3 Polymer/carbon nanotube composite fibers - An overview

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Abstract
Carbon nanotubes have exceptional mechanical, electrical, and thermal properties, which are strongly anisotropic. In order to fully utilize these properties, numerous carbon nanotube/polymer composite fibers have been produced and investigated. In this review, we summarize recent developments in terms of methods of fiber formation and their resulting properties. Polymer/carbon nanotube fibers can be processed using melt or solution spinning. Solutions spinning technologies
including wet, dry, dry-jet, and gel spinning. Fibers can also be spun using electro spinning. Carbon nanotubes used can be single-wall, double-wall, multi-wall, or vapor grown carbon nano fibers. Most composite fibers processed to date contain less than 10 wt% carbon nanotubes, though there are a few studies where carbon nanotube content is 60 wt% or higher. In most cases, the addition of carbon nanotube results in increased tensile and compressive properties, enhanced fatigue resistance, increased solvent resistance, as well as increased glass transition temperature. Carbon nanotubes act as a template for polymer orientation and a nucleating agent for polymer crystallization. This ability of carbon nanotubes is expected to have profound impact on polymer and fiber processing, as well as on the resulting morphology and properties. The results of studies carried out to date are briefly reviewed in this paper.

1. Introduction

At the end of nineteenth century, only natural fibers such as cotton, wool, and silk were available. Man-made fibers were being developed at that time. Most man-made or synthetic fibers that we know today have been developed in the last 70 years or so. In the category of polymeric fibers, these include polyester, nylon, polyethylene, polypropylene, acrylic, spandex, Nomex®, Kevlar®, and Zylon®. This list of polymeric fibers is not complete. The category of other fibers includes carbon fibers, silicon carbide, alumina, glass, alumina-borosilicate, and boron. More than 50% of the fibers used in the world today did not exist just hundred years ago. A ten-fold increase in fiber tensile strength has been achieved over last hundred years (from about 0.5 GPa hundred years ago to more than 5 GPa today). The decision by the DuPont Co’s board in 1927 at the prodding of its chemical director Charles Stine [1] to invest in the unproven concept of macromolecules transformed the company into a major fiber producer of the world for the 20th century. The importance of this decision by the DuPont’s board must be viewed in the light of the following facts: (a) In early 1900, DuPont was a gun powder company. Why would a company in the gun powder business invest in the unproven concept of macromolecules? No one at that time could have predicted that you can take crude oil and convert it into fine textiles, bullet proof vests, fuselage of an airplane, or a medical suture. (b) The Chemistry Nobel laureate (1902) Emil Fisher had proclaimed that there are no molecules with molecular weight greater than 5000. (c) Fisher’s authority in the field was so great that no one dared question him. However, by 1920s there was significant evidence for high molecular weight compounds that compelled Hermann Staudinger (Chemistry Nobel prize 1953) to champion the concept
of macromolecules [2]. (d) Hermann Staudinger was ridiculed by most academic chemists at that time and they stated that Staudinger was corrupting Chemistry and that there were no such large molecules. (e) Nearly half a dozen academic chemists turned down job offers from DuPont to head their program for investigating macromolecules, before a young lecturer from Harvard (Carothers) accepted the job.

Polypropylene, first made in 1930s, was not very useful until 1950s when Ziegler and Natta developed catalysts that made isotactic polypropylene possible. For this discovery Ziegler and Natta shared 1963 Chemistry Nobel prize. Polyethylene, which has been extensively used since 1930s, was processed into high-performance fibers by gel spinning in 1970s.

The concept of nanotechnology is perhaps at the similar development level today as was the concept of macromolecules in 1930s. We believe that just as the development of polymers revolutionized the materials field in the twentieth century, similarly the developments in the field of nanotechnology will revolutionize the materials field in the twenty-first century. It is expected that nanotechnology will enable fibers, films, coatings, and bulk materials that will have major impact on energy harvesting, energy storage, CO2 consumption, and health care.

Carbon nanotube (CNT) research represents a sub-field of nanotechnology. The carbon nanotubes were first recognized in 1991, though they existed before this period but were not recognized as such. During this 17 years period (as of June 2008), more than 32,000 research papers have been published on the topic of carbon nanotubes and over 1800 of these papers address the issue of carbon nanotube fiber or carbon nanotube containing fiber. This suggest that the topic of nano technologically driven fibers is rather large, and even the somewhat narrower topic of CNT containing fibers is also quite vast to be comprehensively covered in this article. Therefore only a brief overview of carbon nanotube containing polymeric fibers is presented here.

