Available online at www.sciencedirect.com
SCIENCE DIRECT
Polymer 46 (2005) 2419–2423
polymer
www.elsevier.com/locate/polymer

Polymer Communication

Continuous yarns from electrospun fibers

Eugene Smit[a], Ulrich Bűttner[b], Ronald D. Sanderson[a,*]

[a]Department of Chemistry and Polymer Science, Stellenbosch University, Private Bag X1, Matieland, 7602, South Africa
[b]Department of Electrical Engineering, Stellenbosch University, Private Bag X1, Matieland, 7602, South Africa

Received 1 September 2004; received in revised form 1 February 2005; accepted 2 February 2005

Abstract

A technique for making continuous uniaxial fiber bundle yarns from electrospun fibers is described. The technique consists of spinning onto a water reservoir collector and drawing the resulting non-woven web of fibers across the water before collecting the resulting yarn. Yarns from electrospun fibers of poly(vinyl acetate), poly(vinylidene difluoride) and polyacrylonitrile are used to illustrate the process of yarn formation and fiber alignment within the yarn. A theoretical production rate of 180 m of yarn per hour for a single needle electrospinning setup makes the process suitable for lab-scale production of electrospun yarns.

Keywords: Electrospinning; Nanofiber; Yarn

1. Introduction

Electrospinning is a simple technique for producing micro- and nanofibers of organic polymers and inorganic oxide materials. It has potential application in filters, tissue engineering scaffolds, wound dressings, drug delivery materials, biomimetic materials, composite reinforcement and many others. A comprehensive review by Huang et al. [1] shows a phenomenal increase in the number of publications on electrospinning in recent years. Since electrospun fibers find application in both nanotechnology and biotechnology, this certainly can be seen as a driving force behind the recent renewed interest in a technique that has been known since the 1930's [2].

The principle behind electrospinning is relatively simple: A solution of a polymer flows out of the tip of a capillary, where a droplet forms under the influence of the surface tension of the solution. A sufficiently large electric charge (+5–25 kV DC) is applied to the solution, which causes repulsive electrostatic forces between polymer and solvent molecules to overcome the surface tension, and a jet of polymer shoots away from the capillary towards a grounded collector. In the space between the capillary tip and the collector, the jet becomes unstable and a rapid whipping of the jet follows. This leads to evaporation of the solvent, leaving a polymer fiber, which undergoes stretching and thinning as a result of the whipping, and finally collects on the grounded collector as a randomly oriented web of micro- or nanofibers.

The random orientation of the electrospun fibers in the typically obtained non-woven webs is acceptable in some applications such as filters, wound dressings and tissue scaffolds. However, nanofibers need to be obtained as continuous single nanofibers or uniaxial fiber bundles to make their commercialisation in the fiber and textile industry viable [1].

Various approaches have been taken to obtain aligned electrospun fibers. These include: spinning onto a rotating drum [3], spinning onto the sharp edge of a thin rotating wheel [4], introducing an auxiliary electrode or electrical field [5,6], rapidly oscillating a grounded frame within the jet [7], and using a metal frame as the collector [8]. With these approaches, various degrees of alignment of the electrospun fibers can be achieved but all invariably suffer from the drawback that only relatively short tows of aligned fibers can be obtained.

In a recent paper, Fennessey and Farris [9] linked and twisted unidirectional tows of electrospun nanofibers into yarns using an electric twister. This allowed the testing of

* Corresponding author. Tel.: +27 21 808 3172; fax: +27 21 808 4967.
E-mail address: rds@sun.ac.za (R.D. Sanderson).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.02.002

the effects of twist on the tensile strength and other properties of the yarn. Ko et al. [10] manufactured continuous yarns of composites of polylactic acid and polyacrylonitrile with single wall carbon nanotubes but no detailed description or discussion of the process or the resulting yarns were given. In a conference abstract, Kataphinan et al. [11] briefly refer to collecting nanofibers off the surface of non-wetting liquids and a figure is included of a PAN nanofiber yarn collected in such a way. In a recent paper, Kim et al. [12] reported on the electrospinning of poly(lactide-*co*-glycolide) onto a liquid reservoir collector to change the morphology of membranes and to simultaneously crystallize the polymer by solvent during electrospinning.

