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Electrospinning of Continuous Nanofiber Bundles and Twisted Nanofiber Yarns

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1. Introduction

Spinning is a prehistoric technology in which endless filaments, shorter fibers or twisted fibers are put together to produce yarns that serve as key element to assemble multifarious structural designs for diverse functions. Electrospinning has been regarded as the most effective and versatile technology to produce nanofibers with controlled fiber morphology, dimension and functional components from various polymeric materials (Dersch et al., 2007, Frenot and Chronakis, 2003, Schreuder-Gibson et al., 2002). However, most electrospun fibers are produced in the form of randomly-oriented nonwoven fiber mats (Doshi and Reneker, 1995, Madhavamoorthi, 2005). The relatively low mechanical strength and difficulty in tailoring the fibrous structure have restricted their applications. With the rapid development in nanoscience and nanotechnology, yarns composed of nanofibers may uncover new opportunities for development of well-defined three dimensional nano fibrous architectures. This chapter focuses on recent research and advancement in electrospinning of nanofiber bundles and nanofiber yarns. The preparation, morphology, mechanical properties and potential applications of these fibrous materials are discussed in details.

2. Nanofibers and yarns

Nanofibers are defined as one dimensional nanomaterials with diameters less than 1 μm (1000 nm), and an aspect ratio (length/diameter) larger than 100:1. They are also named superfine or ultrathin fibers in some literatures (Supaphol et al., 2005, Alborzi et al.). When the fibers are in the range of 100–1000 nm, they are also referred to as submicron fibers (Bellan et al., 2006, Keun Kwon et al., 2005, Givens et al., 2007). This intrinsic feature offers them drastically increased surface to volume ratio and high aspect ratio. There are several methods to prepare nanofibers, encompassing top-down (melt-blown (Ellison et al., 2007), melt electrospinning (Dalton et al., 2007, Lyons et al., 2004), islands-in-the-sea (Nakata et al., 2007), and electrospinning (Bhardwaj and Kundu)), and bottom-up (interfacial polymerization (Xing et al., 2008), self-assembly (Viney, 2004), and phase separation (Zhao et al.)) approaches. Nanofibers produced from electrospinning have a naturally formed porous structure with excellent pore interconnectivity and the pores are in the range between tens of nanometers to a few micrometers. The open pore structure and high permeability to gas, along with the high surface area make them ideal porous membranes. Compared with other one-dimensional nanostructures (e.g. nanotubes or nano-rods),

continuous nanofibers are advantageous in terms of fabrication cost and the possibility of being integrated into other desired assembly in one-step.

Ascribed to the high surface area, porous structure, and the ability to adopt functional molecules and nanomaterials (e.g. nanoparticles, nanotubes), nanofiber nonwoven webs have been used in areas as diverse as batteries (Norris et al., 2000), biomedical (Liang et al., 2007, Agarwal et al., 2008, Yoshimoto et al., 2003, Cao et al., 2009, Xu et al., 2004), filtrations (Gibson et al., 2001, F. DOTTI and MAZZUCHETTI*, October 2007), medical prostheses (Buchko et al., 1999, Buchko et al., 2001), sensors (Wang et al., 2002b, Wang et al., 2002a), fuel cells (Shabani et al., Li et al.), nanocomposites (Huang et al., 2003, Chronakis, 2005), and protective clothing (Lee and Obendorf, 2007, Ramakrishna et al., 2006).

Electrospun nanofibers are generally collected as nonwoven or randomly arranged structures, due to the “whipping instability” of the electrospinning jet. Early studies on fiber deposition and its assemblies were focused on controlling the fiber alignment. A few typical ways to electrospun-aligned nanofibers are shown in Figure 1. Aligned nanofibers can be collected using a dynamic mechanical collector such as cylindrical drum (Ding et al., 2002, Li and Xia, 2004), wired drum (Katta et al., 2004) or a tapered wheel (Xu et al., 2004), either grounded or negatively charged (Theron et al., 2001). When the collector rotates at a high surface speed, such as 8 m/s, fibers start to align along the rotating axis. However, it is yet difficult to obtain perfect fiber alignment with this method, because the residual charge accumulation on the deposited fibers interferes with the incoming ones.

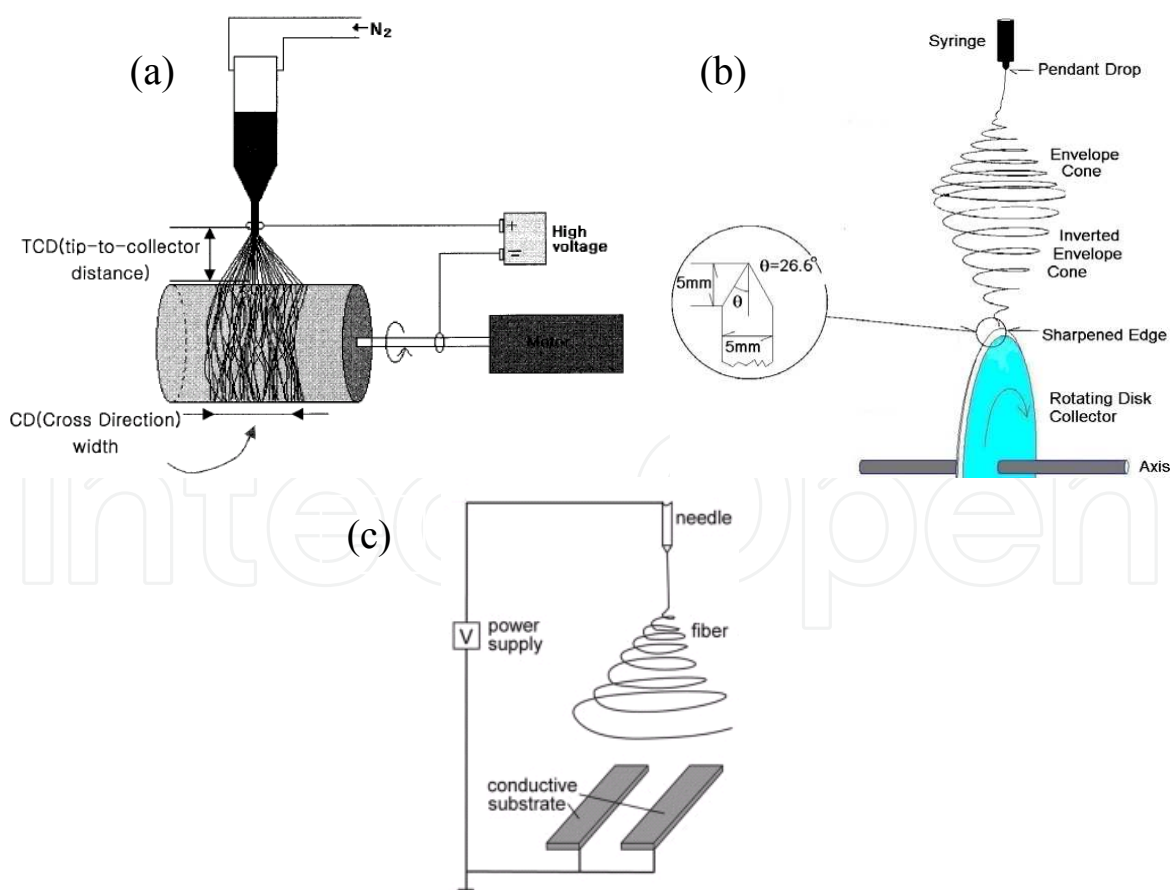


Fig. 1. Basic methods for controlling the alignment of electrospun nanofibers. (a) High speed rotating drum collector, b) a tapered wheel, c) stationary gap collector.

