be substantially improved by the addition of nanotubes. The very high aspect ratio of some carbon nanotubes may also enable them to be aligned with one axis of the composite for fabricating conducting polymers. Carbon nanotubes could replace conventional conductive fillers for a range of application like electrostatic discharge (ESD) and electromagnetic interference (EMI) shielding and a much lower loading of carbon nanotubes can be used to achieve desired conductivity levels[16].

However, the effective utilization of carbon nanotubes in composite applications depends strongly on the ability to homogeneously disperse them throughout the matrix without destroying their integrity. Furthermore, good interfacial bonding is required to achieve load transfer across the CNT-matrix interface, a necessary condition for improving the mechanical properties of the composite[17]. Load transfer from matrix to CNTs plays a key role in the mechanical properties of composites. If the adhesion between the matrix and the CNTs is not strong enough to sustain high loads, the benefits of the high tensile strength of CNTs are lost. Load transfer depends on the interfacial shear stress between the fibre and the matrix[18]. A high interfacial shear stress transfer the applied load to the fibre over a short distance and a low interfacial shear stress will require a long distance.

Dispersion of CNTs with polymer matrix: There are three main mechanisms of interaction of polymer matrix with carbon: (a) **Micro-mechanical interlocking:** This could be difficult in nanotube composites due to their atomically smooth surface. Local non-uniformity along a CNT, including varying diameter and bends/kinks at places as a result of non-hexagonal defects, contribute to CNT-polymer adhesion by mechanical interlocking[19]. (b) **Chemical bonding between the nanotubes and the matrix:** This improves interfacial interaction through ionic or covalent bond that enables a stress transfer. (c) **Weak van der Waals bonding between the fibre and the matrix:** Under no chemical bonding between CNT- polymer, the origins of CNT-polymer interactions are electrostatic and van der Waals forces. There are several techniques to improve the dispersion of CNTs in polymer matrix, such as by optimum physical blending, *in situ* polymerization and chemical functionalizations.

Optimum physical blending: The widely used compounding technique to prepare conventionally filled polymers is still the most convenient and practical way when nano-sized fillers are considered to replace micron-sized fillers for high-performance polymers. But the dispersion of nano-fillers in polymer matrix is more difficult than that of micro-fillers due to the strong tendency to agglomerate for the nano-fillers. For polymer/CNT composites, the high power dispersion methods, such as ultrasound and high speed shearing, are the simplest and most convenient to improve the dispersion of CNTs in a polymer matrix. For example, Qian *et al.*[20] made use of a simple solution-evaporation method assisted by high energy sonication to prepare polystyrene (PS)/MWCNT composite films, in which MWCNTs were dispersed homogeneously in the PS matrix. Similarly, Sandler *et al.*[21] dispersed CNTs in epoxy under high speed stirring (2000 rpm) for 1 h and proved that intense stirring was an effective process to achieve dispersed CNTs uniformly in epoxy segment. Besides, adding a proper compatibilizer to polymer/CNT composites is also another efficient method. Xie *et al.*[22] prepared polypropylene (PP)/CNT composites compatibilized with maleic anhydride grafted styrene-(ethylene-co-butylene)-styrene copolymer (MA-SEBS) by using a combination of ball milling and melt mixing. The viscosity of PP melts increases with CNTs loading but appears to flatten beyond 5 wt. %. When MA-SEBS is added to PP/CNT composites, the melt viscosity of PP/CNT/MA-SEBS composites is further increased. The addition of MA-SEBS improves further their electrical conductivity. Thereby, the static electrical charges on the surface of the nanocomposites are easy to remove. Thus, the anti-static property of the nanocomposite is improved. These results confirm that MA-SEBS acts as a compatibilizer to enhance formation of a perfect percolation network and dispersion of CNTs in the matrix. In a further study on ultra-high molecular weight polyethylene (UHMWPE)/CNT composites, Xie *et al.*[23] have also confirmed that MA-SEBS is an effective compatibilizer, enhances the dispersion of CNTs in the UHMWPE matrix and speeds up crystallization of the UHMWPE phase. Similarly, Jin *et al.*[24] coated MWCNTs by poly(vinylidene fluoride) (PVDF) and then melt-blended with poly(methyl methacrylate) (PMMA). PVDF was found to be a compatibilizer and assist dispersion of MWCNTs in PMMA and served as an adhesive to increase their interfacial bond strength, hence greatly improving the mechanical properties of PMMA/MWCNT composites. Additionally, surfactants can be used as a dispersing agent to improve the dispersion of CNTs in processing polymer/CNT composites. Gong *et al.*[25] used a non-ionic surfactant, polyoxyethylene-8-lauryl, as a processing aid for epoxy/CNT composites due to the strong interactions between carbon of CNTs and the hydrophobic segment of the surfactant *via* van der Waals forces, as well as epoxy and the hydrophilic segment of the surfactant *via* hydrogen bonding. The homogeneous dispersion of CNTs in epoxy improved the thermomechanical properties of the composites. With only 1 wt. % CNTs in the epoxy/CNT composites, the glass transition temperature was increased by 25 °C (from 63 to 88 °C) and the elastic modulus by over 30 %. In some cases, good dispersion of CNTs in polymer matrices can be achieved by means of high power dispersion, compatibilizer, polymer-assisted melt blending and surfactants. The addition of compatibilizers, surfactants, *etc.*, in conjunction with melt blending is most effective and will be widely used to enhance the dispersion and interfacial bonding of many polymer/CNT composites.