It has been a challenge to make macro-scale CNT structures in the form of continuous fiber to fully utilize their outstanding mechanical properties. Poulin and co-workers [3] introduced protocols that enabled well-dispersed CNTs to be injected into a "non-solvent" (coagulation bath) to obtain continuous fibers using the process known as wet-spinning [4]. Baughman and co-workers [5, 6] took significant strides forward to improve the production and processing led to fibers composed of 60 wt% of CNTs with strength that equals the highest performance spider silk and with higher toughness than previously reported for any organic fiber.

Neat CNT fibers can also be processed from liquid media [7, 8]. Alternatively, they may be pulled from nanotube “forests” [9] or drawn as an aerogel fiber from the gas phase in a reactor [10, 11]. The latter process
appears to be particularly promising. The specific strength of this fiber is up to 2.5 times that of the strongest commercial fiber today. There have been many reports [7, 8, 10-18] on the preparation and properties of neat CNT fibers or yarns, but this section focuses only on the CNT/polymer composite fibers. The CNT composite fibers have been dealt with partly in several reviews on CNT composites [19-21]. This review mainly focuses on the composite fiber formation and applications thereof.

2. Formation of CNT/polymer composite fibers

Commodity textile fibers such as poly(ethylene terephthalate) (PET), polypropylene, nylon 6, nylon 66, and polyethylene are processed using melt spinning and have a tensile strength in the range of 0.3 to 1.0 GPa, modulus in the range of 2 to 10 GPa, and elongation-to-break in the range of 10 to 50%. High-performance polymeric fibers on the other hand are processed either from lyotropic liquid crystals (Kevlar® and Zylon®) or by gel spinning (Spectra®), and have strength, modulus, and elongation to break in the ranges of 3 to 6 GPa, 100 to 280 GPa, and 2 to 5%, respectively. Despite significant developments in the polymer synthesis and processing, the basic molecular structure of synthetic fibers such as PET and nylon has not changed since their introduction to the world more than half-a-century ago [22]. Approximately 70 billion kg fibers are consumed annually world-wide, of which nearly 55% are man-made fibers.

Technical and industrial applications, such as ropes and tire cords, among other properties require high strength and high modulus. The cost of high-performance fibers is generally above $40/kg, while the cost of commodity textile fibers is typically below $5/kg. There is a significant performance and price gap between the commodity textile fibers such as PET, nylon, and polypropylene on one hand, and high-performance polymeric fibers such as Kevlar® and Zylon® on the other. Use of carbon nanotube in polymeric materials has the potential to close the performance gap between these two classes of fibers.

2.1. The CNT composite fibers by solution spinning

As the dispersion of nanotube in polymer matrix is an important factor in preparation of polymer/CNT composite fibers, solution processing has been extensively used to prepare these fibers. One of the benefits of this method is that agitation of the nanotube powder in a solvent facilitates nanotube dispersion. In general, agitation is provided by magnetic stirring, shear mixing, reflux, or most commonly, ultrasonication. Sonication can be provided in two forms, mild sonication in a bath or high-power sonication using a tip or horn
[20]. Vigolo et al. [3] demonstrated fiber formation by injecting CNT solution into a rotating bath of poly(vinyl alcohol) (PVA)/water solution, showing enhanced CNT alignment. This method was further improved by Dalton et al. [23, 24] Furthermore, Miaudet et al. [8] have shown that these fibers can be drawn at above the glass transition temperatures of PVA, resulting in improved nanotube alignment and polymer crystallinity.

There have been a number of reports on the composite fibers using various types of polymers and CNTs as summarized in Table 1 [8, 13, 23-57].

Table 1. Polymer/CNT composite fiber formation through solution spinning [8, 13, 23-57].

<table>
<thead>
<tr>
<th>Polymer</th>
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<th>Focus of the research</th>
<th>Reference</th>
<th>Year</th>
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<td>Supercapacitors, artificial muscles</td>
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<td>[53]</td>
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<td>2008</td>
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<td>SWNT</td>
<td>Stabilization and carbonization</td>
<td>[27]</td>
<td>2007</td>
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<td>2007</td>
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<td>PVA</td>
<td>SWNT</td>
<td>CNT fibers through wet spinning into PVA solution as coagulant</td>
<td>[23]</td>
<td>2003</td>
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Figure 1. SEM micrographs of the carbonized (a) PAN and (b) PAN/SWNT (1 wt% SWNT) [27].