Since the electrostatic forces dominate the electrospinning process, it is also possible to obtain aligned nanofibers through the manipulation of the electric field. Electric field was manipulated by using two split parallel flat plates (Gap Collector) connected with grounded electrode (Li et al., 2004, Liu and Dzenis, 2008, Dan Li, *June 20, 2003*, Bazbouz and Stylios, 2008a, Kameoka et al., 2004, Ishii et al., 2008), or a frame-shaped collector (Dersch et al., 2003). The distance between two conductive electrodes is up to centimeters. A high degree of fiber alignment can be achieved with this method, and the produced fibers can be easily transferred to other substrates for device fabrication. However, the fibers thus produced are of limited length and thickness.

Yarns can be assembled or interlaced into many fibrous structures by the process of weaving, knitting or embroidery (P. J Denton and Daniels, 2002). Single nanofibers are too fragile and too thin for such processes, and it also requires sophisticated equipment for precise handling of these fibers (Tan et al., 2005). Attempts to produce nanofiber yarns from electrospun nanofibers were reported by Formhals as early as in 1934. In a series of patents (Anton, 1934, Anton, 1938b, Anton, 1944, Anton, 1938a), he described the experimental setups to produce polymer filaments by using electrostatic forces. Most of the early works on electrospinning of nanofiber yarns were actually focused on non-twisted nanofiber bundles. Although twist can be inserted by a post-electrospinning treatment, it is now highly preferred that twists can be added to continuous nanofiber yarns directly from an electrospinning process.

3. Discontinuous nanofiber bundles and twisted yarns

Generally, electrospinning produces random nanofiber mats, if a planar stationary plate is used as a collector. However, by manipulating the electric field or using moving collecting or spinneret systems, one can collect non-continuous nanofiber bundles or twisted yarns rather than mats.

3.1 Short nanofiber bundles

In 2001, Deitzel et al (Deitzel et al., Deitzel et al., 2001) demonstrated the deposition of nanofibers in a more targeted fashion by a series of charged rings in the electrospinning zone, as shown in Table 1A. The charged rings had the same polarity as the surface charge on the jet, which increased the downward force on the jet. This method resulted in nanofiber deposition in a narrow strip (0.6 cm wide) when the target was a rotating drum. The average diameter of fibers was 300 nm. The prepared short bundles of polyethylene oxide were analyzed using wide angle X-ray diffraction (WAXD) technique and some molecular orientation but poor crystalline microstructure was found in the fibers.

Theron et al (Theron et al., 2001) described an electrostatic field-assisted assembly technique in combination with the dynamic rotating collector to position and align individual nanofibers. Bundles of nanofibers were collected on a tapered wheel-like disc as shown in Table 1B. The disc was made of aluminum with a diameter of 200 mm, a thickness of 5 mm and a tapered angle of 26.6°. The tapered edge of the wheel collector had a strong converging electric field, thus enabling the jet emerged from the droplet to form an envelope cone at the start and then shrink and form an inverted cone, once it approached the sharp edge. As a result, nanofibers of polyethylene oxide (PEO) with a diameter varying within 100-300 nm would preferentially deposit on the wheel edges, which were assembled in a parallel array due to the rotation of the wheel.

Teo and Ramakrishna (Teo and Ramakrishna, 2005) demonstrated the fabrication of nanofiber bundles by collecting them across two negatively charged steel blades (3 cm apart) as shown in Table 1C, and then dipping them in water. During electrospinning, the fibers were preferentially deposited between the blades due to the concentration of electrostatic charges on the sharp edges. The fibers were first deposited on one blade, and then stretched to the other with the aid of electrostatic forces acting on the fibers. As a result, fibers were deposited across the gap. However, “stray” fibers could not be eliminated during the electrospinning process. A further step of dipping fibers in water was thus required to cluster the fibers together, by the force of water surface tension. The resulting fiber bundles had two fixed ends, which were of limited length, but they were free to be transferred to other substrates, and to be twisted or braided manually.

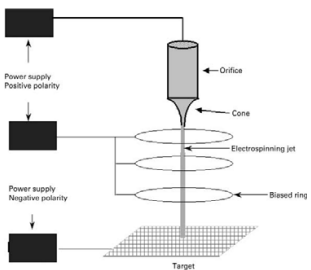
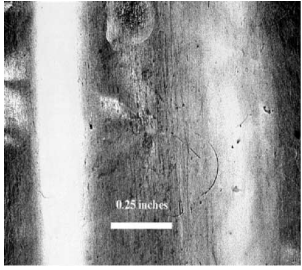
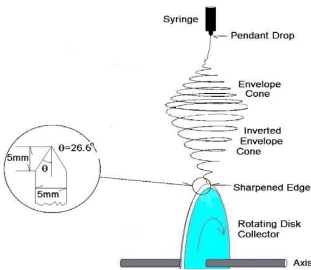
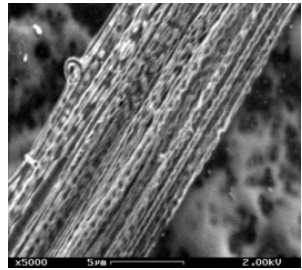
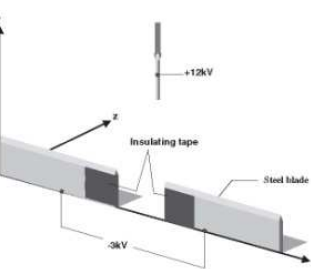
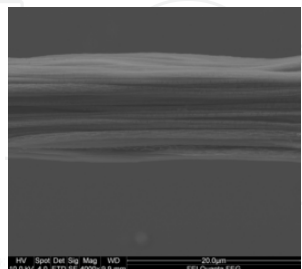
Year	Author	Setup	Morphology	Fiber Bundling/Polymer
A. 2001	Deitzel et al.			Jet was stabilized by placing a series of charged rings in the electrospinning zone and the rings were charged to have the same polarity to the spinneret; PEO
B. 2001	Theron et al.			Electric field is concentrated on the tapered wheel which rotates for fiber alignment. The collector has a limited fiber deposition area; PEO
C. 2005	Teo et al.			Gap collector using sharp blades for concentration of electric field; PCL

Table 1. Short Nanofiber Bundles.

