High Strength Electrospun Nanofiber Mats via CNT Reinforcement: A Review

Bishweshwar Pant*, Mira Park**, Soo-Jin Park*†, Hak Yong Kim**,**†

Abstract: The development of electrospun nanofibers with improved mechanical properties is of great scientific and technological interest because of their wide-range of applications. Reinforcement of carbon nanotubes (CNTs) into the polymer matrix is considered as a promising strategy for substantially enhancing the mechanical properties of resulting CNTs/polymer composite mats on account of extraordinary mechanical properties of CNTs such as ultra-high Young's modulus and tensile strengths. This paper summarizes the recent developments on electrospun CNTs/polymer composite mats with an emphasis on their mechanical properties.

Key Words: Electrospinning, Nanofibers, Carbonnanotubes (CNTs)/polymer composite, Reinforcement

1. INTRODUCTION

Nanotechnology is a rapidly emerging technology with vast potential to create new materials with unique properties for numerous applications. It is the field of applied science that is focused on the synthesis, characterization, design and application of materials and devices on the nanoscale. Generally, nanotechnology deals with structures of the size 100 nanometers or smaller in at least one dimension, and involves developing materials or devices within that size. As one of the most important nanomaterials, one-dimensional (1D) nanomaterials have steadily attracted growing interest in the past decades because of their unique shape, fundamental properties, and potential applications in many different areas [1,2]. A variety of 1D nanostructure in the form of fibers, wires, rods, belts, tubes from various materials have already been developed for the different applications [1,3,4]. In particular, the fiber form of nanostructure has been extensively investigated due to its unique properties and wide areas of potential applications [5-12]. If the diameters of fiber materials are shrunk from micrometer to sub-micrometer or nanometers, there appear several amazing characteristics such as high surface area to volume ratio, flexibility in surface functionalities, and superior mechanical performance compared with any other known nanomaterials [7]. These outstanding properties make the nanofibers to be an optimal candidate for many important applications such as fiber-reinforced composite, membranes, biosensor, optical devices, wound dressing, enzyme and catalytic support, and so on [5,13-17]. However, the relatively low mechanical performance of the electrospun nanofibers greatly limits their applications in areas such as aerospace, protective clothing, armor, advanced composites, etc. Many applications require high mechanical property nanofibers for better performances. Carbon nanotubes (CNTs) reinforcement is one of the widely utilized approaches for improving the mechanical properties of the electrospun fiber mats to widen their applications.

2. ELECTROSPINNING

A variety of advanced techniques such as electrospinning, template synthesis, drawing, self-assembly and phase-separation techniques have already been developed to fabricate 1D nanostructures in the form of fibers from various materials [18]. In comparison with other methods of fiber fabrication, electrospinning has proven to be currently the best method for
producing continuous, nonwoven mats of nanofibrous material from polymeric solutions [19]. The popularity of electrospinning can be ascribed to its simple, versatile, and single-step process to produce well-tailored fibers with diameter ranging from sub-micron to the nanometer scale. A variety of precursor such as synthetic and natural polymers, polymer blends, composite with metal or ceramic particles, nanoparticles, and ceramics can be electrospun into the fiber/nanofiber structures [20-22].

The standard electrospinning setup consists of three main components: (1) a high voltage supply, (2) a capillary tube containing the polymer solution, and (3) a metallic collector. In the typical electrospinning process, to create an electrically charged jet of polymer solution out of the needle, an electrical potential is applied between droplets of a polymer solution or melt held at the end of a capillary tube and a grounded target. An increase in the electrical potential initially leads to the elongation of the hemispherical surface of the solution at the tip of the capillary tube to form a conical shape which is known as Taylor cone [24]. A further increase in the electric potential causes the electric potential to reach a critical value, at which it overcomes the surface tension of the polymer solution and causes the formation of a jet that is ejected from the tip of the Taylor cone. The charged jet undergoes bending instabilities and gradually thins up in air primarily due to elongation and solvent evaporation. The charged jet eventually forms randomly oriented nanofibers that can be collected on a stationary or rotating grounded metallic collector of the electrospinning set up. The electrospun nanofibers are categorized into two classes depending on the material composition, polymeric nanofibers and ceramic nanofibers. The schematic of typical electrospinning process and SEM image of electrospun poly acrylonitrile (PAN) nanofibers are given in the Fig. 1.