***In situ* polymerization:** To improve the processability, electrical, magnetic and optical properties of CNTs, some conjugated or conducting polymers are attached to their surfaces by *in situ* polymerization. Tang and Xu[26] synthesized poly(phenyl acetylene)-wrapped carbon nanotubes (PPA-CNTs), which were soluble in organic solvents, such as tetrahydrofuran, toluene, chloroform and 1,4-dioxane. Meanwhile, the fullerene tips and graphene sheets of CNTs may undergo nonlinear optical (NLO) absorption processes and the cylindrical bodies of CNTs with a high aspect ratio may also function as light scattering centers. Both NLO absorption and light scattering of CNTs protect dramatically the PPA chains from being photo-degraded under severe laser irradiation. Therefore, PPA-CNTs show strong photo-stabilization effect. It is interesting that PPA-CNTs can be macroscopically processed and shearing of their solutions readily aligns CNTs along the applied mechanical force direction. Fan *et al.*[27] synthesized conducting polypyrrole-coated carbon nanotubes (PPY-CNTs) and found that the magnetization of PPY-CNTs is the product of the two components, PPY and CNTs. Star *et al.*[28] synthesized poly(metaphenylenevinylene)-wrapped single-walled carbon nanotubes (PmPVSWCNTs) and UV-Vis absorption spectra confirmed p-p interactions between SWCNT and fully conjugated PmPV backbone. The results indicate that the photo-excited PmPV has a dipole moment that alters the local electric field at the surface of SWCNTs. Cochet *et al.*[29] synthesized polyaniline (PANI)/MWCNT composites by *in situ* polymerization in the presence of MWCNTs. Their results reveal the site-selective interaction between the quinoid ring of PANI and MWCNTs, thus opening the way for charge transfer processes and improving the electric properties of PANI/MWCNT composites. Xiao and Zhou[30] deposited polypyrrole (PPY) or poly(3-methylthiophene) (PMeT) on the surfaces of the MWCNTs by *in situ* polymerization.