Short nanofiber bundles with parallel orientated short fibers can also be prepared by cutting an aligned nanofiber membrane into narrow strips. In this case, preparing aligned nanofiber membranes is the focus. Different fiber alignment techniques have been used, such as using

a rapidly oscillating frame (Fong et al., 2002, Dersch et al., 2003), and a copper comb collector in needleless electrospinning (Jiri Chvojka and Lukas, 2009).

3.2 Short nanofiber yarns

High-speed rotating drum has been recognized as the easiest way to get highly aligned nanofibers. Fennessey et al (Fennessey and Farris, 2004) prepared short nanofiber yarns using aligned PAN nanofiber membranes. The nanofiber membrane was cut into short tows (approximately 32 cm × 2 m) and then linked together. An electric spinner was used to insert twist and the action of twist on yarn tensile strength and modulus was studied. They found that increasing the twist angles led to increased yarn ultimate strength and modulus. Liu et al (Liu et al., 2008) also used a high speed annual shaped collector to prepare aligned nanofiber membrane, and the membrane was cut and twisted in a similar way into short yarns. Later on, PAN nanofibers reinforced by carbon nanotubes (CNTs) were also prepared into short nanofiber yarn by Farouk et al (Farouk et al., 2009) who used a high speed rotating drum collector. They found that well dispersed CNTs in the polymer solution for electrospinning led to high yarn mechanical properties. Recently, Moon et al (Moon and Farris, 2009) prepared short PAN nanofiber yarns using a similar method for making carbon nanofiber yarns. They reported that the carbon nanofiber yarns had a tensile strength as high as 1 GPa.

Researchers have also paid attention to directly getting short twisted nanofiber yarns. For instance, Dalton et al (Dalton et al., 2005) used two parallel grounded rings to get aligned nanofibers (Table 2A). Nanofibers were first deposited at the lower part of the rings, which then proceeded upward to the ring top, aligning across the gap. By rotating one of the rings the suspended fibers were converted into a multi-filament yarn with a diameter of less than 5 μm and a length of 4 ~ 10 cm. The yarn length was limited by the distance between the two electrodes. Later on Liu et al (Liu et al., 2007) prepared nanofiber-based composite ropes of poly(methyl methacrylate) (PMMA)/MWCNT by using a gap collector (Table 2B). Nanofibers were electrospun vertically downward and bridged between the two electrodes. By rotating the point electrode, the as-spun PMMA/MWNT nanofibers were converted into yarns of 30 ~ 40 cm in length and 13 ~ 23 μm in diameter. This method was difficult to spin yarns longer than 40 cm, as the constant distance between two collectors had to be maintained so that nanofibers can be continuously deposited.

Gu et al (Gu et al., 2007) described a method of directly fabricating single twisted nanofibers by controlling the electric field around an auxiliary electrode (Table 2C). A polygon with several faces was placed in between the needle and the collecting plate. Each face of the polygon was subjected to an applied voltage. By switching the voltage rapidly, a rotated electric field was created, changing the direction of the electrostatic force which led to the twisted nanofibers.

Lotus et al (Lotus et al., 2008) also adopted the concept of rotating an electrode in the gap collector to produce twisted nanofiber yarns. The set-up consists of a rotating hollow hemisphere and a non-rotating but translating tapered metal rod. The tapered end of the rod and the edge of the hemisphere are conductive so fibers would preferentially deposit on their edges, and form a conical cone with its apex lying on the rod tip, as shown in Table 2D. by rotating the hollow the hollow hemisphere, and translating the metal rod away, 10cm long zinc oxide and nickel oxide yarns can be fabricated. The yarns are 5~30 μm in diameter and consist of nanofibers 60~100nm in diameter.

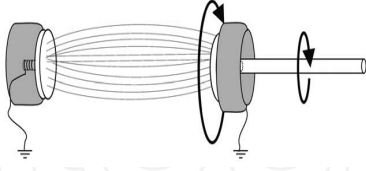
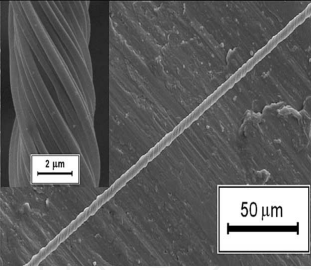
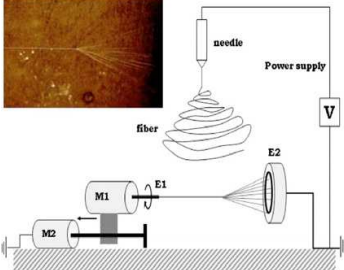
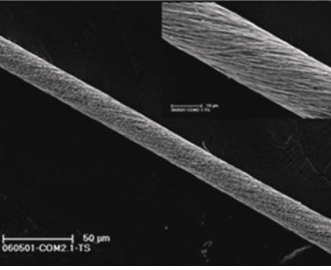
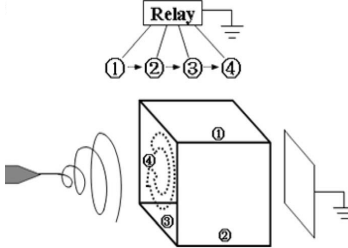
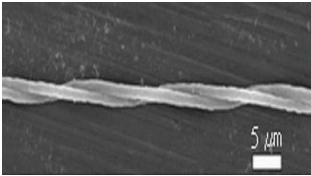
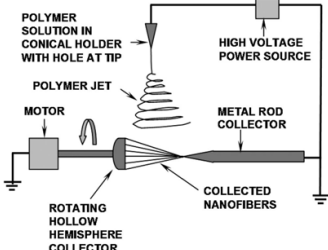
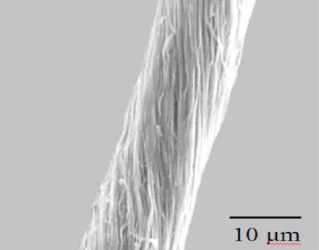
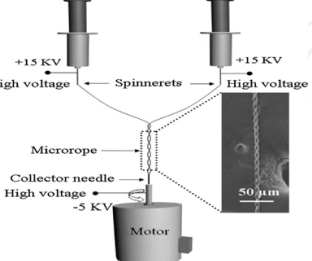
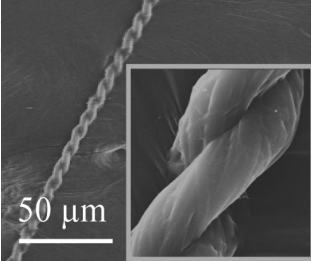
Year	Author	Setup	Morphology	Fiber Twisting/Polymer
A. 2005	Dalton et al.			Aligned nanofibers were collected between the electrodes (gap collector) and twisted by rotating one electrodes; PCL
B. 2007	Liu et al.			Aligned nanofibers collected by twisting needle electrode; PMMA/MWNTs
C. 2007	Gu et al.			Nanofibers were twisted by electric field using an auxiliary polygon electrode; PEO
D. 2008	Lotus et al.			(Gap collector) aligned NFs twisted by rotating the round electrode; ZnO, NiO
E. 2010	Chang et al.			Helical ropes were prepared with two needle spinnerets and one rotating needle collector; PVP

Table 2. Short Nanofiber Yarns.