Kumar et al. [29] demonstrated the possibility to prepare super-strong fibers by using poly(p-phenylene benzobisoxazole) (PBO). They also suggested that polyacrylonitrile (PAN)/single-wall carbon nanotube (SWNT) composite fibers can be used as a precursor for carbon fibers with enhanced mechanical properties [27, 31]. They reported that carbonized PAN/SWNT
(1 wt% SWNT) fibers exhibited 64 % higher tensile strength and 49 % higher tensile modulus than the carbonized control PAN fiber.

Figure 1 shows scanning electron microscopy (SEM) images of the carbonized PAN and PAN/SWNT fibers. High-resolution transmission electron microscopy (HR-TEM) and Raman spectroscopy evidenced the graphitic structure formation in the vicinity of SWNT at a relatively low carbonization temperature (~ 1100 °C). Electrically conductive fibers are also one of major applications of CNT composite fibers [4, 35]. Recently fibers were also made from the solution of natural polymers such as DNA, chitosan, and gelatin for application as biomaterials such as artificial muscles [34].

2.2. The CNT composite fibers by melt spinning

Melt processing is particularly useful for dealing with thermoplastic polymers. A number of studies have focused on production of composite fibers by melt processing as summarized in Table 2 [58-79]. One of the earliest studies on melt processing of polymer–nanotubes composites was carried out by Hagenmueller et al. [66] Main target of the melt-spun fibers is enhancement of mechanical properties and electrical conductivity. However, in the fabrication of CNT-reinforced composites, the CNT dispersion in the matrix is one of the most critical issues. As the dispersion of CNT in polymer melt is much more difficult than in solution, many kinds of methods have been investigated to enhance the dispersion.

Meng et al. [72] incorporated multi-wall carbon nanotubes (MWNT) into the shape memory polyurethane fiber by in-situ polymerization with treatment of MWNT in concentrated nitric acid and sulfuric acid. They demonstrated that through the mechanical stirring, ultrasonic vibration, melt blending, extrusion and melt spinning, the MWNT were distributed homogeneously and preferentially aligned along the fiber-axial direction. Shen et al. [77] premixed CNT with poly(ethylene terephthalate) (PET) in a solvent followed by melt spinning after drying the mixture. They demonstrated that the tensile strength of the composite fibers increased by 36.9 % (from 4.45 to 6.09 cN/dtex), and the tensile modulus increased by 41.2 % (from 80.7 to 113.9 cN/dtex) by adding 0.02 wt% of acid treated MWNT.

Meng et al. [73] suggested that the aligned MWNTs provided shape memory fiber with much higher shape recovery ratio and shape recovery force because the aligned MWNTs could help storing and releasing the internal elastic energy during stretching and shape recovering. Besides, it was also found that compared with pure shape memory polymer (SMP) (polyurethane is the SMP used in this study) fiber, SMP-MWNT fibers recovered the original length more quickly providing the possibility of producing more sensitive smart instruments.
Table 2. Polymer/CNT composite fiber formation through melt spinning [58-79].

<table>
<thead>
<tr>
<th>Polymer</th>
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<th>Focus of the research</th>
<th>Reference</th>
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</table>
2.3 Polymer/CNT composite fibers by electro-spinning

Another method used recently to form polymer/CNT composite nanofibers from solution is electro-spinning. Electro-spinning allows the fabrication of fibers with diameters down to a few tens of nanometers. Electro-spinning is not only the focus of intense academic investigation; the technique is already being applied in many technological areas.

Ko et al. [80] firstly described electro-spinning as a method to fabricate polymer/CNT composite fibers and yarns. Fibers with diameters between 10 nm and 1 µm can be produced in this method. In a similar study, Sen et al. [81] formed fiber based membranes by electro-spinning solution of SWNT dispersed in either polystyrene or polyurethane. Kim et al. [82] prepared electro-spun composite fibers based on polycarbonate with MWNT. They reported that the membrane composed of the composite fibers exhibited strong and tough properties. They suggested that the results may provide a feasible consideration of such electro-spun composite fibers for use as the reinforcing elements in a polymer based composite of a new kind.

