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Polymer 47 (2006) 4901-4904

www.elsevier.com/locate/polymer

polymer

Polymer Communication

Continuous aligned polymer fibers produced by a modified electrospinning method

Huan Pan, Luming Li *, Long Hu, Xiaojie Cui

School of Aerospace, Tsinghua University, Beijing 100084, People's Republic of China

Received 8 November 2005; received in revised form 29 April 2006; accepted 7 May 2006 Available online 26 May 2006

Abstract

A novel and simple technique of manufacturing uniaxially aligned electrospun fibers with diameter of sub-micrometers is described. Compared with typical electrospinning setup, two oppositely placed metallic needles are used, and they are connected to positive and negative voltages, respectively. Fibers coming out of the two needles combine in a yarn, which is wound by a cylinder collector rotating at a high speed. Fibers manufactured by this method are continuous, well-aligned, and can be deposited over a large area. Poly(vinyl alcohol) (PVA) and poly(vinyl pyrrolidone) (PVP) are used to manufacture aligned fibers. An analysis of the possible mechanism of the fibers alignment is given. The influences of the concentration of the solution and the take-up velocity on the alignment of fibers were investigated.

Keywords: Electrospinning; Polymer; Nanofibers

1. Introduction

Recently, electrospinning has attracted a lot of interest as a technique that is very simple and inexpensive to manufacture sub-micron fibers and nanofibers [1]. It provides a potential way to fabricate infinite, continuous nanofibers. A variety of polymers have been electrospun as uniform fibers, and continuous ceramic nanofibers and fibers with a core/shell or hollow structure have also been manufactured by modified electrospinning setups [2]. The as-spun fibers have already been employed for composites, protective clothing, filtration, catalysis, electronics, implants, tissue engineering, drug delivery, agriculture and many other areas [3].

A typical electrospinning setup usually includes a metallic capillary, which is connected to a high voltage, and a collector grounded or charged to a negative voltage. When the electric field exceeds a critical value, the electrostatic force will overcome the surface tension of the polymer solution (or melt), causing a thin jet ejection from the needle tip. As this jet travels through the air, the solvent evaporates leaving behind a polymer fiber deposited on the collector. Due to initial instability of the jet, fibers are often collected as randomly oriented structures in the form of nonwoven mats, which are acceptable only for some applications such as filters, wound dressings and tissue scaffolds. Meanwhile, obtaining continuous aligned nanofibers and high-volume production is very important for many areas such as fiber reinforcement and device manufacture.

Several techniques have been developed to align electrospun nanofibers and some breakthroughs have been obtained. The results are promising, but these methods need to be further improved for practical applications. In the technique of using a rotating drum as the collector [4,5], only partial fiber alignments have been achieved. Some newest techniques can produce well-aligned fibers, but only of limited length [6,7], area [8,9], and thickness [10,11].

In this paper, a simple and versatile technique is described to manufacture aligned polymer nanofibers with infinite length and over large collector area. Unlike the conventional technique, two needles with opposite voltages spray simultaneously. The spun fibers with opposite charges will attract each other, stick together and form a yarn. Then the yarn, which is neutral as a whole can be easily collected. It is an advantage compared with the conventional technique in which an electrode used as the collector is grounded or connected to a negative voltage.

^{*} Corresponding author. Address: School of Aerospace, Tsinghua University, Room 803, 8th floor, Beijing 100084, People's Republic of China. Tel./fax: +86 10 62 78 5716.

E-mail address: lilm@tsinghua.edu.cn (L. Li).

^{0032-3861/}\$ - see front matter © 2006 Elsevier Ltd. All rights reserved. doi:10.1016/j.polymer.2006.05.012

Table 1

Electrospinning nonomete

2. Experimental

2.1. Materials

Poly(vinyl alcohol) (PVA, degree of polymerization is 1700, 88% hydrolyzed) and poly(vinyl pyrrolidone) (PVP, $M_w = 1,300,000$) chosen for the experiment were obtained form Beijing Organic Chemical Plant, China and used without further purification. PVA and PVP solution with different concentrations were prepared with distilled water and ethanol as the solvent, respectively.

2.2. Electrospinning setup

The schematic setup for electrospinning is shown in Fig. 1(a). Two 9-gauge (0.9 mm OD), flat-tipped, stainless steel needles were installed in opposite direction at a distance of about 14 cm. Polymer solutions were pumped to needles by a dual syringe infusion pump. High voltages of several kilovolts were applied to the two needles, respectively. Three collector designs were tested: a teflon tube of 8 mm in diameter; an aluminum shaft of 40 mm; a plastic cylinder of 125 mm in diameter. The vertical distance between the needles and collector was several centimeters. The collector rotated at a very high speed from hundreds to thousands rpm. Some parameters of electrospinning are given in Table 1.