Recently Chang et al (Chang and Shen) prepared helical ropes of polyvinyl pyrrolidone (PVP) by using two needle electrospinning spinneret and a rotating needle collector (Table 2E). The diameter of the needle collector plays a key role in determining the formation of the ropes. A stable fiber bundle was formed when the diameter of the needle was smaller than 0.5 mm. The pitch of the ropes could be adjusted through the distance between the two

spinnerets. When a needle collector of the diameter greater than 5 mm was used, fibers travelled randomly and deposited as a mat on the collector.

4. Continuous nanofiber bundles

Continuous nanofiber bundles are defined as a group of loosely assembled nanofibers, which have no twist. The main techniques to get continuous nanofiber bundles are described in Table 3.

A liquid medium was used separately by Khil et al (Khil et al., 2005) and Smit et al (Smit et al., 2005) to collect nanofibers and subsequently wind into continuous nanofiber bundles (Table 3A). Nanofibers initially formed a random web on the liquid surface, which were drawn and lifted off with a rotating mandrel to form a fiber bundle. Under the action of liquid surface tension, the bundle was elongated and collapsed into a round cross-section. By continuously depositing nanofibers into the liquid, while at the same time collecting them with the winder, a continuous nanofiber bundle was obtained. The fiber bundles could be drawn at a rate of 0.05 m/s ~ 0.5 m/s. To make the fiber suspend on the liquid surface could help the collection, and a liquid having a high density or high surface tension was normally selected as the collecting medium.

To obtain continuous nanofiber bundles, Pan et al (Pan et al., 2006) used a special electrospinning setup consisting of a pair of spinnerets with opposite polarities and a rotating shaft collector (Table 3B). In the process, the nanofibers from the two spinnerets carried opposite charges. They attracted to each other to form a fiber bundle and the fibers aligned within the bundle. The fiber bundle production rate was dependent on the rotating speed of the collector, the polymer material used and the fiber diameter produced. The yarn diameter can be controlled by the number of spinneret pairs. For PVP nanofibers with an average diameter of 670 nm, the maximum production speed was 14.9 m/s. Later, Li et al (Li et al., 2008) and Yao et al (Yao et al., 2009) respectively prepared nanocomposite yarns of poly(L-lactide)(PLLA)/nanotritanium phosphate and PLLA/Zein using this electrospinning setup. Li et al also studied the effect of electrospinning distance and found that nanofibers bonded tightly to each other at an electrospinning distance of 20 cm, however longer electrospinning distance resulted in loosely packed nanofiber bundles.

Okuzaki et al (Okuzaki et al., 2008) observed the formation of poly(p-phenylenevinylene) (PPV) precursor fiber bundles using just a conventional electrospinning setup (Table 3C). The spinneret was placed vertically on top of the grounded flat collector. The unusual bundle formation was explained by the conductive nature of the PPV precursor. The deposited fibers discharged through polyelectrolyte chains to the grounded target, which preferred the gravitated deposition so as to decrease the gap between the fibers and the needle. Centimeter-long nanofiber bundles were formed spontaneously between the spinneret and the grounded plate within a minute. Subsequent thermal conversion led to bundles of PPV nanofibers.

In 2008, Wang et al (Wang et al., 2008b) reported a method to self assemble continuous nanofiber bundles (Table 3D). A grounded needle tip was incorporated into the collecting system to induce self-bundling of nanofibers. It was observed that the liquid jet was a straight line initially, and then whipped around until it got close to the tip of the needle collector, splaying fibers to converge on the needle collector due to the large electrostatic attraction. By pulling back the bundle and winding it on a grounded rotating collector,

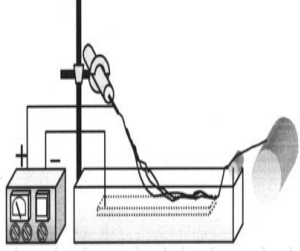
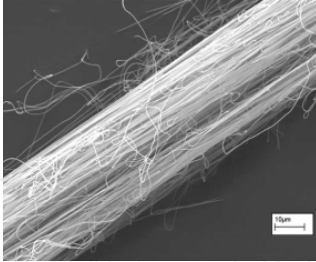
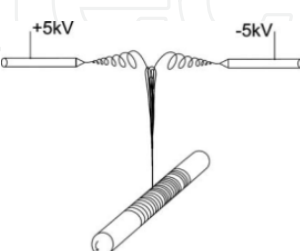
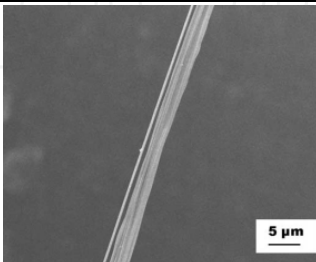
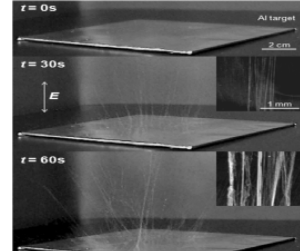
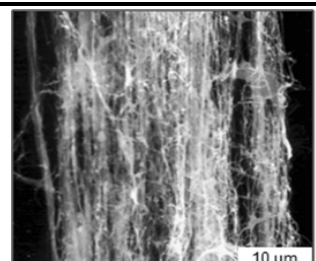
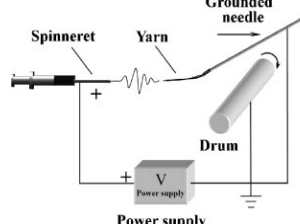
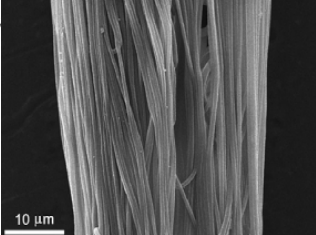
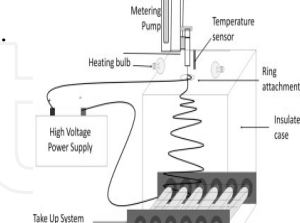
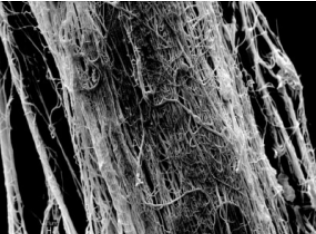
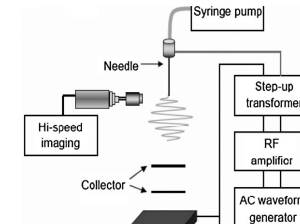
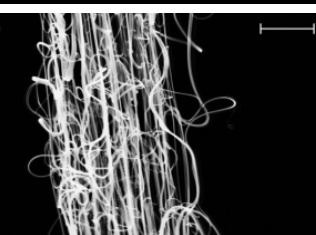
Year	Author	Setup	Morphology	Yarn Bundling/Polymer
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2005	Smit et al.			
B. 2006	Pan et al.			Nanofibers electrospun from opposite charged spinneret attract each other to form bundles; PVA; PVP
2007	Li et al.			
2009	Yao et al.			
C. 2006	Okuzaki et al.			Conductive fiber induces self-bundling; PPV
D. 2008	Wang et al.			Needle collector induced self-bundling of nanofibers; PHBV
E. 2008	Mondal et al.			Ring induced self bundling of nanofibers; PAN
F. 2009	Maheshwari et al.			AC induced self-bundling of nanofibers; PVP

