Developments in Electrospinning of Nanofiber Yarns

Baoming Zhou¹, Xiaodong Jiang¹, Rui Wang¹ *, Xiaoting Yuan¹, Yong Liu¹
School of Textile Science and Engineering, Tiangong University, Tianjin, 300387, China
*Corresponding author and e-mail: Rui Wang, wangrui@tiangong.edu.cn

Abstract. Electrospinning technology has great advantages in the preparation of continuous nanofiber materials. Nanofiber yarn has better performance in fiber orientation and mechanical properties than traditional nanofiber membrane. In this paper, the spinning principle and yarn structure of electrospun nanofiber yarns in recent years are summarized. In terms of yarn structure, nanofiber yarns can be divided into pure nanofiber yarns and micro/nanofiber composite yarns. Based on the spinning principle, pure nanofiber yarns are divided into orientation type and twist type, and micro/nanofiber composite yarns are divided into core-spun yarn, wrapped yarn, and blended yarn. Through the analysis of devices and microstructure of nanofiber yarns, it is found that the micro/nanofiber composite yarns can not only retain the functionality of nanometer fibers but also meet the requirements of weaving and knitting processes, which are expected to be used in practical production as high-performance functional yarns.

1. Introduction
Nanofibers have nano-effect, high specific surface area, and other characteristics, which make them have great application prospects in areas as diverse as filtration and separation [1], catalysis [2], battery separator [3], sensor [4], biomedicine [5] and composite materials [6]. At present, electrospinning is one simple and efficient technique for the preparation of continuous nanofibers. Electrospun products are mainly nonwoven thin films, which restricts their wide application [7-10]. Therefore, a series of electrospinning techniques based on the principle of traditional spinning have been developed for the preparation of nanofiber yarns in order to improve the product strength and broaden the application field [11-13].

In this paper, based on the classification and summary of yarn structure and spinning principle, the research results of electrospun yarns in recent years are analyzed. In terms of yarn structure, nanofiber yarns can be divided into pure nanofiber yarns and micro/nanofiber composite yarns. In terms of yarn forming mechanism, pure nanofiber yarns are divided into orientation type and twist type, and micro/nanofiber composite yarns are divided into core-spun yarn, wrapped yarn and blended yarn.

2. Pure nanofiber yarns
Pure nanofiber yarns are made of electrospun nanofibers through spinning process such as collecting, orienting, twisting, and winding. According to the spinning principle, the yarns that have not been twisted are called oriented nanofiber yarn, and the yarn that have been twisted are called twisted nanofiber yarn. In addition, the spinning methods of oriented nanofiber yarn includes double electrode method, auxiliary electrode self-cluster method and static water bath method. The spinning methods of twisted nanofiber yarn include fluid twist method, rotating disk twist method and rotating winding
device twist method.

2.1. Oriented nanofiber yarn

2.1.1 Conjugate electrode method. Figure 1(a) briefly illustrates the conjugated electrodes device. High voltages of 5 kilovolts were applied to the two needles, respectively. Under the attraction of positive and negative electric charges, nanofibers ejected from the needle stick to the center of the spinneret and formed a long strand, which is then wound onto the winding roller. Pan [15] used Poly (vinyl alcohol) (PVA) and Poly (vinyl pyrrolidone) (PVP) as raw materials to prepare nanofiber yarn by the conjugate electrode method. The nanofibers in the yarn are aligned neatly, and few of them are messy, as shown in Figure 1(b).

Figure 1. (a) Conjugate electrode device. (b) SEM image of PVA/PVP nanofiber yarn.

2.1.2 Self-bundling electrospinning method. In the self-bundling electrospinning method, a grounded needle tip is used as an auxiliary electrode to guide the nanofibers ejected from the spinneret into yarn. Wang [16] used this method to prepare Polyacrylonitrile (PAN) nanofiber yarn successfully. A thin metal needle is placed between the spinneret and the winding roller, which is grounded to change the electric field distribution, then the fibers are bundled under the action of electric field, and finally wound on the winding roller, as shown in Figure 2(a). Most of the fibers in the yarn are arranged in the axial direction of the yarn, as shown in Figure 2(b). In addition, compared with traditional yarns, the nanofiber yarn exhibits lower strength due to no twist and low cohesion between fibers.

Figure 2. (a) Self-bundling electrospinning device. (b) SEM image of PAN nanofiber yarn.