High-performance structural composites based on CNTs and polymer have also been prepared by *in situ* polymerization. Jia *et al.*[31] first synthesized PMMA/CNT composites by *in situ* polymerization of MMA with CNTs present. Later, Park *et al.*[32], Velasco-Santos *et al.*[33] and Jang *et al.*[34] polymerized *in situ* polyimide (PI)/SWCNT, PMMT/MWCNT and liquid crystalline epoxide (LCE)/MWCNT composites. PI/SWCNT composite films were anti-static and optically transparent with significant conductivity enhancement (10 orders) at a very low loading (0.1 vol. %). For PMMA/MWCNT composites containing 1 wt. % MWCNT, the storage modulus at 90 °C is increased by an outstanding 1135 % and the glass transition temperature is raised exceptionally by *ca.* 40 °C. For LCE/ MWCNTcomposites containing 1 wt. % MWCNT, the nematic phase temperature of liquid crystalline epoxide (LCE) is decreased. When the MWCNTs are modified by chemical surface oxidation (oxMWCNT), this LCE nematic phase temperature of LCE/oxMWCNT composites is shifted to a lower temperature. This is because the molecular alignment of the LCE for evolution of the LC phase is partially restricted by the interaction between the MWCNTs and LCE. In LCE/oxMWCNT composites, the LC domains form at a lower temperature.

Chemical functionalization: In addition, the surfaces of CNTs have to be chemically functionalized (including grafting copolymerization) to achieve good dispersion in polymer/CNT composites and strong interface adhesion between surrounding polymer chains, even though the interface area is very large. Carbon nanotubes are assembled as ropes or bundles and there are some catalyst residuals, bucky onions, spheroidal fullerenes, amorphous carbon, polyhedron graphite nano-particles and other forms of impurities in as grown CNTs. Thus, purification, "cutting" or disentangling and activation treatments are needed before chemical functionalization.

Purification: The first method to purify MWCNTs is based on oxidation[35], which is observed to occur preferentially at the nanotube ends and on nano-particles that have a high concentration of topological defects. Multi-walled carbon nanotubes (MWCNTs) are purified by burning away of these tube ends, nano-particles and amorphous carbon at > 700 °C in air or oxygen. However, the yield is extremely low (< 5 %). Hiura *et al.*[36] purified CNTs by a mixture of concentrated sulfuric acid and potassium permanganate, but this is still not proven to be a good method for large-scale separation. Tohji *et al.*[37] suggested a purification method that included hydrothermal treatment along with extraction of fullerenes, thermal oxidation and dissolution in 6 M hydrochloric acid. To prevent CNTs from being destroyed during purification, Bonard *et al.*[38], Bandow *et al.*[39] and Duesberg *et al.*[40] dispersed the CNTs in polar solvents assisted by surfactants, such as sodium dodecyl sulfate, followed by micro-filtration and size exclusion chromatography. These methods may be possible to separate CNTs in selected sizes without destruction. Yamamoto *et al.*[41] used AC electrophoresis to treat the CNTs dispersed in iso-propyl alcohol. They found that the separation from impurity particles depended on the frequency of the applied field. At the same time, it is worth noting that CNTs align along the electric field direction. Coleman *et al.*[42] and McCarty *et al.*[43] used a functional organic polymer, poly(*m*-phenylene-co-2,5-dioctoxy-phenylenevinylene) (PmPV), as a filtration system to purify CNTs. They found that the solution of PmPV is capable of suspending nanotubes indefinitely whilst the accompanying amorphous graphite separates out. Although these novel techniques are only suited to treat small amounts of the nanocomposite, they are definite advances to manipulate CNTs. Liu *et al.*[44] developed a purification method that consisted of refluxing in 2.6 M nitric acid and re-suspending CNTs in pH 10 water with surfactant followed by filtration with a cross-flow filtration system. This may be an efficient method to purify CNTs owing to the combined advantages of the chemical and physical methods.

Disentangling of carbon nanotube: Carbon nanotubes are long and entangled as ropes or in bundles. The ‘cutting’ process is necessary for CNTs to disentangle, open up the tubes and provide active sites for chemical functionalization. Liu *et al.*[44] chose a 3:1 mixture of concentrated sulfuric acid and nitric acid to "cut" CNTs into *ca.* 150 nm in length (Fig. 1). The short and open-ended CNTs are then treated by a 4:1 mixture of concentrated sulfuric acid and 30 % aqueous hydrogen peroxide. Thus, more functional groups such as carboxylic acid and hydroxyl groups are formed on the CNT surface. Later, Shaffer *et al.*[45,46] used a 3:1 mixture of concentrated sulfuric acid and nitric acid to "cut" CNTs and produced an electrostatic stabilized dispersion of CNTs in water with an average length of 1.1 mm (Fig. 2). Chen *et al.*[47] also obtained disentangled SWCNTS with an average length > 1 mm. Obviously, it is necessary to control and adjust the processing conditions to obtain short CNTs with different length.

