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RESEARCH ARTICLE

Aligned polymer fibers produced via an additive electric field

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Electrospinning is known to be a highly versatile method to produce nanofibers, and several techniques have been developed to align nanofibers. In this paper, poly(vinyl alcohol) (PVA), poly(vinylpyrrolidone) (PVP), poly(propylene carbonate) (PC), poly(ethylene oxide) (PEO), PVA/Chitosan and PVA/Fe_3O_4 uniaxially aligned ultrafine fibers were obtained with electrospinning method by adding another electric field in the collection area. Alignment of the nanofibers was characterized by the use of digital cameras and field emission scanning electron microscopy, polarized Fourier transform infrared spectroscopy (FTIR), and wide-angle X-ray diffraction (XRD). The mechanism of fiber alignment was investigated as well.

Keywords align, electrospinning, electrostatic field, orientation

1 Introduction

Electrospinning is one of the most effective methods for the preparation of polymer nanofibers [1]. 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 [2–5]. In electrospinning process, fiber instability or "whipping" makes it difficult to control the orientation of the nanofiber and resulted in a non-wave structure.

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 [6–8], only partial fiber alignments have been achieved. Some of the newest techniques can produce well-aligned fibers, but only of limited length [9,10], area [11,12], and thickness [13,14].

In this paper, the initial investigation result of the additive electric field electrospinning is reported to generate aligned fibers along the direction of the additive electric field. It demonstrated a new way, unlike the conventional technique, to produce highly oriented fibers, which could control the orientation by the additive electric field.

2 Experimental

2.1 Materials

Poly(vinyl alcohol) (PVA, whose degree of polymerization is 3500), poly(propylene carbonate) (PC, Mw = 700,000), poly (vinylpyrrolidone) (PVP, K-30, Mr $\approx 1.0 \times 10^4 - 7.0 \times 10^4$), poly(ethylene oxide) (PEO, Mw = 5,000,000) and PVA/Chitosan and PVA/Fe_3O_4 composite were chosen for this experiment.

2.2 Preparation of polymer nanofibers by electrospinning

The schematic setup of the electrospinning processes is shown in Fig. 1 (a). Polymer solutions were put in a syringe (stainless steel needles OD 0.5 mm) equipped with an infusion pump. High voltages of 20 kV were applied to the syringe needles, and 30 V was applied to two metallic flats with 10 cm gap. When voltages were applied to the needles, a jet was ejected. Then the fibers were collected as aligned arrangement between the two metallic flats. Because there was an additive electric field between the positive metallic flat (DC +) and negative metallic flat (DC −), fibers with charge would be induced by the electrostatic force when they entered this electric field. This electrostatic force is F1. Similarly, there

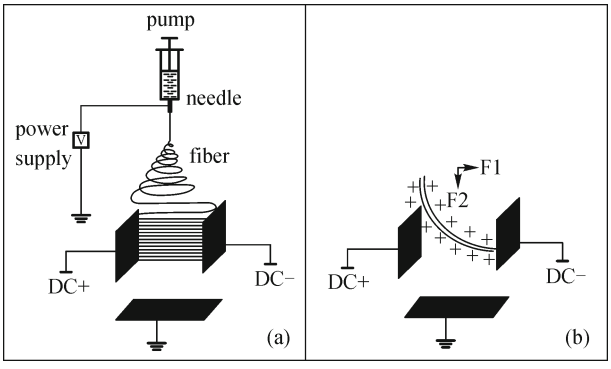

Figure 1 (a) Schematic illustration of the setup for electrospinning. The collector contained two pieces of metallic flats with a 10 cm gap. (b) electric force analysis of a charged nanofiber spanning across the gap

F1: electrostatic force between positive metallic flat (DC +) and negative metallic flat (DC −); F2: electrostatic force of electrospinning.

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was another electric field between the needle and grounded collector, and fibers with charge would be induced by the electrostatic force when they were located in this electric field. This electrostatic force is F2.

Some parameters of electrospinning are given in Table 1.