In this paper continuous uniaxial fiber bundle yarns are obtained by electrospinning onto a liquid reservoir collector. The method is used to obtain yarns of poly(vinylidene difluoride) (PVDF), poly(vinyl acetate) (PVAc), and polyacrylonitrile (PAN).

2. Experimental

2.1. Materials

The polymers used were poly(vinylidene difluoride) $M_v = 2500$ amu (Elf Atochem), poly(vinyl acetate) $M_w = 500{,}000$ amu (Aldrich) and polyacrylonitrile $M_w = 210{,}000$ amu (Acordis Kelheim GmbH, Dolanit ®). The solvents used were *N*,*N*-dimethylacetamide (DMAc) (Aldrich) for the PVDF and *N*,*N*-dimethylformamide (DMF) (Saarchem South Africa) for the PVAc and PAN. All materials were used as received. The electrospinning solutions were obtained by dissolving the required amounts of polymer in the solvents at 40–60 °C.

2.2. Yarn spinning

2.2.1. Spinning setup

The polymer solution was placed in a glass pipette and gravity-fed through the tip. A copper wire electrode was inserted into the solution. The pipette used was a 150 mm Volac disposable glass Pasteur pipette (Poulten & Graf Ltd, UK). A Gilson Yellow 200 µl polypropylene pipette tip (Greiner Bio-one) with a 10° tapering end was placed on the glass pipette tip to reduce the capillary opening size to approximately 0.5 mm. A solution flow rate of approximately 1 ml/h was observed.

The grounded collector electrode water bath consisted of a round glass petri dish (150 mm diameter × 15 mm depth). A round metal plate (140 mm diameter × 0.42 mm thick) was placed inside the bath and covered with distilled water to a depth of 5 mm. A thin copper wire was trailed over the edge of the bath to connect the metal plate to the ground electrode.

The high voltage power supply used was a model ES30-0.1P from Gamma High Voltage Research, Ormond Beach, FL. A diagrammatic representation of the electrospinning setup is given in Fig. 1. The electrospinning conditions for the yarn samples discussed here are given in Table 1.

2.2.2. Yarn formation

A motorised take-up roller was set to run at a rotary speed equivalent to a linear take-up speed of 0.05 ms^{-1}. The initial non-woven web of fibers that formed on the surface of the water was then drawn, with the aid of a glass rod, across the surface of the water and scooped off into air. The resulting yarn was drawn slowly by hand to the revolving take-up roller and it was then attached by wrapping the yarn once around the roller.

2.3. Characterization

The morphology of the gold sputter-coated yarns was studied with a scanning electron microscope (LEO 1430VP). The cross-section image of the yarn was obtained by embedding the yarn in a silicone resin and cutting cross-sections with a razorblade by hand.

3. Results and discussion

Figs. 2–5 show that all the yarns obtained using this method exhibit very high degrees of fiber alignment. The average diameters of the fibers in the obtained yarns are given in Table 2. Bent fiber loops were observed in all the yarns, as indicated with arrows in Fig. 2(b).

When electrospinning onto a solid collector, fiber diameters are generally observed to increase with an increase in solution concentration [13]. Bead-like structures are sometimes observed on electrospun fibers and these have been shown to decrease in size or disappear with an increase in solution concentration [14]. Both these trends are also observed when spinning onto a water bath collector. When a yarn from a 20 wt% solution of PVDF (Fig. 3) is compared to a yarn from a 15 wt% solution (Fig. 4), it is observed that the higher solution concentration results in

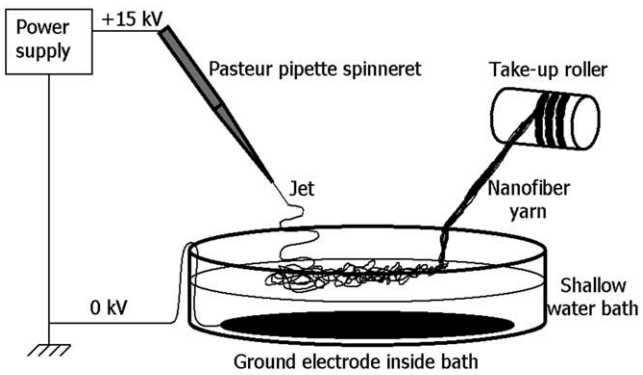

Fig. 1. Yarn-spinning setup with water bath grounded collector electrode.