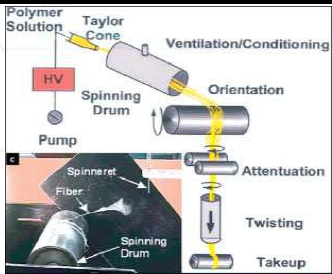
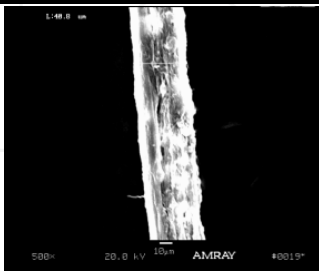
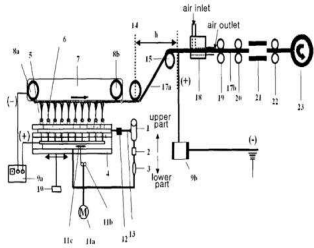
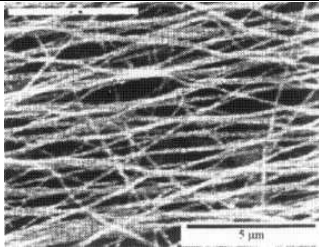
Table 3. Continuous Nanofiber Bundles.

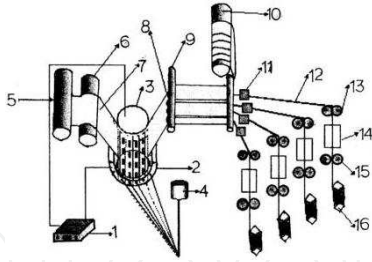
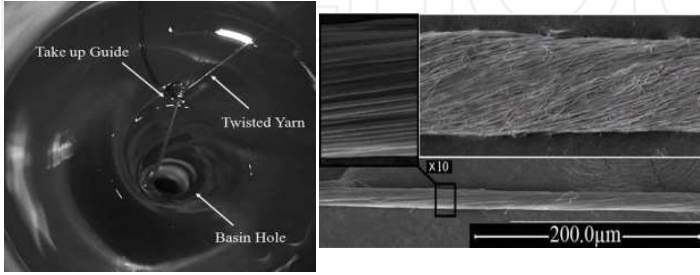
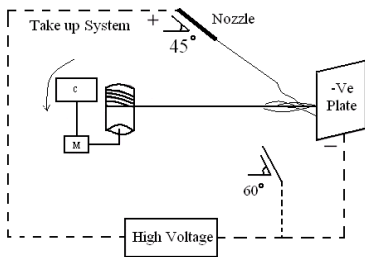
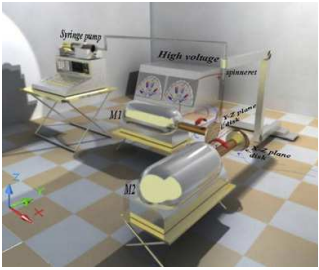
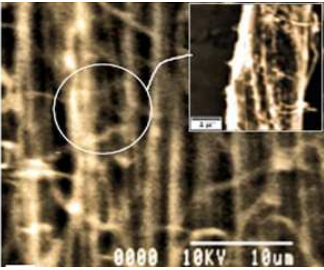
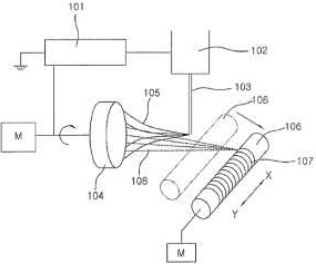
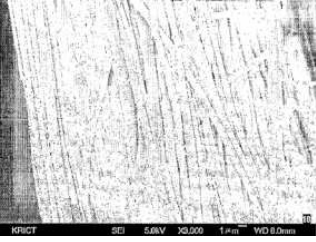
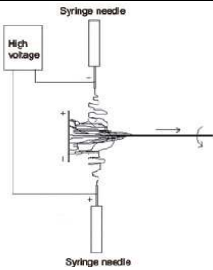
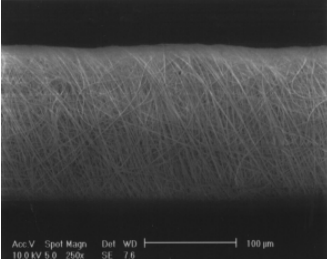
continuous nanofiber bundle was generated, provided that the surface velocity of the rotating drum matched the velocity of the bundle growth. The self-bundling became easier when increasing the conductivity of polymer solution. When the solution conductivity was larger than $400 \mu\text{S}/\text{cm}$, self-bundling occurred automatically without the induction of a needle collector. Greater fiber alignment was observed with the increase in the solution conductivity. Another approach to prepare electrospun nanofiber yarn was introduced by Mondal et al (Mondal et al., 2008). In their design, the electric field was manipulated by attaching a ring to the spinning nozzle just above the orifice to self-assemble the fibers for yarn formation (Table 3E). To initiate the yarn formation, a glass rod was introduced to attract yarn on the glass rod end. By moving the glass rod away from the spinning zone, a continuous nanofiber yarn was prepared manually. The formation of nanofiber yarn was controlled by temperature, polymer concentration and applied voltage.

Maheshwari et al (Maheshwari and Chang, 2009) reported an assembly of multi-stranded nanofiber threads via AC electrospinning (Table 3F). Nanofibers with both positive and negative segments were electrospun because of polarity switching during electrospinning. The fibers experienced an alternation of attractive and repulsive forces, resulting in increased alignment. A visible thread was observed emerging downstream from the spinneret. The thread could be easily deflected away and collected because of the small attraction toward the counter electrode. The authors also showed how the AC voltage and frequency affected the fiber collection. Increasing the frequency suppressed the jet whipping instability, thus giving smaller thread width (thread with lower fiber density), but more beaded fibers. An opposite effect was seen with the increase in the voltage.