On the other hand, electro-spinning is a useful method to obtain an effective structure for biomedical application like scaffold. McCullen et al. [83] investigated electro-spinning of poly (L-D-lactic acid) (PLA) with the addition of MWNT for development of a scaffold for tissue engineering. Meng et al. [84] reported the nano fibrous scaffold of MWNT/polyurethane composite with an average fiber diameter of 300 - 500 nm by electro-spinning. They demonstrated that the composite scaffold exhibited enhancement not only to the cell adhesion and proliferation but also to the cell migration and aggregation. Hence, the nano fibrous architecture and MWNT incorporation provided favorite interactions to the cells, which implied the applicable potential of the nano fibrous composite for tissue repair and regeneration. The studies on the polymer/CNT composite nano fibers by electro-spinning including of the most recent reports are summarized in Table 3 [80-98].

2.4. CNT as a nucleating agent in polymer composite fibers

Nucleating agents for polymer crystallization play an important role in processing polymer/CNT fibers. There are no other nucleating agents as long and as narrow as carbon nanotubes and particularly SWNT. The work utilizing this ability of carbon nanotubes has gained momentum since 2001.

In 2007 alone, more than 100 research papers appeared addressing some aspect of polymer crystallization aided by CNT. Initial attempts in fabricating polymer/CNT composites focused on achieving mechanical properties based on
the rule-of-mixtures. In this early work, carbon nanotube content used in the polymer matrix was as high as 60 wt% [99]. While improvements occurred in many physical and mechanical properties, the absolute properties of the composites, particularly mechanical properties were not as high as expected.

Table 3. Polymer/CNT composite fiber formation through electro-spinning [80-98].

<table>
<thead>
<tr>
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<td>2008</td>
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<td>MWNT</td>
<td>Electro-spun fiber</td>
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This was generally attributed to the following three factors: (a) poor CNT dispersion, (b) impurity in the carbon nanotube, (c) poor interfacial strength between the polymer and the carbon nanotube. However when high purity nanotubes are well dispersed and exfoliated in the polymer matrix, good to excellent tensile property composites can be obtained [26, 27, 29, 51, 66, 100-103]. It is being increasingly recognized that only when a small quantity of carbon nanotube, particularly SWNT, are dispersed and exfoliated in polymer matrix, then it can affect the polymer orientation and crystallization [26, 76, 104-110].

Both SWNT and MWNT have been shown to act as a nucleating agent for polymer crystallization [104, 107, 111-119]. Such studies have been carried out on more than ten polymer systems. These include polypropylene [120], polyethylene [105], nylon 6, nylon 66, poly(ethylene terephthalate) (PET) [121], poly(butylene terephthalate) (PBT), poly(vinyl alcohol) (PVA) [108, 122-124], poly(ε-caprolactone) [125], and poly(m-phenylenevinylene-co-2,5 dioctyloxy-p-phenylenevinylene) [126]. Carbon nanotube concentration for the study of crystallization has often been in the range of 0.01 to 1 wt%. In PET/SWNT composites with SWNT content ranging from 0.03 to 3 wt% the rate of crystallization compared to neat PET samples increase as the SWNT content increases [127]. In some cases higher nanotube concentration (e.g. 15 wt%) has been used. Polymer structure and CNT type (e.g. SWNT or MWNT, pristine tube vs. functionalized tube, etc.) affect the interaction between the two entities, which ultimately affect the polymer orientation and crystallization. The use of CNTs at low concentrations results in faster crystallization rates at higher temperatures than would be possible without CNT in the same system. Isothermal crystallization studies of polyethylene/SWNT composites show that onset of crystallization can occur earlier in the composites than the neat polymer, and the crystallization rate is faster in the composite [128]. In-situ polymerization of ε-caprolactone in the presence of SWNT leads to the formation of film nanocomposites containing ε-caprolactone functionalized SWNT in the polymer matrix with concentrations from 0.5 to 4.6 wt%. Differential scanning calorimetry (DSC) results implied that the presence of SWNT in the ε-caprolactone matrix increased crystallinity, and the crystal growth was much faster [113]. WAXD studies of melt-spun polyethylene and polyethylene/SWNT fibers show that after melting and recrystallization neat polyethylene fibers are isotropic while polyethylene/SWNT fibers retain some orientation [105]. Melt-processed injected molded PBT/SWNT composites show that SWNT template polymer orientation during shearing and also template polymer crystallization [129, 130].
When the SWNT and surrounding material have high interaction templating behavior is observed. Small molecules such as H₂SO₄ have been shown to form ordered structures induced by SWNT [131]. X-ray diffraction gives evidence of orientation. Proteins have been shown to crystallize in an ordered helical fashion on the surfaces of MWNT [132]. The MWNT that induces protein crystallization are of a specific size, and protein crystallization occurred consistently throughout the system. SWNT has also been shown to induce crystallization and orientation in the sheared polymer melt [129], and polymer melt containing aligned SWNT [133].