Table 1
Electrospinning parameters

Polymer	Concentration (wt%)	Spinning voltage (kV)	Tip-to-collector distance (cm)
PVDF	15 and 20	20	20
PVAc	18	15	20
PAN	5	15	20

fibers with an average diameter of 1 μm and a few beads, while the lower concentration leads to an average fiber diameter of 294 nm and extreme bead formation.

In Fig. 4(b), arrows indicate large beads on the electrospun fibers. These beads exhibit an indented surface morphology, which is most likely caused by skin formation on contact with the non-solvent water bath, followed by collapse of the skin as the solvent diffuses out of the polymer. This phenomenon is commonly observed with polymers and also resembles observations by Kim et al. [12], where poly(lactide-*co*-glycolide) fibers electrospun onto a liquid reservoir collector showed an indented surface morphology.

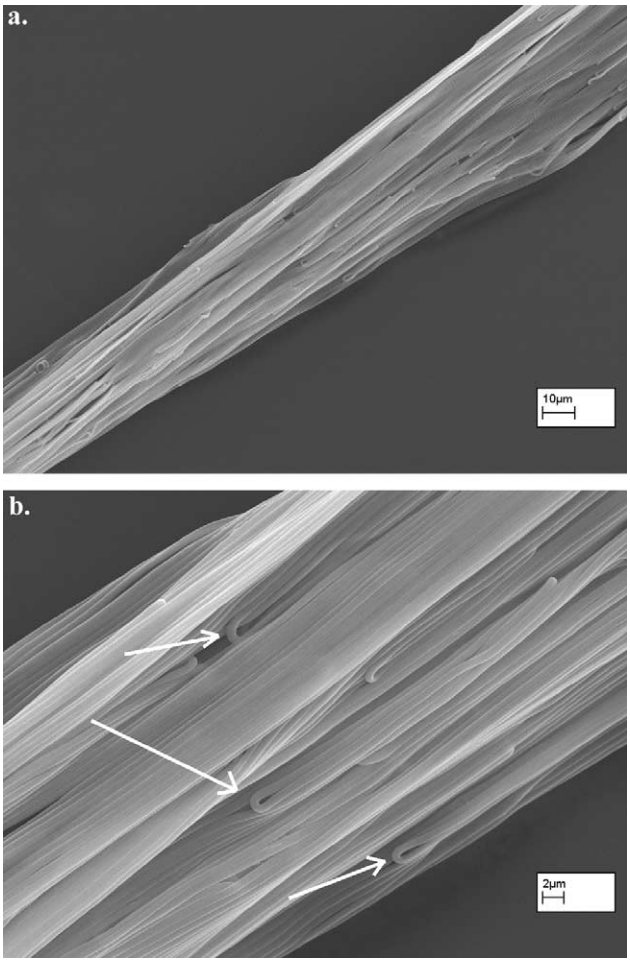

Fig. 2. (a) Electrospun fiber yarn of PVAc showing high degree of fiber alignment. (b) Higher magnification image of the PVAc yarn with bent fiber loops indicated by arrows.

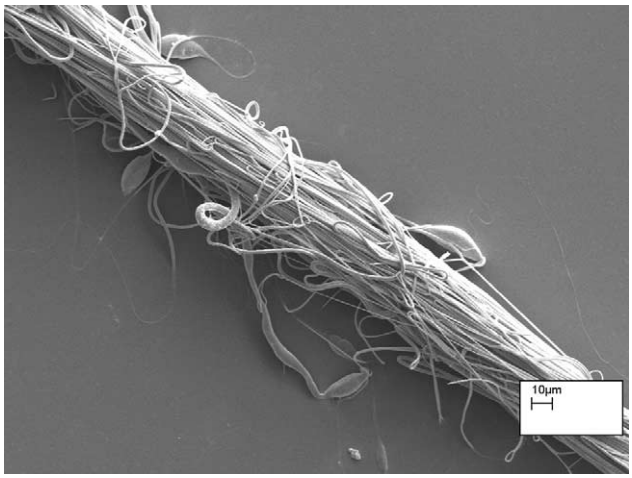

Fig. 3. Electrospun fiber yarn from 20 wt% PVDF solution exhibiting a small number of beads and high fiber diameter.