5. Continuous nanofiber yarns

A nanofiber yarn can be formed by twisting a thin strand of nanofibers around the axis. The fibers after twisting show a helical configuration. Twist functions to increase the fiber to fiber cohesion and strength of the yarn. In electrospinning research, considerable effort has gone into making continuous twisted nanofiber yarns in recent time. Table 4 summarizes the main techniques that have been developed to electrospin continuous nanofiber yarns.

Year	Author	Setup	Morphology	Yarn Twisting/Polymer
A. 2003	Ko et al.			Twisting of nanofibers with a special setup; PAN,PLA
B. 2005	Kim et al.			Manually drawing and twisting nanofibers electrospun from a multi-needle setup; Poly urethane

Year	Author	Setup	Morphology	Yarn Twisting/Polymer
C. 2006	Kim et al.			Manually drawing and twisting nanofibers electrospun from a needless electrospinning setup;
D. 2007 2010	Teo et al. Yousef. et al.			Nanofibers twisted due to rotation of liquid water; polymer (Helix angle 19.76°)
E. 2007	Dabirian et al.			Nanofiber stream redirected and twisted by a twist winder; PAN
F. 2007	Bazbouz et al.			Nanofibers twisted by rotating the left disk and then taken up by the right disk; Nylon6/MWNT
G. 2008	Lee et al.			Nanofiber web directly twisted by rotating the disk collector; PAI
H. 2009	Dabirian et al.			Nanofibers produced from two oppositely charged spinneret and twisted by using an electronic twister; PAN

Year	Author	Setup	Morphology	Yarn Twisting/Polymer
I. 2009	Kim et al.			Single and multi nozzles are arranged along the circumferential direction. Nanofibers are drawn and twisted; Nylon6, Nylon66 (Helix angle up to 15°)
J. 2010	Afifi et al.			Fiber web was twisted by an earthed rotating funnel; PLLA
K. 2011	Ali et al.			Nanofiber yarns were directly produced from an un-earthed fibrous cone formed on a rotating funnel; PVDF-HFP, PCL, PAN, PS (twist angle up to 0 - 61°)

Table 4. Continuous Nanofiber Yarns.

The concept of using nanofiber yarns to make complex fibrous structures for a new generation of composites was firstly presented by Frank Ko (Ko et al., 2003). Continuous poly(lactic acid) (PLA) and PAN nanofiber yarns filled with carbon nanotubes in the fibers were produced by applying a yarn twisting and subsequent winding method (Table 4A). However, no details were presented to explain how the yarns were twisted and continuously wound, considering in particular that the twisting arrangement resembles a false twist texturing process rather than one that inserts any real twist into the yarn.

Kim et al (Kim, 2010a, Kim, 2009a, Kim, 2008b, Kim, 2009b, Kim, 2010b, Kim, 2005) claimed a series of patents to electrospin continuous filament composed of nanofibers. In one of these techniques, a multiple needle electrospinning system was used to produce nonwoven web on a rotating belt which was then stretched and collected on single winding roller (Table 4B) (Kim, 2008b). The nonwoven web was also prepared by a needleless electrospinning setup using a rotating cylinder spinneret before splitting it into several strips (Table 4C). Later on, the group also prepared continuous nanofiber bundles by collecting nanofibers on the circumference of a disc collector (Kim, 2008a) (Table 4I). By using 16,000 nozzles, the group has achieved a maximum speed of 490 m/min with an average fiber diameter of 480 nm.

Teo et al (Teo et al., 2007) demonstrated a technique for continuous formation of nanofiber bundles using the water vortex. Different from previous fiber bundling techniques (Table

3A), the nanofiber bundles were formed inside a liquid (e.g. water), as shown in Table 4D. A take-up rate of 1.05 m/s could be reached in this experiment. The nanofiber yarn had a maximum twist angle of 19.76° (Yousefzadeh et al.).

Dabirian et al (Dabirian et al., 2007) reported a method of continuous nanofiber yarn formation through the manipulation of the electric field. A negative bar and a negative surface were placed within the electric field to direct the electrospinning jet. A spinning triangle was formed as a result (Table 4E). Nanofibers were collected and twisted with a three-phase motor. The twist level and the take-up speed were inter-related. To increase the twist level, the take-up speed has to be compromised. The yarn production rate was about 14 m/hr, whereas the yarn diameter was in the range of 160~170 μm . Later on in 2009, Dabirian et al (Dabirian and Hosseini, 2009) also produced nanofiber yarns by using two oppositely charged nozzles placed on either side of an uncharged collector (Table 4H), and the yarn take-up velocity was 5.76 m/hr.

Bazbouz et al (Bazbouz and Stylios, 2008b) improved the gap collector by using two perpendicularly disks placed 4 cm apart. One disk was rotated to twist the nanofibers, and the other was for continuous yarn winding and both disks rotated at a constant rate (Table 4F). Different twist rates could be applied to provide fiber bundles with different degrees of lateral cohesion and friction. The yarn diameter was 5 ~ 10 μm and dependent on the number of fibers generated at the spinneret, as well as the twist and take-up speeds. The limitation of the method is the fiber sticking, due to the short spinning distance and the low evaporation rate of the solvent.

Lee's group (Lee, 2009, Lee, 2010b, Lee, 2010a, Lee, 2008) prepared a long filament consisting of nanofibers by using a multi-collector technique (Table 4G). They indicated that the first earthed collector should be made of a conductive metal plate or a metal mesh and the second collector a material capable of generating static electricity. The shape of the first collector was not fixed but the second collector must have a round shape like a tube. Different from previous methods based on gap collection, the glass rod is extendable, making the yarn collection continuous. However, due to its non-conductive nature, the fiber alignment could not be matched with the ones prepared by gap collector, where two electrodes are both conductive and grounded.

Afifi et al (Afifi et al.) used a slowly rotating grounded "funnel" to collect PLLA electrospun fiber yarns (Table 4J). The charged jet was ejected toward the grounded funnel target from a diagonal direction, forming a web on the mouth plane. The web was twisted as it was formed, and pulled upward to the winder. Continuous yarns were fabricated thereby, with diameters of around 164 μm . However, the authors only demonstrated that micro-sized fibers with diameters around 6 μm were electrospun for this yarn production.

Recently, Ali et al (Ali et al.) developed a method to directly electrospin highly twisted continuous nanofiber yarns. The setup combined a rotary funnel collector and two oppositely charged spinnerets, as shown in Table 4K. The funnel collector was not earthed. The deposition of nanofibers onto the funnel was largely due to the electrostatic attractions. Nanofibers mainly deposited to cover the funnel forming a fibrous membrane on its mouth. To initiate a twisted yarn, a plastic rod was first placed near the central area of the rotary membrane. When the rod was withdrawn from the funnel, the membrane formed a "fibrous cone" with its apex attaching to the rod, and its edges connecting to the funnel end. Further withdrawing of the cone apex induced the formation of continuous yarns as shown in Figure 2.