Polyethylene (PE) and nylon 66 have been shown to crystallize on the surface of both SWNT and MWNT to form nano hybrid shish kebab structures [111]. Recently PE oligomers have been shown to decorate the surface of SWNT by a mechanism of “soft-epitaxy” [112]. Polyvinylidiene fluoride, and poly(L-lysine) have also been used to form nano-hybrid shish kebab structures on CNT [134]. CNT also promote smaller crystal size as well as smaller spherulite size [104, 105, 107], and this is indicative of the increased number of nucleation sites due to SWNT. Depending on the processing conditions, at higher carbon nanotube concentrations, crystallization can be hindered.

Polymer containing CNT can also retain their orientation in melt. SWNT induced oriented crystallization is exhibited in PET/SWNT composites [127]. In these samples PET and PET with 1wt% SWNT loading are prepared under identical conditions by melt compounding in a Haake Kneader at 40 rpm for 4 min at 270 °C. Both PET and PET/SWNT 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 SWNT orientation. Wide-angle X-ray diffraction (WAXD) of both materials shows that PET is oriented in the samples (Figure 2A and C). The strained PET and PET/SWNT samples were held at fixed length and heated at 20 °C/min to 300 °C. After melting PET, both samples were allowed to recrystallized at a cooling rate of 10 °C/min. WAXD of the heat-treated samples show that polymer retains its orientation in the PET/SWNT sample but not in the neat PET sample (Figure 2D) [127]. Although polymer melting occurs in the PET/SWNT sample, SWNT maintains its orientation due to its rod-like structure and upon recrystallization acts as a template for reorientation and crystallization of the PET. This is an important observation and shows that carbon nanotubes can be used as nucleating agents in polymer processing to promote polymer crystallization and orientation. This could potentially change the morphology of typical semi-crystalline polymeric fibers produced from polymers like PET, nylon, polyethylene, and polypropylene and pave the way to producing high-performance fibers from these systems.
Figure 2. Wide-angle X-ray diffraction patterns of (A) drawn PET/SWNT (SWNT content 1 wt%) nanocomposite film, (B) PET/SWNT 1 wt% nanocomposite film after melting to 300 °C and subsequently slowly cooled at constant length to room temperature, (C) drawn neat PET film, (D) drawn neat PET film after melting to 300 °C and subsequently slowly cooled at constant length to room temperature. The drawing direction was vertical. After melting and re-crystallization, PET film becomes unoriented as expected (D), while remarkably only at 1 wt% SWNT concentration, PET/SWNT film retains its high orientation [127]. (E) PP transcry stalline interfacial layer on CNT fibers [153]. The development of transcry stallinity provides the evidence of interaction between PP and CNT. Optical micrographs with cross-polarizers of spherulite formation in (F) PP, (G) PP/SWNT (0.1 wt% SWNT), (H) PP/SWNT (1 wt% SWNT), and (I) PP/MWNT (1 wt% MWNT) bulk samples [154].

3. Properties of polymer/CNT fibers
3.1. Thermal shrinkage
The presence of CNT in the polymer matrix restricts the molecular mobility of the chains which results in lower thermal shrinkage in the composite containing the carbon nanotube as compared to the neat polymer (Figure 3a and b). Oriented flexible polymer molecules when heated above their glass transition temperature become coil like resulting in shrinkage.
Figure 3. Schematic showing changes in molecular structure during thermal shrinkage in the (a) neat polymer, and (b) at the polymer-CNT interphase. (c) Thermal shrinkage in PAN and PAN/CNT fibers [149]. CNT content was 5 wt% in each case. The presence of 5 wt% SWNT reduced thermal shrinkage from 14 % in PAN to 7 % in PAN/SWNT at 180 °C. (d) Thermal shrinkage in polypropylene and polypropylene/CNT fibers [135]. CNT content in polypropylene was 0.1 and 1 wt% as indicated. Even 0.1 wt% exfoliated carbon nanotubes, reduced polypropylene thermal shrinkage at 160 °C from over 25 % to below 5 %.