2.3 SEM characterization calculation

The microstructures of the fibers arrangement were characterized with a scanning electron microscope (SEM, Hitachi S-450, Hitachi Co., Tokyo, Japan) using an accelerating voltage of 20 kV.

2.4 FTIR spectroscopy

Polarized Fourier transform infrared spectroscopy (FTIR) (Nicolet FTIR-560) was used in investigating molecular orientation in the aligned fibers.

2.5 X-ray diffraction (XRD)

WAXD (D/max-RB, Japan) patterns were taken by using Ni-filtered Cu Kα radiation. The diffraction scans were collected at $2\theta = 5° - 60°$.

3 Result and discussion

3.1 SEM characterization of aligned nano-micro fibers

In the conventional electrospinning process, the fibers were collected onto a grounded aluminum foil randomly. Because of the chaotic motion of polymer jets forced under the electrostatic forces of electrospinning (F2), the degree of orientation for nanofibers was low. Furthermore, the fibers were directly deposited on a grounded substrate and were often discharged immediately. But in this novel setup as shown in Fig. 1, fibers were collected in an additional electrostatic field. The fibers under a chaotic motion were aggregated by the electrical forces of the collector (F1) to form a highly aligned ultrafine fiber (Fig. 2), and the fibers would not be discharged immediately as the fibers were across the two pieces of metal slices.

In this electrospinning process, well-separated nanofibers could be fabricated because of repulsive interactions between the residual charges. The fibers tended to be separated as far as possible from each other within a short time collection, for example, 2 seconds. (Fig. 2(a)). However, for a long time collection, for example, 30 minutes, a large number of fibers overlapped each other (Fig. 2(b)), which might result from space limitation. This setup can fabricate the micrograph of an array of crossbar junctions by the rotation angle of 90° in terms of the additive electric field, as is shown in Fig. 2(e).

Additive electric field of aligned fibers also concerns other polymers, such as gelatin, PCL, PLGA, PAN, poly(3-hydroxybutyrate) (PHB) and polylactic acid (PLA). After systematical investigation this method has been found to provide a simple route to array nano-micro fibers with relatively high densities and over large areas.

As shown in Fig. 2, the degree of orientation of PVA nanofibers, PC nanofibers and PEO nanofibers were all better than that of PVP nanofibers. The reason may be that the concentration of the PVP solution was higher than that of PVA solution, PC solution and PEO solution. Under the same experimental conditions, the chain entanglement of PVP was more severe than that of the latter three materials, so the chain orientation of PVP was more difficult to be placed in the electric field.

3.2 FTIR analysis

Polarized FTIR spectroscopy was used to investigate the molecular orientation in the PEO nanofibers. The polarized FTIR spectra of anisotropic electrospun nanofibers were obtained by using two mutually perpendicular polarizations (Fig. 3). For aligned PEO fibers, the bands attributed to the C-H stretching at 2890 cm^{-1}, C-H wagging at 1342 cm^{-1}, C-O-C stretching at 1101 cm^{-1}, and C-H rocking at 962 cm^{-1} have lower intensities when the vector was perpendicular to the fiber axis than when it was parallel with the fiber axis. This is due to molecular orientation of the PEO backbones along the fibers' axes. When most of the PEO chains were oriented in the fibers' axes direction, the electric vector along this direction encountered a great number of C-H bonds and C-O-C bonds, together with the change in dipole moment of their

Table 1 Electrospinning parameters

Polymer/ solvent	Concentration/wt%	Spinning voltage /kV	Flow rate /(mL·h^{-1})	Collected voltage /V	Coverage diameter/nm
PVA-chitosan/acetic acid-water solution	7.5 (chitosan/PVA 9/1)	20	0.6	60	185
PVA /Fe_3O_4/H_2O	10 (30 wt% Fe_3O_4)	20	0.6	60	568
PVP/H_2O	50	20	0.3	60	200
PC/CH_2Cl_2	10	16	1.0	60	2400
PEO/ethanol and H_2O (ethanol/ H_2O 2/3)	4	7.5	1.0	60	500