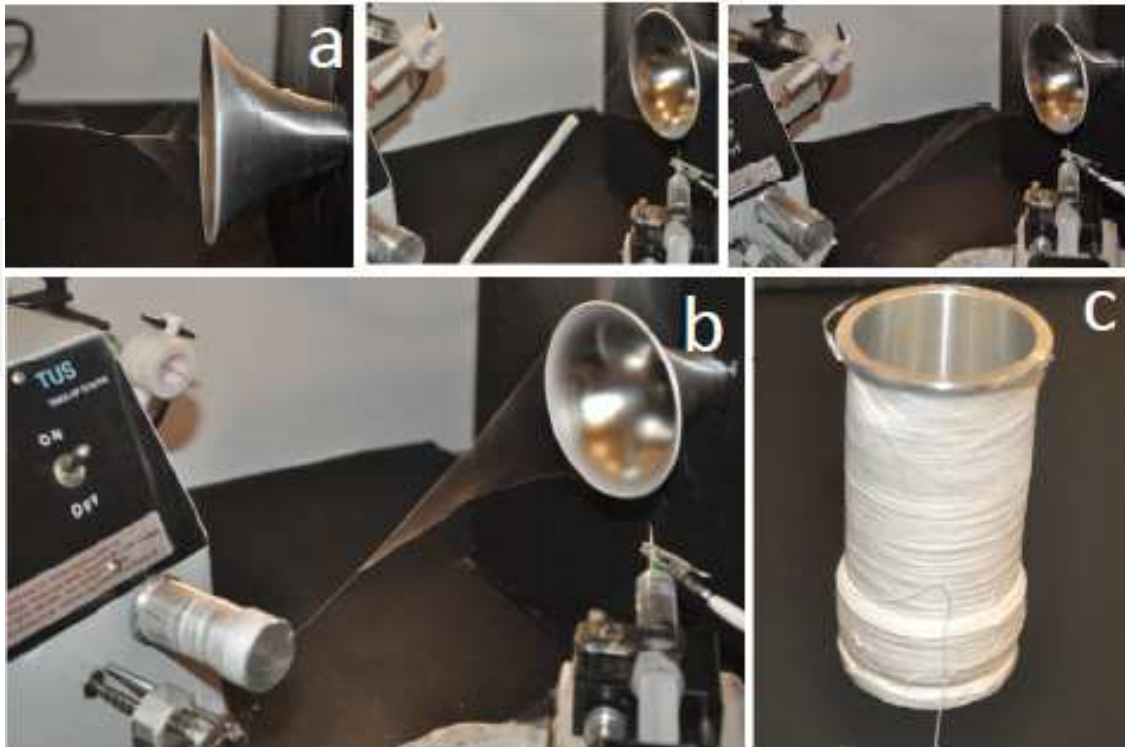


Fig. 2. a) Frames of a video showing the formation of nanofiber cone with the aid of a plastic rod, b) hollow nanofiber cone taken up by continuous drawing with a winder, c) a photograph of as-electrospun nanofiber yarn, d) SEM images of a nanofiber yarn section.

The yarn could be collected and wound incessantly as far as the fibrous cone was maintained dynamically. Kilometers of nanofiber yarns have been drawn from the fibrous cone, with up to 7400 tpm of twist inserted through the rotation of the funnel. The average yarn diameter can be adjusted in the range of 30 ~ 450 μm through the overall solution feeding rate and the twist rate, while the constituent fiber diameter can be changed over a wide range (between 480 - 1500 nm in the study).

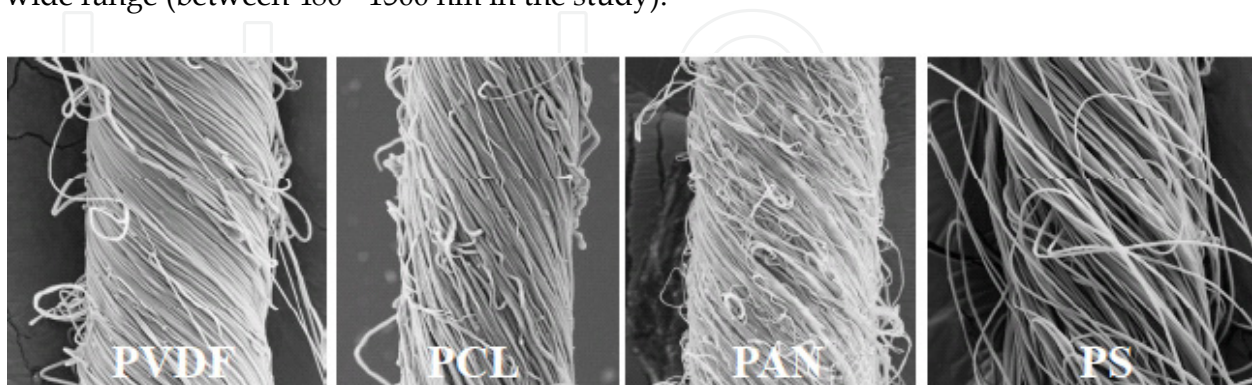


Fig. 3. SEM images of nanofiber yarns produced from different polymers.

Poly(vinylidene fluoride-co-hexafluoropropene) (PVDF-HFP), PAN, polycaprolactone (PCL) and polystyrene (PS) have been successfully electrospun into yarns using this setup. The SEM images of the yarns are shown in Figure 3. This electrospinning mode increased not

only the stability of yarn formation but also the yarn spinning rate. In addition, the two spinnerets provide opportunities for fabrication of hybrid nanofiber yarns.

6. Morphology and mechanical properties

A lot of yarn manufacturing technologies have been explored (Zhou and Gong, 2008). It has been generally recognized that both the structure of fibers and their macroscopic arrangement play key roles in yarn mechanics.

Teo et al (Teo et al., 2007) reported the morphology of individual fibers in the yarns and the control through adjusting the electrospinning parameters, such as solution concentration, flow rate, spinning distance and applied voltage. They also reported that the average diameter of nanofiber yarn increased linearly with increasing the feed rate of polymer solution. Ali et al (Ali et al.) study the effect of applied voltage, solution concentration and flow rate on the morphology of nanofiber yarns in detail and indicated that with an increase in the applied voltage the individual fiber diameter decreased but the overall diameter of yarn increased linearly. Not only the individual fiber but also the yarn increased their diameters linearly with polymer concentration and flow rate. The morphology of nanofiber yarns also depended on the winding rate. It was demonstrated that with increasing the winding rate, the diameters of both the individual fiber and the nanofiber yarn decreased linearly (Ali et al.).

It is well known that the strength of conventional yarns increases with increasing the twist level in the yarn, up to a limit. Ali et al (Ali et al.) systematically studied the effect of twist on the mechanical properties of nanofiber yarns. They found that when the twist level was 420 tpm, the yarn tensile strength and elongation at break were 42.0 MPa and 250%, respectively. However the tensile strength started decreasing when the twist level reached 3500 tpm, as shown in Figure 4a. The maximum average tensile strength of PVDF-HFP nanofiber yarn produced from their method was 60.4 MPa. Figure 4b shows a comparison of stress-strain curves for the aligned twisted nanofiber strip, twisted nanofiber yarn and a yarn braid. It shows that when the nanofiber yarn is braided the tensile strength is improved considerably (Fig. 4b).