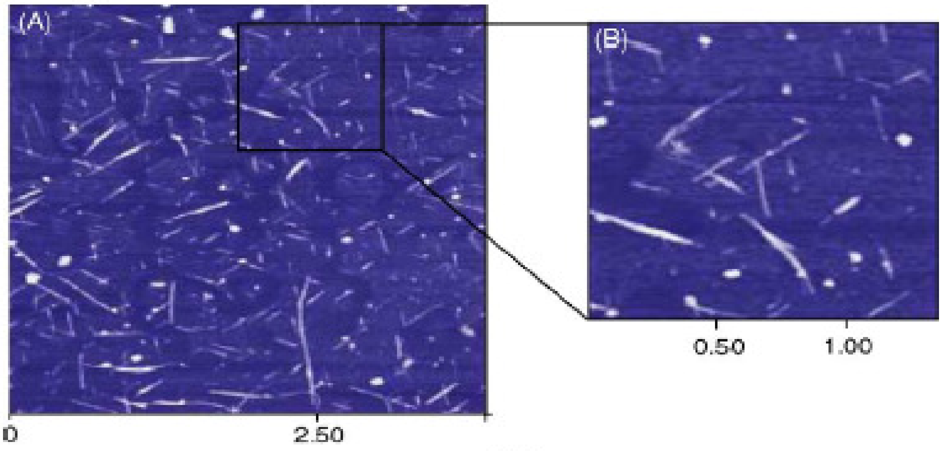


Fig. 1. Tapping mode AFM images of 'cut' CNTs by Liu *et al.*[44]

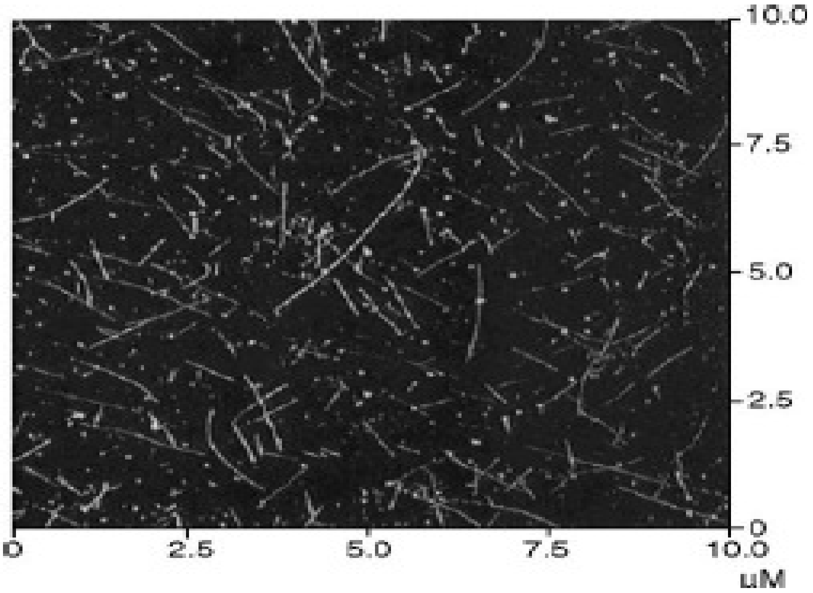
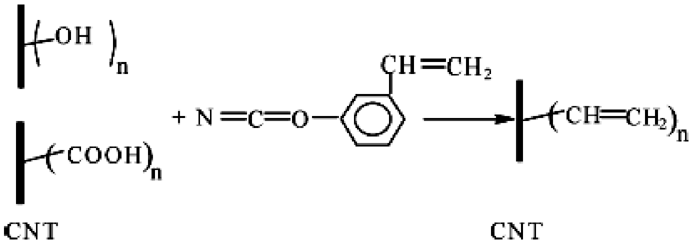