Fig. 5 shows the yarn obtained from a 5 wt% PAN solution. Fibers dangling from the bulk surface of the yarn, such as can be seen in Fig. 5(a), are observed for all three polymers used here. These dangling fibers give the yarn a textured yarn appearance.

The process of yarn formation is illustrated in Fig. 6. It can be described in three phases. The first two phases occur in two dimensions and the third phase occurs in three dimensions. In the first phase, a flat web of fibers forms on the surface of the water bath with randomly looped fibers. In the second phase, when the fibers are drawn over or through the water, the web is elongated and alignment of the fibers takes place. The third phase consists of drawing the web off the water into air. The surface tension of the remaining water on the web pulls the fibers together into a 3-dimensional round yarn structure.

Initial investigations on the effect of conductivity and surface tension of the water showed that addition of NaCl or dishwashing detergent to the distilled water bath leads to sinking of the fibers, which in turn leads to higher drag on the drawn yarn. The increased drag makes it difficult to obtain continuous yarns and further studies on the effects of fluid conductivity and surface tension need to be done.

SEM images of the yarn formed at the beginning of the process show that the fibers are initially bundled in a randomly oriented mess but that the fiber alignment starts

Table 2
Average fiber diameters in the yarns of the polymers studied

Polymer	Concentration (wt%)	Average fiber diameter (nm)
PVAc	18	646
PVDF	20	1000
PVDF	15	294
PAN	5	285

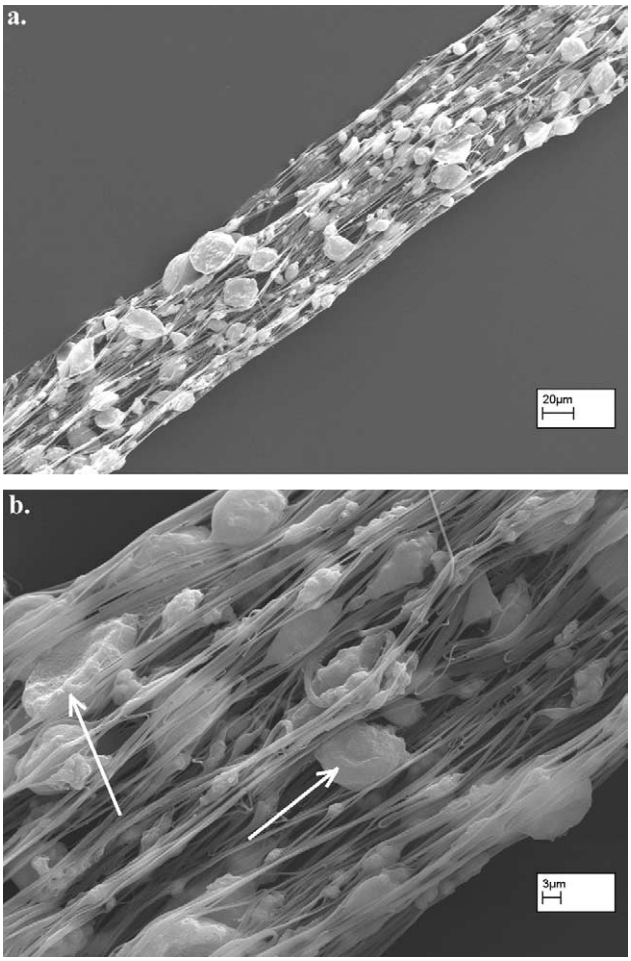

Fig. 4. (a) Electrospun fiber yarn from 15 wt% PVDF solution exhibiting extreme bead formation and low fiber diameter. (b) Higher magnification image of the yarn with arrows showing collapsed bead structures.