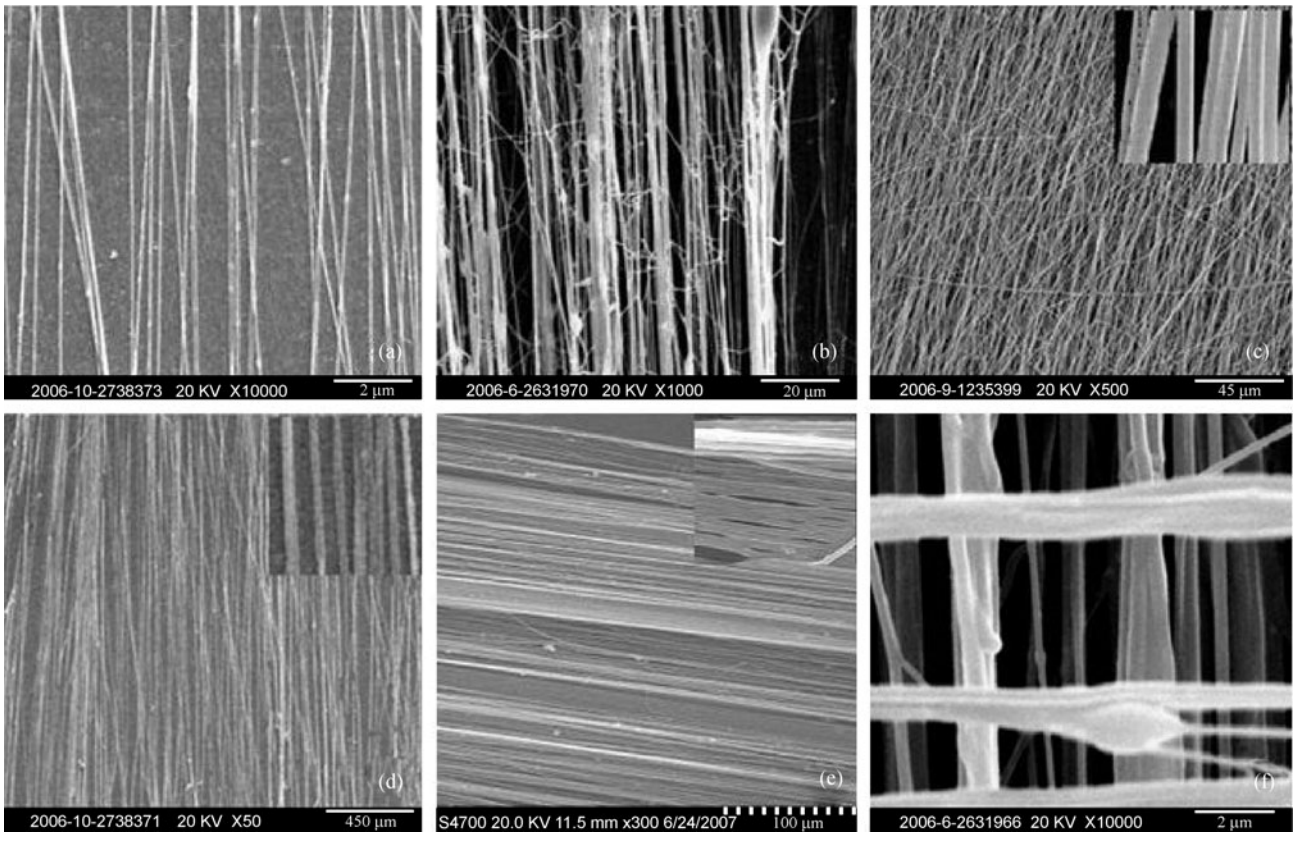

Figure 2 SEM image of uniaxially aligned nano-micro fibers made by various materials: The insets showed enlarged SEM images of these fibers. (a) 7.5 wt% Chitosan/PVA (9/1 w/w) blend solution; (b) 10 wt% PVA with 30 wt% Fe_3O_4 water solution; (c) 50 wt% PVP water solution; (d) 10 wt% PC chloroform solution; (e) 4 wt% PEO solution (solvent: ethanol/water, 2/3); (f) array of crossbar junctions constructed by sequentially transferring the collected electric field of PVA nanofibers

respective vibrations, resulting in higher absorbance intensities in fibers' axes direction [15]. This result demonstrated that there were a large number of orientations of the polymer chains in the nanofibers generated by the additive electric field.