Fig. 2. Tapping mode AFM images of 'cut' CNTs by Chen *et al.*[47]

Activation treatments: In general, carboxylic acid and hydroxyl groups could be formed on the surface or open ends of CNTs during the oxidation process by oxygen, air, concentrated sulfuric acid, nitric acid and 30 % aqueous hydrogen peroxide and concentrated sulfuric acid and its mixture. To further activate the carboxylic acid groups on the surface of CNTs, they are converted into acyl chloride groups by reaction with thionyl chloride at room temperature. Wu *et al.*[48] converted the hydroxyl groups on the surface of CNTs into hydroxymethyl groups ($-CH_2OH$) by the formalization reaction with formaldehyde as below.

By using a redox initiating system, which consists of cerium ions and hydroxymethyl groups ($-CH_2OH$) on the surface of CNTs, free radical graft polymerization of vinyl monomers could occur. Zhou[49] also converted carboxylic acid and hydroxyl groups on the surface of CNTs into vinyl groups ($-CH=CH_2$) by reaction with 3-isopropenyl-α,α-dimethylbenzyl isocyanate:



Because of the presence of these vinyl groups ($-CH=CH_2$) on CNTs, some vinyl monomers could be grafted on the surface of CNTs. Besides the above activation methods, Chen *et al.*[50] activated CNTs surface by plasma modification. Acetaldehyde and ethylenediamine vapours were plasma polymerized on the surface of CNTs, thereby introducing active aldehyde (-CHO) and amino ($-NH_2$) groups. Moreover, Mickelson *et al.*[51] added functional groups to the side walls of SWCNTs by fluorine at elevated temperatures. These fluorinated SWCNTs could be solvated in alcohols and reacted with other species, particularly strong nucleophiles, such as alkylithium reagents. Mawhinney *et al.*[52] reported that carboxylic acids, anhydrides, quinines and esters can also be introduced to CNTs by ozone oxidation. Bahr *et al.*[53] successfully functionalized SWCNTs with electrochemical reduction of aryl diazonium compounds, resulting in a free radical that could attach to the SWCNT surface. Georgakilas *et al.*[54] discovered a method to functionalize SWCNTs with 1,3-dipolar cycloaddition of azomethine ylides. Chen *et al.*[55] and Holzinger *et al.*[56] functionalized SWCNTs by directadditions based on nucleophilic carbenes, cycloaddition of nitrenes and radicals.

Chemical functionalization: Riggs *et al.*[57] and Lin *et al.*[58] synthesized polymer grafted CNTs based on acylated CNTs with poly(propionylethylenimine-co-ethylenimine) (PPEI-EI), poly(vinyl acetate-co-vinyl alcohol) (PVA-VA) and poly(vinyl alcohol) (PVA), respectively. They found that PVA grafted CNTs were soluble in PVA solution, PVA-CNT nanocomposite films so-formed are of high optical quality without any observable phase separation. The result indicates that chemical graft functionalization of CNTs by matrix polymer was an effective way to achieve homogeneous dispersion for high-performance polymer/CNT nanocomposites. Cao *et al.*[59] synthesized dodecylamine grafted CNTs with dodecylamine and acylated CNTs and found that these grafted CNTs were miscible with polyvinylbutyral (PVB) caused by the interaction between functional groups in polymer and long dodecylamine chains attached to the ends of CNTs. Also, Hill *et al.*[60] functionalized CNTs by the grafting reaction between carboxylic acid-bound CNTs and poly(styrene-co-*p*-(4-(4'-vinylphenyl)- 3-oxabutanol)) (PSV). These PSV-grafted CNTs are soluble in common organic solvents and are homogeneously dispersed in the PS matrix. This offers an example for the widely held expectation that the solubility of CNTs will enable the preparation of desirable polymer/CNT nanocomposites. Meanwhile, Mitchell *et al.*[61] synthesized 4-(10-hydroxydecyl)benzoate-SWCNTs by *in situ* reaction of organic diazonium compounds and prepared the composites based on the functionalized SWCNTs and PS. These nanocomposites show a percolated SWCNT network structure at 1 vol. % nanotubes, whilst for the unfunctionalized SWCNT/PS nanocomposites this occurs at twice SWCNTs loading. The reason is that the chemical functionalization of CNTs enhances their interaction with the polymer matrix and improves their dispersion in the composites. Recently, Viswanathan *et al.*[62] reported that introduction of carbanions on the SWCNTs surface by treatment with an anionic initiator served to exfoliate bundles of SWCNTs and provided initiating sites for polymerization of styrene. Qin *et al.*[63] grafted poly(*n*-butyl methacrylate) (PBMA) brushes on the ends and sidewalls of SWCNTs by using atom transfer radical polymerization (ATRP). In summary, chemical functionalization can promote good dispersion in the polymer/CNT composites and will play a dominant role in future development and applications of these nanocomposites.