The presence of nanotube restricts this shrinkage. Polymer molecule wants to shrink, however carbon nanotube at these temperatures (100 to 300 °C) does not go from an oriented state to a coil-like state, and therefore does not shrink. Interaction between polymer molecules and CNT, restricts the polymer shrinkage. In amorphous and semi-crystalline polymers, this behavior can be observed above the polymer glass transition temperature. In semi-crystalline polymers this behavior can even be observed at polymer melting temperature. PAN/CNT and PP/CNT composite fibers show significant reduction in thermal shrinkage with the addition of CNT compared to the neat fiber (Figure 3c and d). PP/CNT fibers heated at 170 °C (above polypropylene melting temperature) shows that PP/CNT fibers retain polymer orientation [135], a result of polypropylene interaction with CNT. In PMMA/carbon nanofiber (CNF) composites thermal shrinkage at 110 °C is reduced from ~35 % in neat PMMA fibers to ~5 % in PMMA/CNF fiber with 5 wt% CNF loading [136].
Increased dispersion and interfacial interaction between the polymer matrix and CNT would lead to even greater improvement in the mechanical properties, and may also contribute to the improvement in thermal, electrical, and optical properties of composite materials. Studies of these systems add to the fundamental understanding of the nucleating capability of CNT, epitaxial polymer-CNT 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 CNT, CNT templating of polymer orientation and crystallinity are all properties that one can build on to develop high-performance fibers from commodity polymers.

3.2. Electrical conductivity

Fabrication of electrically conducting polymer/CNT composites is another potential application of CNTs, whose electrical conductivity is as high as $10^6$ S/m. Depending on the polymer matrix, conductivities of 1 to 10 S/m can be achieved for 5 wt% MWNT loading [137]. Sandler et al. [138] dispersed MWNTs in an epoxy matrix to obtain a composite with an electrical conductivity sufficient for anti-static applications. The percolation threshold was proven to be below 0.04 wt% MWNT, while the overall conductivity increased as compared to carbon black. Sandler et al. [139] carried this study further and obtained an ultra-low electrical percolation threshold of 0.005 wt% by using aligned MWNTs grown from an injection chemical vapor deposition (CVD) process. Kymakis et al. [140] found that doping of a conducting polymer, such as poly(3-octylthiophene), with SWNTs to form a composite increases the electrical conductivity by five orders of magnitude from 0 to 20 wt% nanotube concentration. The percolation threshold was determined to be 11 wt%.

3.3. Thermal conductivity

Although theory predicts the room temperature thermal conductivity of greater than 6000 W/m-K for isolated SWNTs [141], and measurements show higher than 3000 W/m-K and 200 W/m-K for isolated MWNTs [142] and aligned bundles of SWNTs [143], respectively, thermal conductivity has been one of the least explored areas in the study of polymer/CNT composites. Hone et al. [143] made epoxy/SWNT composites whose room temperature thermal conductivity enhanced by 120 % at 1 wt% SWNT loading, as compared to epoxy filled with vapor grown carbon fiber (VGCF). In continuation of the same work, Biercuk et al. [144] reported a 70 % increase in thermal conductivity at 40 K, up to 125 % at room temperature also at
1 wt% SWNT. It is likely that SWNTs are superior to VGCFs because their nano-scale diameter and larger aspect ratio facilitate the formation of extensive network at the same weight loading. Windle et al. work on CNT/epoxy composites show that thermal conductivity is unaffected by increasing CNT loading in samples, and only slight enhancements in thermal conductivity are observed [145, 146]. CNT composites with high thermal conductivity have a number of potential applications, particularly in thermal management, such as heat sinking for electronics and motors.

3.4. Property enhancements due to CNT templated orientation and crystallization

Using orientation and crystallization ability of CNT recently it was shown that by adding only 1 wt% SWNT, tensile strength of oriented PVA film increased from 0.4 GPa to 1.2 GPa (increase of 0.8 GPa) [100], strength of gel-spun PVA fiber containing 1 wt% SWNT increased from 1.6 GPa to 2.6 GPa (increase of 1.0 GPa) [147], and that for PAN-based carbon fibers containing 1 wt% carbon nanotubes it increased from 2.0 GPa to 3.2 GPa (increase of 1.2 GPa) [27]. Analysis of this data shows that effective stress on the carbon nanotube in these cases at failure was in the range of 88 to 120 GPa. These stress values are higher then the theoretical tensile strength of carbon nanotubes [148], and thus lends support to the argument that addition of CNT modifies polymer morphology in terms of higher crystallinity and orientation of the polymer. This results in mechanical properties beyond what is predicted by the rule of mixtures. Direct evidence of increased crystallinity and orientation due to the presence of nanotubes has been obtained in a number of systems [26, 105, 108, 149]. In addition, there is also indirect evidence for the same. The indirect evidence includes, enhanced solvent resistance [26, 48, 149], higher electron beam radiation resistance for the polymer containing CNT than the control polymer [26, 51, 108].