2.1 Mechanical properties of electrospun fibers

Development of polymeric nanofibers is of great scientific and technological interest because of their many interesting properties and wide-range applications. However, despite their outstanding potential properties, the applications of various nanofibers have been limited by their poor mechanical properties. The mechanical property of the nanofiber is important because in most of the applications, the produced nanofiber mats are subjected to stress and strain from surrounding. Generally, the mechanical property of the electrospun nanofibers is moderately higher when compared with their bulk material counterparts. However, compared to corresponding textile fibers made from the same polymers, the mechanical properties of electrospun nanofibers are often found to be poor. Electrospun nanofibers typically display poor mechanical tensile strengths [25-27], which can be mainly ascribed to the low degree of orientation and chain extension of the polymer chains along the fiber axis. Therefore, the development of electrospun nanofibers with improved mechanical properties remains a great challenge for the material scientists. One potential avenue for improving the mechanical properties of the electrospun fiber membranes is to spin fibers from polymer–CNTs composite solutions [28-32].

The objective of this review article is to report on the various research works on enhanced mechanical properties of electrospun nanofibers. For this, herein we have addressed the current developments, including preparation and a brief overview of different concepts to produce conventional high performance electrospun nanofibers via CNT reinforcement. We hope that the review paper will save the readers’ time by making available all the aforementioned information in a single document.

3. CARBON NANOTUBES (CNTS)

Carbon nanotubes (CNTs) which were first reported by Oberlin et al. [33] and later by Iijima [34] have remained the focus of intense academic investigation since early 90’s and brought revolutionary changes in the field of polymer nanocomposites. Carbon nanotubes are basically rolled up graphene sheets (hexagonal structures) into cylindrical form and capped with half shape of fullerene structure. There are two general types of carbon nanotubes: (1) Single walled carbon nanotubes (SWCNTs), which can be considered as single graphene sheet rolled into a tubular form the diameter of which ranges from 0.4 to 3 nm, and (2) Multi walled carbon nanotubes (MWCNTs), it can be considered as stacking of concentric layers of several graphene layers in the form of cylinders with an interspacing of 0.34 nm and diameter from 1.4 to over 100 nm [35]. Owing to their interesting mechanical, electrical, and thermal characteristics, the CNTs are still at the forefront of research in many areas of nanotechnology [36]. The properties of CNTs are highly dependent on their morphology, size, and diameter. It can be metallic or semiconductor, depending on the atomic arrangement.
3.1 Functionalization of CNTs

For the preparation of nanocomposite, a good dispersion of the filler within the host matrix is required. The proper dispersion of CNTs in the polymer matrix and prevention of re-aggregation are challenging because the extremely large surface area leads to a strong tendency to form agglomerates [37]. Currently, there are several methods used to obtain the proper dispersion of CNTs in polymer matrices such as solution mixing, melt blending, and in-situ polymerization. But, the most effective way to solve this problem is the surface functionalization of the CNTs which helps in the better dispersion and stabilization of the CNTs within the polymer matrix [38]. Various methods such as functionalization of defect groups, covalent functionalization, and non-covalent functionalization have been developed for the surface functionalization of CNTs [28,37,38].

4. CARBON NANOTUBES/POLYMER NANOCOMPOSITES

In order to exploit the extraordinary properties of CNTs, CNTs/polymer composites have been developed. There have been various reports on the fabrication of CNTs reinforced fibers or nanofibers for various applications [28,32]. These nanocomposites are being utilized in different fields including transportation, automotive, aerospace, defense, sporting goods, energy and infrastructure sectors. The effective utilization of CNTs for fabricating nanocomposites strongly depends on many factors such as the geometry of CNTs, adhesion between the polymer matrix and the fillers, purity, and dispersion of CNTs throughout the matrix without destroying their integrity. Furthermore, a good interfacial bonding is also required to achieve significant load transfer across the CNT–matrix interface for improving the mechanical properties of composites. CNTs/polymer composites have been fabricated by adopting a number processing approaches such as melt processing, solution blending, and in-situ polymerization [39-42]. However, it is difficult to control the orientation of CNTs within the polymer matrix which is required for the enhancement of the mechanical properties of the composite. CNTs reinforced polymer nanofibers can be prepared by electrospinning a polymer solution containing well-dispersed CNTs. It has been demonstrated that the electrospinning is a promising technique for aligning and debundling CNTs which allows the interactions between CNTs and host polymers [18, 43].

4.1 Mechanical properties of carbon nanotubes/polymer nanocomposite

Owing to the remarkable mechanical properties such as high elastic modulus and tensile strength, CNTs are considered to be the most ideal and promising reinforcements in substantially enhancing the mechanical properties of resulting CNTs/polymer composites. The CNTs/polymer composites are expected to have improved mechanical properties as a result of interactions between CNTs and the polymer matrix. Therefore, several studies have been made in the past to exploit the exceptional mechanical properties of CNTs into the composite. Both SWCNTs and MWCNTs have been utilized for reinforcing the polymer.