Properties of polymer/CNT nanocomposites

Mechanical properties: Incorporation of CNTs into a polymer matrix can potentially provide structural materials with dramatically increased modulus and strength. Biercuk *et al.*[64] have observed a monotonic increase of resistance to indentation by up to 3.5 times on adding 2 wt. % SWCNTs in epoxy resin. Cadek *et al.*[65] also found that adding 1 wt. % MWSNTs to polyvinyl alcohol (PVA) increased the modulus and hardness by 1.8 times and 1.6 times, respectively. The homogeneous dispersion and alignment of CNTs in polymer matrices are significant to enhance the effectiveness of reinforcement. The tensile strength and modulus of melt drawn PS/MWCNT composite films are, respectively, increased by 137 and 49 % compared to the drawn PS film[65].

Thermal properties: The addition of CNTs could increase the glass transition, melting and thermal decomposition temperatures of the polymer matrix due to their constraint effect on the polymer segments and chains. It is important to improve the thermal endurance of polymer composites. Thus, with a surfactant, adding 1 wt. % CNTs to epoxy increases the glass transition temperature from 63 to 88 °C. Similarly, with 1 wt. % well-dispersed SWCNTs, the glass transition temperature of PMMA is increased by *ca.* 40 °C. Because CNTs act as nucleation sites in the matrix, their inclusion enhances polymer crystallization and increases the melting temperature. Kashiwagi *et al.*[66] found that the thermal decomposition temperature of polypropylene (PP) at peak weight loss in nitrogen was increased by *ca.* 12 °C with 2 vol. % MWCNTs and that MWCNTs significantly reduced the PP heat release rate making it as effective a fire-retardant as PP/PP-g-MA/clay.

Electrical properties: The commercial application of carbon nanotubes is their use as electrically conducting components in polymer composites. It is reported that GE Plastics has been using CNTs in a poly(phenylene oxide) (PPO)/polyamide (PA) blend for automotive mirror housings for Ford to replace conventional micron-size conducting fillers, which would require loadings as high as 15 wt. % to have a satisfactory anti-static property but which would impart poor mechanical properties and a high density to the composite. Coleman *et al.*[67] showed that the electric conductivity of poly(*p*-phenylenevinylene-co-2,5-dioctoxy-*m*-phenylenevinylene) (PMPV) polymer could be dramatically increased by up to ten orders of magnitude when 8 wt. % CNTs were added, indicative of percolating behaviour. The *in situ* polymerized polyimide (PI)/SWCNT composite films exhibited significant conductivity enhancement (10 orders) at a very low loading (0.1 vol. %) without significantly sacrificing optical transmission. Since their mechanical properties and thermal stability were also improved by addition of SWCNTs, they are potentially useful in a variety of aerospace and terrestrial applications. Again, alignment of CNTs affects the electrical properties of polymer/CNT nanocomposites. Thus, in epoxy/MWCNT nanocomposites with MWCNTs aligned under a 25 T magnetic field leads to a 35 % increase in electric conductivity compared to those similar composites without magnetic aligned CNTs. Improvements on the dispersion and alignment of CNTs in a polymer matrix could decrease the percolation threshold value.