Shearing of PVA/SWNT dispersions containing 1 wt% SWNT resulted in the formation of self-assembled oriented PVA/SWNT fibers or ribbons, while PVA solution results in the formation of unoriented fibers. Diameter/width and length of these self assembled fibers was 5 to 45 µm and 0.5 to 3 mm, respectively. Both the PVA and PVA/SWNT fibers are composed of fibrils ranging from about 100 to 800 nm in diameter. The PVA/SWNT fibrils also appear to consist of nano-fibrils ranging from 25 to about 100 nm in diameter, while the PVA fibrils did not show the obvious presence of nano-fibrils. These PVA/SWNT nano-fibrils can be used as seed crystals.

WAXD and polarizing optical microscopy, both shows that self assembled PVA fibers are isotropic while self assembled PVA/SWNT fibers
Composite fibers

are oriented, exhibiting SWNT templated orientation. WAXD of the self-assembled PVA fibers show strong intensity equatorial (101) peak, which is also the case for solution spun and drawn PVA fibers [150, 151].

Contrary to this, in the self-assembled PVA/SWNT fibers, a medium intensity (101) reflection is observed as a four-point pattern, a strong intensity (200) reflection is present on the equator, and the (102) plane is on the meridian. This evidence suggests SWNT templated PVA crystallization. HR-TEM of PVA/SWNT nano-fibril sections showed well-resolved PVA lattice with molecules oriented parallel to the nanotube axis.

PVA fibers exhibited about 48 % crystallinity, while crystallinity in PVA/SWNT fibers was 84 % as determined by WAXD [34]. It is noted that crystallinity in gel-spun PVA/SWNT fiber (draw ratio 6), containing 3 wt% SWNT was only ~ 53 % [116]. It is noteworthy that 84 % crystallinity in this work is without annealing or drawing. The presence of SWNT, results in significantly enhanced polymer crystallinity, and that SWNT act as a template for polymer orientation. Polymer orientation facilitated by the presence of fully exfoliated SWNT may have implications for polymer processing.

Mixing MWNT and polypropylene (PP) in the solution results in the formation of PP/CNT particles which consist of PP-coated CNT [152]. The average degree of crystallinity in these PP/CNT particles was determined to be about 80 %. Such a high level of crystallinity is attributed to more complete PP crystallization in dilute solution and PP-CNT interaction.

Individual CNT promote PP crystallization, as a result thick PP interfacial layer is formed on the nanotube surface, and this is confirmed by HR-TEM. Transcrystallization of PP in the presence of CNT fibers has also been studied [153]. 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. The observation of polypropylene transcrystals on CNT is yet another evidence of PP-CNT interaction. In PP/CNT fiber samples melted and recrystallized spherulite growth is influenced by the presence of CNT, where the presence of CNT increase the number of nucleation sites for the polymer and smaller spherulites are observed (Figure 2F to I) even a low CNT loading (0.1 wt %) [154].

4. Applications of CNT/polymer composite fibers

4.1. Stronger fibers

The improved mechanical properties of composite fibers enable them find new application along with the enhanced electrical and thermal conductivity as discussed in following sections, which was not feasible for
pure polymeric fibers. For example, the stronger fibers with relatively low density will lead to the lightweight high-performance composite materials, providing the enhanced fuel economy. The structure of CNT fibers is similar to that of high-strength polymeric fibers. Both types of fibers are strong and stiff along the fiber axis in tension, but relatively weak in axial compression and transverse to the fiber axis [155]. Such changes as fibrillar structure in matrix morphology need to be considered when evaluating the nanocomposite performance with regard to the intrinsic filler properties [156, 157]. Mechanical properties of composites fibers are summarized in Table 4 [3, 26-29, 42, 43, 46, 48, 59, 62, 65, 68, 76, 78, 91, 158].