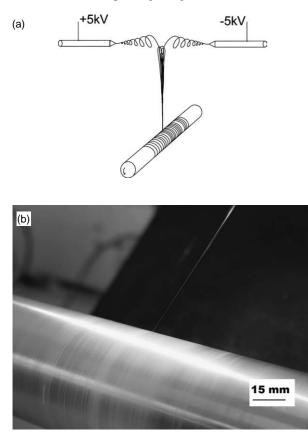


Fig. 1. (a) Schematic electrospinning setup for collection continuous aligned fibers. (b) A yarn of fibers is formed between the needles and a rotating aluminum shaft.

Electrospinning parameters				
Polymer	Concentration (wt%)	Spinning voltage (kV)	Flow rate (µl/min)	Maximum take-up velocity (m/s)
PVA	10	±3.3k	5	3
PVA	13	$\pm 4.5k$	5	4.3
PVP	6	$\pm 3.8k$	16	1.4
PVP	8	$\pm 3.8k$	14	2.8
PVP	10	$\pm 4k$	14	6.4
PVP	12	$\pm 4k$	14	14.9

When voltages were applied to the needles fed with polymer solution, jets were ejected. Then the jets met, a cluster of fibers formed. A yarn of fibers formed between the two needles was towed manually to the collector, which was rotating at a high speed. Fig. 1(b) shows the yarn obtained when using aluminum shaft as the collector. The surface velocity of the shaft is about 0.9 m/s.

2.3. Microscopy

Samples covered with nanofibers were platinum-coated with a JEOL JFC-1200 Coater, and photographed using a scanning electron microscope (JSM-6700F) using an accelerating voltage of 10 kV.

3. Results and discussion

Fig. 2 shows aligned fibers made out of 10 wt% PVA solution. In Fig. 2(a) and (b), the surface velocities of the collector are 1.3 and 2.3 m/s. It demonstrates that with the increasing rotation speed; the degree of fiber alignment becomes better. However, when the rotation speed is too high, the fibers break. The maximum take-up velocity for 10 wt% PVA solution is about 3 m/s. It is proven that the concentration of the solution largely influences the maximum take-up velocity. For 13 wt% PVA solution, the take-up velocity can increase to 4.3 m/s, and very good aligned fibers are collected, as shown in Fig. 3. The average diameter of the fibers is about 346 nm. Using PVP ethanol solution for electrospinning, the results are similar. For 12 wt% PVP solution, continuous fibers can be collected at a highest take-up velocity of 14.9 m/s, and as show in Fig. 4, crooked fibers can hardly be found. The average diameter of the fibers is about 670 nm. Table 1 gives the maximum take-up velocity for different PVA and PVP solution concentrations. The maximum take-up velocity also depends on other parameters such as the type of polymer and solvent, the molecular weight of the polymer, the diameters of the electrospun fibers, and so on, which need to be further investigated. In addition, all the experiments were done in atmosphere, and with the increase of the take-up velocity, the airflow caused by the rotation of the collector made it difficult to tow the fibers yarn onto the collector. It is a limitation for the increase in the take-up velocity, and further work will be done in vacuum environment.

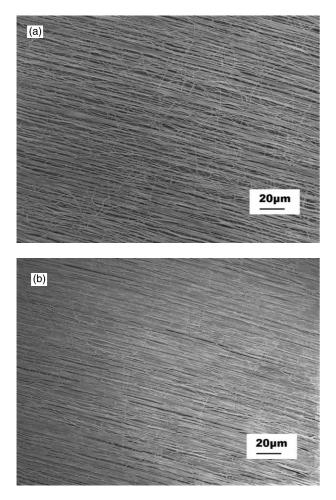


Fig. 2. Well-aligned PVA fibers collected on a Teflon tube with different surface velocity: (a) about 1.3 m/s, (b) 2.3 m/s.

The result suggests a possible mechanism for the alignment of the fibers. Polymer fibers fabricated by electrospinning are electrically charged. Fibers produced from the needle, which is applied with positive voltage are charged positively and vice versa. When a positively charged fiber comes into contact with negatively charged one, they will stick to each other. Because

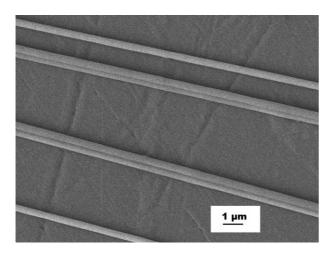


Fig. 3. Well-aligned PVA (13 wt%) fibers collected at the surface velocity of 4.3 m/s.