2.1.3 Water bath collecting method. Water bath collecting method is a method in which a grounded coagulation bath is used as a collection device for electrospun nanofibers, and the fiber membrane deposited on the water surface is wound into yarn by a winding roller, as shown in Figure 4(a). Smit [17] successfully prepared PVA nanofiber yarn using this method. The yarn obtained using this method exhibits high degrees of fiber alignment, but there are a few disordered fibers and bent fiber loop, as shown in Figure 3(b). The winding speed of the yarn prepared by this method can reach 3 m/min, which is suitable for batch production in the laboratory. Pan [18] added a tension guide and a
heat setting device, and prepared continuous Polyamide 66 (PA66) nanofiber yarn, and spin without end breakage for 10 hours. On the basis of this device, Liu [19] bundled the nanofibers by tilting the coagulation bath to make water flow down naturally. The yarn has a higher degree of fiber orientation, but the nanofibers in the yarn have certain folding and adhesion.

2.2. Twisted nanofiber yarns

2.2.1. Fluid twisting method. The fluid twisting method is a spinning technology in which a fluid vortex was formed on the basin to drive the nanofibers bundling, orientation, stretching and twisting. Teo [20] invented a fluid twisting device, as shown in Figure 4(a). Water flows out of the outlet hole at the bottom of the basin to form a vortex that promotes the nanofibers to be spun along the direction of the water flow. Figure 4(b) shows the morphology of Poly(vinylidene fluoride-co-hexafluoropropene) (PVDF-co-HFP) nanofiber yarn prepared by this method. The fibers in the small twist yarn are highly arranged and adhered to each other. The yarn structure is mainly related on the properties of the liquid, such as the surface tension, viscosity, and flow rate. In addition, compared with static water bath collecting method, fluid twist method has a faster yarn winding speed with 63 m/min.

2.2.2. Rotating ring twisting method. The rotating ring twisting method was proposed by Korea Institute of Chemical Technology [21], in this method, the collection and twisting of nanofibers is completed by rotating ring. In recent years, many improvements and deformations have been made on the basis of this method. Lin [22] used a rotary ring collector to collect and twist nanofibers into
continuous yarns. Figure 5(a) and (b) show the diagram of rotating ring twisting device. First of all, the two electrospinning systems are charged with positive and negative charges to form a fibrose web on a rotating circular collector, respectively. Then, fibrose web is pulled out from the center of the disk to form a stable fiber cone. Last, the fibers are continuously pulled out from the top of the fiber cone to form a continuous fiber bundle, which is finally collected by the winding roller. The yarn obtained by the method has significant twist characteristics, and its nanofibers are arranged at an angle along the direction of the fiber bundle, as shown in Figure 5(c). Moreover, the yarn has good mechanical properties, such as surface twist angle of 54.4°, tensile strength of 93.6 MPa, and elongation at break of 242.6%. Afifi [23] improved the rotating ring into a hollow trump-shaped disk, and successfully prepared a kind of twist yarn. Wu [24] obtained continuous PAN nanofiber yarn by the rotating ring twisting method. The yarn was used to manufacture traditional fabrics, including braiding, weaving and knitting, providing an important direction for the application.

2.2.3. Twisting and winding integrated method. Twisting and winding integrated method is realized by using a winding device with a rotating twist disk to twist and wind the fiber bundle simultaneously. Figure 6(a) shows the schematic diagram of the device. Two nozzles with positive and negative voltage are used to spray the nanofibers onto the rollers to form a fiber suspension triangle, where the nanofibers are clustered, twisted, and wound into yarn by means of the twisting and winding integrated device. Maleki [25] created Poly (L-Lactide) (PLLA) nanofiber yarn with this device, as shown in Figure 6(b). The yarn surface is smooth, and the twist angle is large, which indicates that the twisting and winding integrated device can successfully twist the fibers into clusters and produce nanofiber yarns with good mechanical properties. On the basis of this method, the distribution of electric field in the electrospinning system is changed by changing the angle between the spinneret and receiving board, thus changing the twist and density of the yarn [26].

3. Electrospun composite yarn of micro/nanofibers
Pure nanofiber yarns have seriously hindered promotion and application due to its weak strength, low production efficiency and high cost. Therefore, the composite yarn of micro/nanofibers is considered as a new research direction to improve yarn yield and strength. According to the different spinning methods, the composite yarns are divided into core-spun yarn, wrapped yarn and blended yarn.

3.1. Electrospun core-spun yarn
Electrospun core-spun yarn is prepared by electrospinning technology with nanofiber yarn as the sheath and micron fiber filament as the core. The sheath yarn has the characteristics of large specific surface area, high porosity and excellent hydrophilicity, which can be used as a functional layer to improve the performance of the yarn significantly. In addition, the excellent mechanical properties of the yarn are maintained due to the high strength of the core yarn. Liu [27] used polycaprolactone (PLC) nanofibers as sheath yarn and polyglycolic acid (PGA) filament as core yarn to obtain core-spun yarn with controllable surface morphology. The schematic diagram of the equipment is shown in Figure 7(a). On two rotating disk with the same speed, the core yarn is transferred from an unwinding roller to a winding roller at a certain speed, and then the PLC nanofibers are sprayed onto the core yarn to form the core-spun yarn. The microscopic appearance is shown in Figure 7(b). The surface of the core-spun yarn is smooth, and the fibers of the sheath yarn are evenly covered on the core yarn.