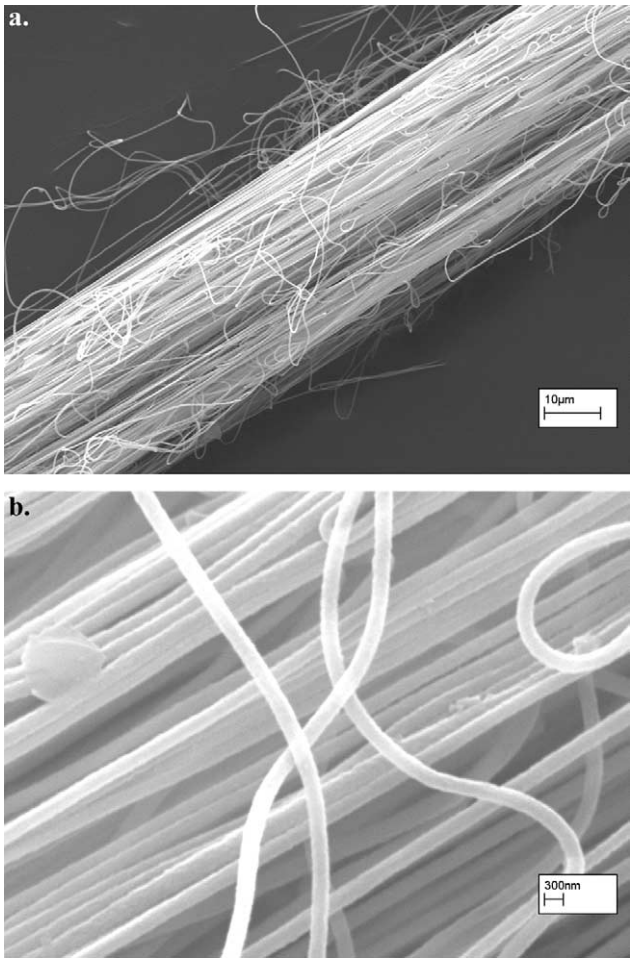

Fig. 5. (a) Electrospun fiber yarn of PAN showing dangling fibers. (b) Higher magnification image of the PAN yarn.

within the first 5 cm or even sooner of the drawn yarn (images not included). At the end of the process, i.e. when the power supply is switched off, the yarn appears similar to a normal break in the yarn, with broken aligned fibers.

During the electrospinning process, the polymer flows through the spinneret at a flow rate of approximately 1 ml/h. Taking the PAN solution used here as an example, a 5 wt% solution flowing at 1 ml/h implies 0.05 g of polymer spun per hour. With the density of PAN equal to 1.17 g/ml, a total polymer volume of 0.043 ml is obtained. When this volume of polymer is electrospun into fibers with a diameter of 285 nm, the total length of fibers spun per hour is 669 km. This implies that a total of 186 m of nanofiber is spun per second onto the collector bath surface. If the majority of these fibers are deposited onto a circular area with a diameter of 5 cm, as has been frequently observed in our laboratory when spinning onto a water bath, the web of fibers formed will consist of loops that overlap hundreds of times per second. When the resulting web is drawn away from the target area at a rate of 0.05 ms^{-1}, a continuous web of fibers that roughly contains 186 m of electrospun fiber per 5 cm length is obtained. In a single-needle electrospinning setup this implies that the average yarn should contain approximately 3720 fibers per cross-section and that approximately 180 m of yarn can be spun per hour. Fig. 7(a) and (b) show a cross-section of the PAN yarn embedded in a silicone resin. Visual comparison and rough calculations with image-processing software show that 3720 fibers per cross-section is a reasonable estimate for this example.

The allowable drawing rate of the yarn was observed to depend on parameters such as the diameters of the

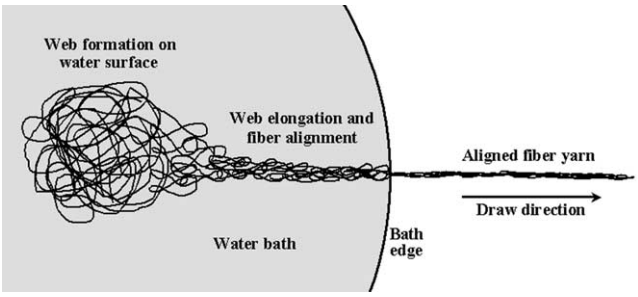

Fig. 6. Top-view of the yarn formation process.