Ko et al. [44] described electrospinning as a method to fabricate CNTs reinforced PAN and PLA fibers. The TEM observation (Fig. 2) showed that the SWNTs were parallel to the axis direction of polymer fiber maintaining their straight shape. The alignment of CNTs in polymer matrix had a significant effect on the properties of resulting nanocomposites. Kim et al. [45] prepared MWNTs embedded polycarbonate nanofibers by electrospinning method. They reported that the nanocomposite exhibited strong and tough properties. Further, they suggested that the results may provide a feasible consideration of such electrospun composite fibers for use as the reinforcing elements to produce a new kind of composite.

The proper interactions between CNTs and polymer matrix and orientations of CNTs into the nanofiber play important role to enhance the mechanical properties of the composite membrane. Reneker’s group [46] developed highly oriented, large area continuous composite nanofibers composed of MWCNTs and PAN by electrospinning. They found that the orientation of MWCNTs within the electrospun NFs was much higher than that within the PAN polymer crystal matrix. Their finding showed that the orientation of the CNTs was not only determined by the surface tension and jet elongation, the slow relaxation of the CNTs in the nanofibers also played an important role in the orientation of CNTs in the polymer matrix. As a result of the high anisotropic orientation of the MWCNTs in the polymer matrix, the resulting composite mats possessed enhanced mechanical properties.

Sen et al. [47] fabricated SWNTs reinforced polymer comp-
Composite by electrospinning a solution of SWNTs dispersed poly-styrene or polyurethane solutions. They observed that the small SWNT bundles were oriented parallel to the nanofiber axis. Mechanical tests showed that the tensile strength of these SWCNT reinforced nanofiber membranes were improved by 104%, and the elastic moduli were increased by 250% compared to pure PU membranes, with improvements of these properties being mainly attributed to alignments and improved interfacial interactions between SWCNTs and the polymer matrix.

The elastic properties (Young’s modulus and yield strength) of the CNTs/polymer composites are found to be dependent on the effects of the aspect ratio of carbon nanotube reinforcements. Various studies have proved that incorporation of a very small amount of CNTs into the polymer matrix can lead to structural materials with significantly high modulus and strength. Significant advancement has been made in improving the mechanical properties of polymer matrix by mixing small fraction of CNTs. In this regards, Hou et al. [48] prepared PAN-MWCNT composite sheets of aligned nanofibers containing different concentrations of MWCNTs by electrospinning. The investigated improved tensile modulus by 144% at 20% MWCNTs by weight, and the tensile strength by 75% at 5% MWCNTs. Similarly, McCullen et al. [49] investigated electrospinning of poly (L-D-lactic acid) (PLA) with the addition of MWNF for development of a scaffold to be applied in tissue engineering. Further, they studied the effect of MWNT concentration on the mechanical properties of the composite mats. The findings can be summarized in the Table 1.

Baji et al. [50] used electrospinning technique to align and disperse multi-walled carbon nanotubes in nylon 6,6 to obtain high strength composite. The thermal and mechanical properties of the synthesized nanocomposite were characterized as a function of the weight fraction of the CNTs. Tensile and nanoindentation experiments were performed to investigate the mechanical deformation behavior of the composite. The results suggested that incorporation of high strength and high aspect ratio CNTs into the fiber matrix significantly enhanced the stiffness and strength of nylon 6,6 fibers. The mechanical test showed the remarkable increase in the tensile strength from 0.32 GPa to 0.65 GPa and Young’s modulus from 1.2 GPa to 3.5 GPa, respectively for CNT concentrations of 7.5 wt%.

Papila et al. [51] prepared composite electrospun fibers of multi walled carbon nanotubes and reactive poly(styrene-co-glycidyl methacrylate) (St-co-GMA) nanofibers to strengthen epoxy matrices. The incorporation of MWCNTs into the (St-co-GMA) nanofibers was successfully carried out by electrospinning. The addition of a very low weight fraction of composite fibers at 0.2 wt % increased the flexural modulus of epoxy composites by more than 20%. They claimed that the increase was attributed to the inherent strength of the well-dispersed MWCNTs and the surface chemistry of the electrospun fibers. Liu et al. [52] prepared epoxy composites by the impregnation of epoxy resin with thermoplastic polyurethane (TPU/MWCNTs) nonwoven mats. With only 3 wt % MWCNTs embedded in mats, a significant increase in the mechanical response was observed, up to 29% in tensile strength, 4% in elastic modulus, and 19% in tensile strain, in contrast with those of neat epoxy.

The composite of CNTs/polymer can also be obtained by the post-treatment of electrospun nanofibers followed by successful loading of CNTs. Recently, Gao and co-workers [53] synthesized CNT/polymer composites by post-treatment of electrospun nanofiber membrane. Ultrasonication was employed to induce the uniform decoration CNTs onto electrospun polymer nanofiber surfaces. It was found that the hardness and Young’s modulus of the composite mat significantly increased, which originated from the perfect dispersion of CNTs as well as the strong interaction between CNTs and nanofibers. The hydrogen bonding may occur between the amino groups of polyurethane chain and the carboxylic groups of CNTs surface which led to the enhanced mechanical properties of the composite membrane.