Optical and photovoltaic properties: The carbon nanotubes, both SWCNTs and MWCNTs, have been studied. O'Flaherty *et al.*[68] noted that the optical limit saturated at carbon nanotubes exceeding 3.8 wt. %, relative to the polymer mass. Goh *et al.*[69] found that the aqueous MWCNT suspension showed only weak optical limit towards laser at 532 nm operating at 20 Hz, but its mixture with double-C60-end-capped poly(ethylene oxide) (FPEOF) solution displayed enhanced optical limiting responses at 532 and 1064 nm. Polymer/CNT composites could also be used to protect human eyes, optical elements, optical sensors and optical switching. Chen *et al.*[70] demonstrated the ultra-fast optical switching property of polyimide (PI)/SWCNT composites at 1.55 μm.

Applications of polymer/CNT nanocomposites: Carbon nanotubes have been proposed for many potential applications including conductive and highstrength composites; energy storage and energy conversion devices; sensors; field emission displays and radiation sources; hydrogen media and nanometers-sized semiconductor devices, probes and interconnects, *etc*. The incorporation of CNTs could improve the thermal transport properties of polymer composites due to the excellent thermal conductivity of CNTs. This offers an opportunity for polymer/CNT composites for usages as printed circuit boards, connectors, thermal interface materials, heat sinks, lids and housings and high-performance thermal management from satellite structures down to electronic device packaging.

The super-capacitors are attracting great attention because of their high capacitance and potential applications in electronic devices. It has been reported[71] that the performance of supercapacitors with MWCNTs deposited with conducting polymers as active materials is greatly enhanced compared to electric double-layer supercapacitors with CNTs due to the Faraday effect of the conducting polymer. Besides these, polymer/CNT nanocomposites could have many potential applications in electrochemical actuation, electromagnetic interference shielding (EMI), wave absorption, electronic packaging, self-regulating heater and PTC resistors, *etc*. Polymer/CNT nanocomposites represent an alternative class of organic semi-conducting materials that are promising for organic photo-voltaic cells and devices with improved performance. Sun *et al.*[72] and Feng *et al.*[73] prepared lotus-like and honeycomb-like aligned CNT films with a combination of micro- and nano-structures (Fig. 3) and they all displayed super-hydrophobicity. Thus, it is expected that well-aligned CNT compounded polymer films or coatings should have wide applications including super-hydrophobic surfaces to textiles, coatings, gene delivery, micro-fluid channels, non-wetting liquid transfer and so forth.

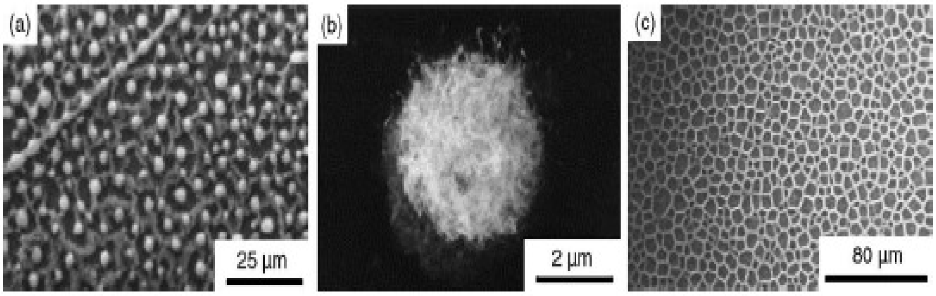


Fig. 3. SEM images of lotus-like and honeycomb-like aligned CNT films: (a) top view of lotus-like aligned CNT films; (b) enlarged view of single micro-papilla of the lotus-like aligned CNT films; and (c) top view of honeycomb-like aligned CNT

Conclusion

Polymer/CNT nanocomposites are accepted as novel materials due to its versatile application and commercialization. In spite of the obstacles in the development of nanotube-based composites, the good load transfer measured between a matrix and CNTs is very encouraging for the future. Now that these problems have been identified, it is believed that solutions will be found for making CNT polymer composites in which the exceptional mechanical properties and strength of CNTs will be reflected in the overall physical properties even with a very low CNT content.

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