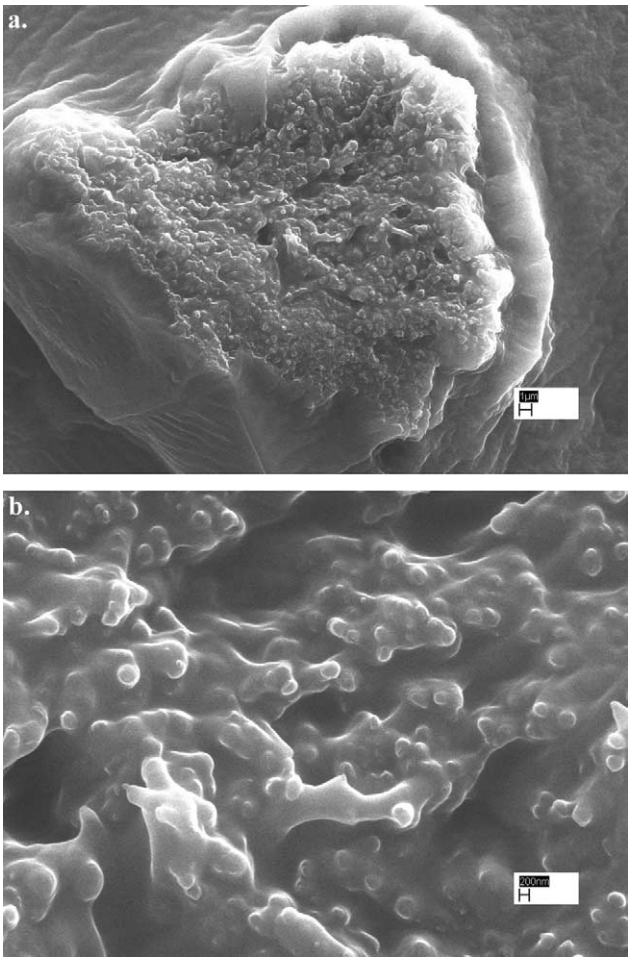

Fig. 7. (a) Cross-section of PAN yarn in a silicone resin. (b) Higher magnification image of the PAN yarn cross-section.

electrospun fibers, surface tension of the water in the collector bath, type of polymer and various other parameters, which need to be further investigated.

4. Conclusion

In this work we describe a method for making continuous yarns from electrospun fibers of poly(vinyl acetate), poly(vinylidene difluoride) and polyacrylonitrile. The fibers in the obtained yarns are aligned and exhibit typical electrospinning fiber characteristics, such as concentration dependence on fiber diameter and bead formation. The technique is easy to use and the yarn production rate makes it most useful for the lab-scale production of electrospun nanofiber yarns.

References

[1] Huang Z-M, Zhang Y-Z, Kotaki M, Ramakrishna S. Compos Sci Technol 2003;63:2223–53.
[2] Formhals A. US Patent 1,975,504: 1934.
[3] Doshi J, Reneker DH. J Electrostat 1995;35:151–60.
[4] Zussmann E, Theron A, Yarin AL. Appl Phys Lett 2003;82(6):973–5.
[5] Bournat A. US Patent 4,689,186: 1987.
[6] Deitzel JM, Kleinmeyer JD, Hirvonen JK, Beck Tan NC. Polymer 2001;42:8163–70.
[7] Fong H, Weidong L, Wang C-S, Vaia RA. Polymer 2002;43: 775–80.
[8] Dersch, Liu T, Schaper AK, Greiner A, Wendorff JH. J Polym Sci, Part A: Polym Chem 2003;41:545–53.
[9] Fennessey SF, Farris RJ. Polymer 2004;45:4217–25.
[10] Ko F, Gogotsi Y, Ali A, Naguib N, Ye H, Yang G, Li C, Willis P. Adv Mater 2003;15(4):1161–5.
[11] Kataphinan W, Dabney S, Smith D, Reneker D. Fabrication of electrospun and encapsulation into polymer nanofibers. Book of Abstracts. The Fiber Society, Spring Meeting, May 23–25, 2001.
[12] Kim H-S, Kim K-Y, Jin H-J, Chin IJ. Polym Preprints 2004;45: 843–4.
[13] Deitzel JM, Kleinmeyer J, Harris D, Tan NCB. Polymer 2001;42: 261–72.
[14] Fong H, Chun I, Reneker DH. Polymer 1999;40:4585–92.