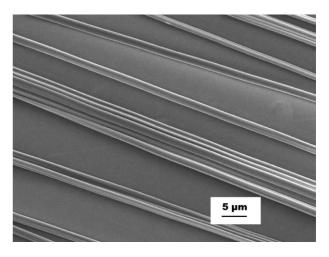


Fig. 4. Well-aligned PVP (12 wt%) fibers collected at the surface velocity of 14.9 m/s.

the fibers are insulated, their charges will not be totally neutralized [12]. Then a third charged fiber joins the two fibers, it sticks to the oppositely charged fiber. A yarn of fibers forms in a similar way at the center of the two needles after a short time. This yarn of fibers is neutral as a whole and it will not be attracted by either needle. Fibers in the original yarn are curly. After towing the yarn of fibers manually to the rotating collector, the yarn is elongated by the mechanical force and alignment fibers begin to form. With the increase of the rotation speed, the degree of the alignment of fibers becomes better and the number of fibers in a yarn reduces. Finally, when the take-up velocity is high enough, there are only two fibers deposited on the collector, and the alignment of fibers should be perfect.

Fig. 5 shows two parts of a PVA (10 wt%) yarn obtained during electrospinning with a collection velocity of about 2.3 m/s. Fig. 5(a) shows some curly fibers in the yarn, this is a reason that fibers did not align well with a low take-up velocity. In Fig. 5(b), the fiber yarn is made of several aligned fibers, which were tightly clustered together, and there is also a fiber not linked to the fiber yarn tightly. It is also found that a few fibers usually do not stick tightly on the yarn. Thus, when the yarn lands on the collector, the separate fibers will align freely, or be attracted and link to other fibers charged oppositely. This is another reason why there are some free-aligned fibers between the aligned fibers. The results agree with the analysis of the process of the fiber alignment. The most practical way to improve the alignment of the fibers is to increase the take-up velocity. It is proven that the take-up velocity and the maximum take-up velocity are the key parameters for this technology.

In the conventional technique of collecting fibers onto a rotating drum, which is an electrode and is grounded or connected to a negative voltage, the degree of the orientation for nanofibers is far from perfect mainly because that the chaotic motion of polymer jets are not likely to be consistent and are less controllable [3]. When fibers and their charges accumulate on the conducting collector, the electrostatic field may be changed, thus this will affect the fiber alignment. This

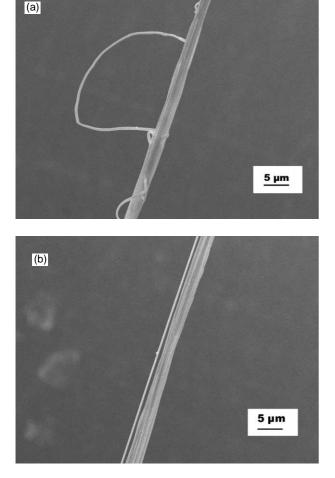


Fig. 5. Two part of a PVA (12 wt%) yarn collected at the surface velocity of 2.3 m/s.

is a reason that some techniques cannot manufacture wellaligned fibers for a long time. In our method, two needles are used and the collector is separate from the electrical equipments. Fibers under a chaotic motion are aggregated by the electrical forces between fibers to form a yarn, which is neutral as a whole, so they are stable, controllable, and can be wound continuously. Because fibers can be wound on collector taking no account of its size and material, and the alignment of fibers does not change with time, it is possible to fabricate wellaligned fibers in large amounts.

Although the experience described in this paper demonstrates good potential for manufacture of continuous and wellaligned nanofibers, further investigation is required. Morphology and internal structure of the fibers collected at different condition need to be investigated systematically. This method also needs to be used for more materials and different settings.

4. Conclusion

In this work a novel technique based on electrospinning for generating uniaxially aligned fibers with diameters of submicrometers is demonstrated. Continuous, well-aligned PVA and PVP fibers have been obtained by this technique. It has been proven that the fiber alignment becomes better at increasing take-up velocity; and fibers of more concentrated solutions can be collected continuously at higher velocity. This method can be developed and used for a variety of applications.

References

- [1] Li D, Xia YN. Adv Mater 2004;16:1151-70.
- [2] Dzenis Y. Science 2004;304:1917-9.
- [3] Huang ZM, Zhang YZ, Kotaki M, Ramakrishna S. Compos Sci Technol 2003;63:2223–53.
- [4] Matthews JA, Wnek GE, Simpson DG, Bowlin GL. Biomacromolecules 2002;3:232–8.
- [5] Fennessey SF, Farris RJ. Polymer 2004;45:4217-25.
- [6] Li D, Wang YL, Xia YN. Adv Mater 2004;16:361-6.
- [7] Dalton PD, Klee D, Moller M. Polymer 2005;46:611-4.
- [8] Theron A, Zussman E, Yarin AL. Nanotechnology 2001;12:384-90.
- [9] Zussman E, Theron A, Yarin AL. Appl Phys Lett 2003;82:973-5.
- [10] Sundaray B, Subramanian V, Natarajan TS, Xiang RZ, Chang CC, Fann WS. Appl Phys Lett 2004;84:1222–4.
- [11] Katta P, Alessandro M, Ramsier RD, Chase GG. Nano Lett 2004;4: 2215–8.
- [12] Kessick R, Tepper G. Appl Phys Lett 2004;84:4807-9.