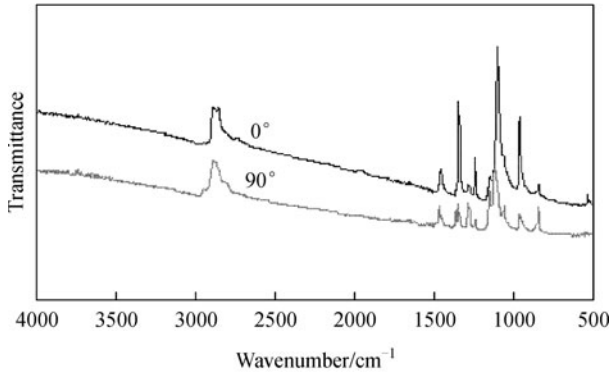

Figure 3 Polarized FTIR spectra of aligned PEO nanofibers 0° (and 90°) means that polarized radiation is parallel with (perpendicular to) the fiber direction. For aligned PEO nanofibers, the peak intensities of 0° are greater than those for 90°.

3.3 XRD characterizations — crystal orientation within the fibers

The XRD patterns obtained for a pure PEO powder, bundles of oriented nanofiber and nonwoven mat nanofiber are shown in Fig. 4, respectively.

For PEO powder, a peak at 2θ = 19.0° from the 120 reflection and another stronger peak at 2θ = 23.6° were obtained. As shown in Fig. 4, the pattern of PEO nonwoven mat was similar to that of PEO powder. Yet the main crystalline peak at 2θ = 19.0° was sharp and the crystalline peak at 2θ = 23.6° was absent due to the high fiber orientation. The sharp 120 reflections indicated that the PEO crystals were oriented with the chain axis preferentially aligned along the nanofiber axis [16]. Also, the crystalline peak at 2θ = 23.6° was absent precisely because of the fiber orientation.

4 Conclusions

This study has demonstrated that various uniaxially oriented nanofibers were obtained when an additive electric field was

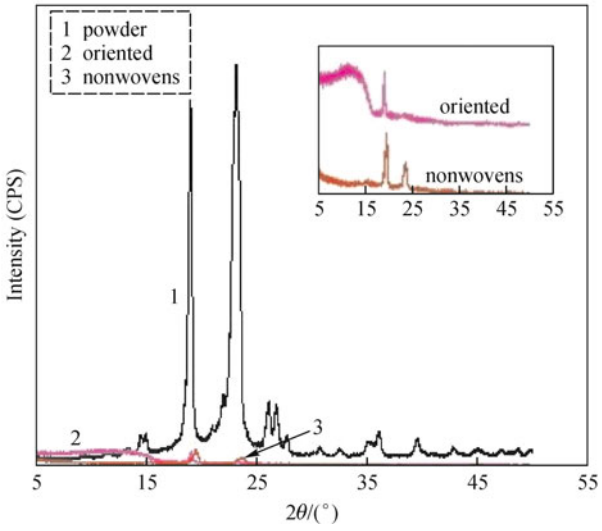

Figure 4 XRD patterns of PEO powder (1), oriented nanofiber (2) and nonwoven mat nanofiber (3)

introduced in the electrospinning process. This setup can also be used for other polymers to prepare oriented nanofiber arrangement over the gap between the two pieces of metal slices, and allows the construction of structure based on the rotation of the direction of the additive electric field, such as the crosslink structure. The results of polarized FTIR and XRD indicated that the electric field aligns not only the fibers but also the polymer chains in the fibers. This technology, which leads to an anisotropic property, can be easily applied to wider areas.

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