Non-woven fabric from the composite fibers could be used for making distributed sensors, antennas, capacitors, and even batteries. Commercial applications such as artificial muscles, structural fibers, and electronic textiles require development of a continuous spinning process [23]. It is likely that next-generation carbon fibers used for structural composites will thus likely be processed not from PAN alone but from its composites with CNTs [22, 27].

4.2. Electrically conductive fibers

Electrically conductive textile composites, representing a family of newly developed composites, have many potential applications such as: sensors, static charge dissipation, filters, electro-magnetic interference shield, and special purpose clothing acting as protection or dust and germ free purpose [55]. Demand for electrically conductive textiles has increased in recent years. The fabrication of CNT composite fibers is of special interest not only for mechanical but electronic textile application. Wang et al. [52] presented new battery materials that consist of a solid polyaniline (PANI)/CNT composite fibers which exhibited a discharge capacity of 12.1 mAh/g with a CNT content of 0.25 wt%. Mottaghitalab et al. [34] also demonstrated that PANI/CNT composite fibers containing 2 wt% CNTs had improved mechanical, electrical and electrochemical properties compared with the neat PANI fibers. They suggested that these improved properties resulted in significantly improved electromechanical actuation performance of the composite fibers when compared with neat PANI fibers. Xue et al. [55] showed that electrically conductive yarns from CNT and PVA could be prepared by two different methods, wet spinning and coating process. The electrical resistance of the CNT/PVA (40 wt% CNT) composite fiber by the wet-spinning process was about tens of kΩ/cm. They also demonstrated that PVA/CNT-coated yarns had linear resistivity of 250 Ω/cm. The electrical conductivity of these textiles is very important because the conductive fibers would be transformed into textile structures by weaving, knitting or other
manufacturing processes for smart and intelligent textiles. Multifunctional CNT composite fibers are currently of interest in applications where actuation and energy-storage functions are highly desirable, such as electronic textiles.

4.3. Fibers for biological applications such as artificial muscle or scaffold

The enhancement of mechanical properties along with the improvement in electrical and electrochemical properties by the inclusion of CNT can be used to produce low voltage actuators which can exert significant force and/or movement as compared to neat polymer. Spinks et al. [47] reported a novel dual mode actuation in the fibers composed of chitosan, PANI, and SWNT. They demonstrated that the actuation of the fibers during pH switching in acidic or basic electrolyte solutions with and without applied electrical potential exhibited a dual mode actuation which is useful in practice, as it allows independent small scale adjustment of the pH induced large strains. In another report, Spinks et al. [46] showed that the addition of small amounts of CNT to PANI fibers produced significant improvements in their electro-activity that translates to enhanced actuation performance. The improved strength and stiffness of the composite fibers can be utilized in various applications where high-force operation is required, such as in strain-amplification systems or bio-mimetic musculoskeletal systems.

Polyurethane/MWNT composites [72, 73] for the application of shape-memory materials have outstanding mechanical properties and may find broad applications such as in smart textiles and apparels, biomedical materials, high performance sensors, actuators, micro-grippers, etc. Lynam et al. [4] suggested that combining the conductivity of CNT with biomolecules such as chitosan or heparin involved in tissue repair should produce novel platforms, that is, scaffolds, with the properties of expediting cell growth.

5. Conclusions

This review summarizes studies on a number of polymeric fiber systems containing carbon nanotubes. Composite fibers have been processed using solution spinning, melt spinning, as well as electro-spinning. Carbon nanotube containing polymeric fibers exhibit improved mechanical and physical properties such as tensile strength, tensile modulus, strain to failure, torsional modulus, compressive strength, glass transition temperature, solvent resistance, and reduced shrinkage. In addition, carbon nanotube based fibers will also have electrical and thermal properties. These fibers will also find
applications for biomedical scaffolds as well as for various types of sensors such as gas, strain or stress, and heat, among others. These results point to the enormous potential for carbon nanotubes/polymer composite fibers.

Understanding the nature of polymer-SWNT interaction will lead to a more efficient use of CNT in composites as well as better processing methods, which may in turn contribute to lower cost of these materials, more widespread use, improvement in properties of composite fibers, as well as the production of functional polymer/CNT composite fibers tailored for specific applications. In addition, there is also need in industries like the aerospace or automotive, where the growing use of composites will lead to faster, more functional, lighter, stronger, and more fuel efficient means of transportation.

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