Tijing et al. [54] reported the two-nozzle electrospinning of (MWNF/PU)/PU nanofibrous composite mat with improved mechanical and thermal properties. They fabricated the composite nanofibrous mat composed of neat polyurethane (PU)

![Fig. 3. Stress-strain curves for various membranes. The SWNT to PU weight ratio is 1:100 in the composite membranes (b and c) [47](Image 62x562 to 275x730)](Image 62x562 to 275x730)
and multi-walled carbon nanotubes/polyurethane (MWNTs/PU) nanofibers by one-step angled two-nozzle electrospinning. Good interfacial interaction occurs between MWNTs and PU which enhanced the tensile strength by 25-64% and tensile strain by a maximum of 73% depending on the amount of MWNTs. Chen et al. [55] reported the successful preparation of polyimide (PI) and PI nanocomposite fibers containing different amounts of MWNTs for the first time by electrospinning. They compared the mechanical properties of thus obtained electrospun nanocomposite fibers with the membrane prepared by conventional solution-casting method and it was found that the mechanical property was significantly enhanced after incorporation of MWNTs in the case of electrospun composite membrane than that of solution-casting membrane. This can be considered as a good example for the preparation of high performance CNTs/polymer composites by electrospinning method.

Since it is difficult to disperse CNTs in the solvents for biopolymers, there are few reports on the reinforcing effects of CNTs into the natural biopolymers [56]. Jonathan et al. [57] reported nanocomposite fibers of Bombyx mori silk and single walled carbon nanotubes prepared by electrospinning process. The regenerated silk fibroin dissolved in a dispersion of CNTs in formic acid was electrospun to obtain composite nanofibers. They examined the morphology, structure, and mechanical properties of the electrospun nanofibers. The mechanical properties of the SWNTs reinforced fiber show an increase in Young's modulus up to 460% in comparison with the un-reinforced aligned fiber, however, the produced composite lacks proper distribution of nanotubes throughout the fibers. Lu and Hsieh [56] synthesized MWCNTs incorporated ultrafine cellulose fibers by electrospinning MWCNTs-loaded cellulose acetate (CA) solutions, followed by deacetylation of CA to cellulose (cell). The composite exhibited well-aligned MWCNTs along the fiber axes. The mechanical properties of the fibers were also greatly enhanced with increased MWCNTs loading levels. They have mentioned that the fibers loaded 0.55 wt % MWCNTs had doubled Young's modulus (553 to 1144 MPa) and tensile strength (21.9 to 40.7 MPa) while slightly increased elongation (from 8.04 to 10.46%).

Jose et al. [59] reported the fabrication of aligned nanofibrous nanocomposites of nylon 6 and surface-modified MWNTs via electrospinning process, using a rotating mandrel. The combination of carbon nanotubes and nanoscale processing results in structural and mechanical enhancements of nylon 6. Our research group [58] reported the preparation and characterization of MWCNTs incorporated electrospun nylon66 composite nanofibers by electrospinning. We observed that a good interaction between the polymer matrix and CNTs can be obtained by the surface treatment of CNTs. The mechanical properties of the composite nanofibers such as Young's modulus, tensile strength and elongation at break were improved than that of the pristine nylon66 nanofibers.

5. CONCLUSIONS

Electrospinning has become one of the most acceptable methods for preparing nano scale fibers, both in laboratory and industrially. This review summarizes studies on a number of electrospun polymeric fiber composite containing CNTs. The CNTs/polymer nanocomposites processed by electrospinning exhibit improved mechanical and physical properties. These nanocomposite fibers find applications in a wide range of areas such as filtration, biomedical, catalysis, sensor, aerospace, automotive, and so on. There are several factors affecting the development and quality of CNTs/polymer composite
such as types of CNTs, aspect ratio, dispersion of CNTs into the polymer matrix, alignments, anti-agglomeration of CNTs into the matrix, interaction between the CNTs and matrix, etc. The major obstacle in preparing CNTs/polymer nanocomposite is the homogeneous dispersion of CNTs into the polymer matrix. Functionalization of the CNTs is the most effective approach to overcome the agglomeration for homogeneous dispersion of the CNTs into the polymer matrix with good interactions which lead to the enhanced mechanical properties of the resulting nanocomposite. The CNTs reinforcement into the polymer matrix can produce a new generation of composite materials. Alignment of CNTs in the polymer matrix shows a predominant role in the mechanical response of the composites. To further enhance the mechanical properties, a lot of research work could be done in the future.

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