3.2. Electrospun wrapped yarn
Nazife [28] successfully spun a wrapped yarn through an improved electrospinning device to strengthen the abrasion resistance of yarns. Firstly, the untwisted ring-spun yarn is subjected to conductive treatment, then nanofibers are sprayed onto the surface of the yarn by electrospinning technology. Finally, the yarn is twisted to prepare the wrapped yarn. The microscopic images of the ring-spun yarn and the wrapped yarn are shown in Figure 8(a) and (b), respectively. The nanofibers in the twisted yarn are evenly wrapped on the surface of the ring-spun yarn. Oldrich [29] added a heat treatment device based on the above method to protect the nanofiber layer. Moreover, the wrapped yarn with excellent mechanical properties can be used for weaving and knitting.
3.3. Electrospinning blended yarn
Yang [30] prepared PAN nanofiber/viscose fiber blended yarn by using electrospinning and traditional spinning technology. The spinning process is shown in Figure 9. The nanofibers are sprayed onto the surface of the micro-fiber web by electrospinning technology to form composite web. The composite web is processed into Nano-fiber/micro-fiber blended yarn after drawing, roving and ring spinning processes. Nanofibers are evenly distributed in the yarn, which greatly protects the structure and functionality of the nanofibers. PAN nanofiber/cotton fiber blended yarn is prepared by this method, which has good mechanical properties and meets weaving process requirements [31]. In addition, the problem of strength and wear resistance of nanofibers in the yarn can be solved by this yarn structure, which provides a new direction for the application of nanofibers in the field of clothing.

4. Conclusion
As a new nanofiber material, nanofiber yarns have broad application prospects in the fields of filtration, sensors, tissue engineering, composite materials, and flexible electronic products. Micro/nanofiber composite yarns can be obtained by electrospinning on the basis of traditional spinning, and has mechanical properties similar to traditional yarns, which can not only retain the functionality of nanofibers but also meet the various technological requirements of weaving. Therefore, micro/nano fiber composite yarns have lower cost, higher strength and higher efficiency than pure nanofiber yarns, becoming an important direction for nanofibers in practical applications.

References
[1] Ma W, Guo Z, Zhao J, et al. Polyimide/cellulose acetate core/shell electrospun fibrous membranes for oil-water separation[J]. Separation and Purification Technology, 2017,177:71-85.
[2] Gupta A, Dhakate S R, Pahwa M, et al. Geranyl acetate synthesis catalyzed by Thermomyces lanuginosus lipase immobilized on electrospun polyacrylonitrile nanofiber membrane[J]. Process Biochemistry, 2013, 48(1):124-132.

[3] HAN Ling, LU Chun, Chen Ping, etc. The effects of in situ generated titanium dioxide on the mechanical and electrochemical properties of electrospun polyvinylidene fluoride separator for lithium-ion battery[J]. Acta Polymerica Sinica, 2012(11):1319-1325.

[4] Akbarinejad A, Ghoorchan A, Kamalabadi M, et al. Electrospin soluble conductive polypyrrole nanoparticles for fabrication of highly selective n-butylamine gas sensor[J]. Sensors and Actuators B: Chemical, 2016, 236:99-108.

[5] Wu T, Huang C, Mo XM. A new vascular tissue engineering material: Electrospun small-diameter nanofibrous scaffolds. Zhongguo Gongchén Yanyu. 2013;17(29): 5387-5394.

[6] Chen Q, Wu W, Zhao Y, et al. Nano-epoxy resins containing electrospun carbon nanofibers and the resulting hybrid multi-scale composites[J]. Composites Part B: Engineering, 2014, 58:43-53.

[7] Mohamed Basel Bazbouz G K S. Nove. Mechanism for spinning continuous twisted composite nanofiber yarns[J]. European Polymer Journal, 2008(44):1-12.

[8] Usman Ali Y Z X W. Direct electrospinning of highly twisted, continuous nanofiber yarns[J]. Journal of The Textile Institute, 2012, 1(103):80-88.

[9] Dabirian F, Ravandi S A H, Sanatgar R H, et al. Manufacturing of twisted continuous PAN nanofiber yarn by electrospinning process[J]. Fibers and Polymers, 2011, 12(5):610-615.

[10] He J, Qi K, Zhou Y, et al. Fabrication of continuous nanofiber yarn using novel multi-nozzle bubble electrospinning[J]. Polymer International, 2014, 63(7):1288-1294.