Electrospun fibers normally possess poorly developed crystalline structure owing to the quick solidification of the spinning jet. Post-treatment such as drawing and annealing used for improving crystalline structure and mechanical strength of conventional fibers has also been applied to increase the crystallinity and yarn tensile strength. By uniaxial drawing PAN nanofiber yarns in boiling water under tension and annealing, higher molecular orientation and increased degree of crystallinity were observed (Wang et al., 2008a). It was indicated that drawing plus annealing was an effective way to improve the strength of nanofiber yarns, approaching the value equivalent to conventional fibers.

Jalili et al (Jalili et al., 2006) also studied the mechanical properties after carrying out a post treatment in boiling water under tension. They found that fiber bundles became stronger but relatively low elongation after the post-treatment. The average values of E-Modulus and tensile strength before the treatment were 2786 ± 200 MPa, $99 \pm 12\%$ and after the post-treatments were 4575 ± 220 MPa and $178 \pm 15\%$, respectively.

Apart from twisting, immersing nanofiber yarns in some solvents can also improve yarn strength. For example, when electrospun MWNT/PMMA rope was immersed in methanol overnight and then dried for 8 hours at 40 °C (Liu et al., 2007), the yarn strength was much improved, approaching that of the bulk material. This was attributed to the increased

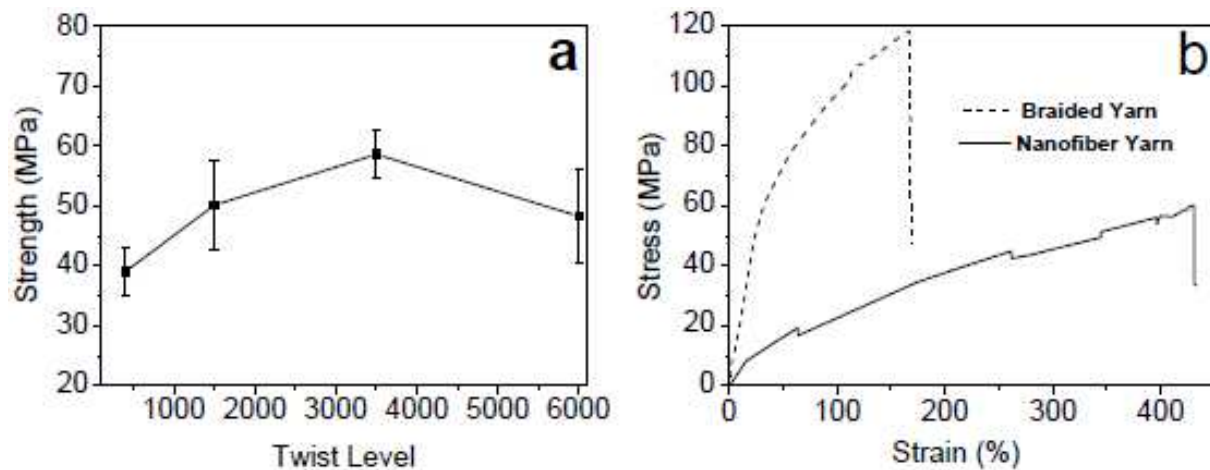


Fig. 4. (a) Influence of twist level on the tensile properties of nanofiber yarns, (b) Typical stress-strain curves of a nanofiber yarn (twist level 3500 tpm), a nanofiber yarn braid (four-ply).

packing density within yarns by reducing the repulsive interactions from the residual surface charge.

Carbon nanotube has been extensively used as a filler material to reinforce polymer nanofibers, as demonstrated and reviewed by many groups. Ko et al (Ko et al., 2003) used CNTs to improve the strength and toughness of nanofiber yarns. A two-fold increase in the modulus was observed in SWNT/PAN yarns. It was explained that polymer matrix was stiffened as a result of interaction with SWNTs. The structural changes of the polymer caused by nanotubes could also be seen from the improved thermal stability. Farouk et al (Farouk et al., 2009) reported that yarn tensile strength increased by about 35% due to MWCNT reinforcement in the PAN polymer with surfactant-aided CNT dispersion. Also the mechanical properties of the well-dispersed sample were improved relative to those of the poorly dispersed samples. Similar effects were also observed with MWNT/PMMA composite ropes (Liu et al., 2007).

7. Potential applications

Through weaving, knitting, or other embroidery processes, nanofiber yarns can be assembled into many new fibrous structures, which may find uses in high performance clothing, filters and composites. Nanofiber yarns have been shown their potential for carbon fiber production, electronic devices, and tissue engineering. Many attempts have been devoted to making high quality PAN nanofiber yarns to produce super-strong carbon nanofibers (Moon and Farris, 2009). By twisting yarns composed of metal oxide nanofibers, which displays semi-conducting behavior, a novel p-n junction can be fabricated (Lotus et al., 2009). The typical rectifying current-voltage characteristics of the yarn have potential for constructing sensors and transistor devices. A plain woven fabric of PCL nanofibers has been shown successful for cell cultures, and used as a woven tissue scaffold (Khil et al., 2005).

Another application for yarns is composite reinforcement, to enhance the fracture toughness and damage tolerance. Yarns composed of nanofibers are also envisioned to have such

potential, as nanofibers possess much greater surface area and stiffness. Besides these, nanofibers with diameters smaller than the wavelength of visible light should reinforce composite without changing the composite color. However, electrospun nanofibers haven't been used much in composite reinforcement so far.

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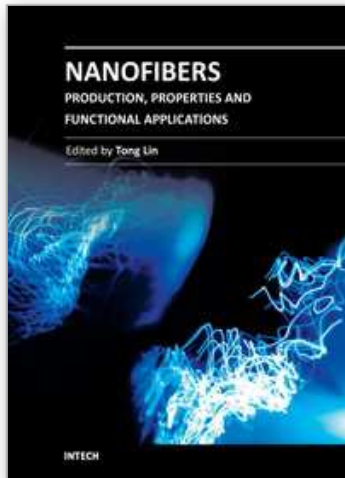
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As an important one-dimensional nanomaterial, nanofibers have extremely high specific surface area because of their small diameters, and nanofiber membranes are highly porous with excellent pore interconnectivity. These unique characteristics plus the functionalities from the materials themselves impart nanofibers with a number of novel properties for advanced applications. This book is a compilation of contributions made by experts who specialize in nanofibers. It provides an up-to-date coverage of in nanofiber preparation, properties and functional applications. I am deeply appreciative of all the authors and have no doubt that their contribution will be a useful resource for anyone associated with the discipline of nanofibers.

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