[11] Bazbouz M B, Stylios G K. A new mechanism for the electrospinning of nanoyarns[J]. Journal of Applied Polymer Science, 2012, 124(1):195-201.

[12] Dabirian F, Ravandi S A H, Hinestroza J P, et al. Conformal coating of yarns and wires with electrospun nanofibers[J]. Polymer Engineering & Science, 2012, 52(8):1724-1732.

[13] He J, Zhou Y, Wang L, et al. Fabrication of continuous nanofiber core-spun yarn by a novel electrospinning method[J]. Fibers and Polymers, 2014, 15(10):2061-2065.

[14] Shaohua Wu; Yue Zhang; Penghong Liu; Xiaohong Qin. Polyacrylonitrile nanofiber yarns and fabrics produced using a novel electrospinning method combined with traditional textile techniques[J]. Textile Research Journal. 2016, Vol. 86(No. 16): 1716-1727.

[15] Pan H, Li L, Hu L, et al. Continuous aligned polymer fibers produced by a modified electrospinning method[J]. Polymer, 2006, 47(14):4901-4904.

[16] Wang X, Zhang K, Zhu M, et al. Continuous polymer nanofiber yarns prepared by self-bundling electrospinning method[J]. Polymer, 2008, 49(11):2755-2761.

[17] Smit E, Böttner U, Sanderson R D. Continuous yarns from electrospun fibers[J]. Polymer, 2005, 46(8):2419-2423.

[18] Pan Z, Liu H, Wan Q. Morphology and Mechanical Property of Electrospun PA 6/66 Copolymer Filament Constructed of Nanofibers[J]. Journal of Fiber Bioengineering and Informatics, 2008, 1(1):47-54.

[19] Hong-bo, Liu; Qian-hua, Wan; Zhi-juan, Pan. Electrospinning of polyamide 6/66 copolymer nano-scale fiber yarns and their structure and mechanical properties[J]. RESEARCHES AND PROGRESSES OF MODERN TECHNOLOGY ON SILK, TEXTILE AND MECHANICALS I. 2007: 352-357.

[20] Teo W, Gopal R, Ramaseshan R, et al. A dynamic liquid support system for continuous electrospin yarn fabrication[J]. Polymer, 2007, 48(12):3400-3405.

[21] LEE J R, JEE S Y, KIM H J, et al. Filament bundle type nanofiber and manufacturing method thereof: WO, 123995[European Patent] 2005, 12-29.

[22] Shuaat M N, Lin T. Direct electrospinning of nanofibre yarns using a rotating ring.
collector[J]. The Journal of the Textile Institute, 2016, 107(6): 791-799.

[23] Afifi A M, Nakano S, Yamane H, et al. Electrospinning of Continuous Aligning Yarns with a ‘Funnel’ Target[J]. Macromolecular Materials and Engineering, 2010, 295(7): 660-665.

[24] Shaohua Wu; Yue Zhang; Penghong Liu; Xiaohong Qin. Polyacrylonitrile nanofiber yarns and fabrics produced using a novel electrospinning method combined with traditional textile techniques[J]. Textile Research Journal, 2016, Vol.86(No.16): 1716-1727.

[25] Maleki H, Gharehaghaji A A, Moroni L, et al. Influence of the solvent type on the morphology and mechanical properties of electrospun PLLA yarns[J]. Biofabrication, 2013, 5(3): 035014.

[26] Dabirian F, Hosseini Y, Ravandi S A H. Manipulation of the electric field of electrospinning system to produce polyacrylonitrile nanofiber yarn[J]. Journal of the Textile Institute, 2007, 98(3): 237-241.

[27] Liu C, Li B, Mao X, et al. Controllable Aligned Nanofiber Hybrid Yarns with Enhanced Bioproperties for Tissue Engineering[J]. Macromolecular Materials and Engineering, 2019, 304(7): 1900089.

[28] Korkmaz Memiş N, Kayabaşı G, Yılmaz D. Development of a novel hybrid yarn production process for functional textile products[J]. Journal of Industrial Textiles, 2019, 48(9): 1462-1488.

[29] Jirsak O, Sanetrnik F, Chaloupek J. Nanofiber-covered yarns[J]. Chemical Fibers International, 2011, 61(2): 38-40.

[30] Yang Y, Zhao Y, Quan Z, et al. An efficient hybrid strategy for composite yarns of micro-/nano-fibers[J]. Materials & Design, 2019, 184: 108196.

[31] Guojun Jiang; Junrui Zhang; Dongxiao Ji; Xiaohong Qin; Yeqian Ge; Sheng Xie. A novel approach for fabricating antibacterial nanofiber/cotton hybrid yarns[J]. Fibers and Polymers, 2017, Vol.18(No.5): 987-992.