Well-aligned Polycaprolactone Fiber by Stable Jet Electrospinning

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Abstract. In this work, polycaprolactone (PCL) fiber membrane with random, partially aligned and well-aligned morphology by conventional electrospinning, high speed drum electrospinning and stable jet electrospinning, respectively. By adjusting PCL polymer solution (solution viscosity and conductivity) and electrospinning parameter (voltage, temperature, humidity et al.), well-aligned PCL membrane with fibers arranged in one direction under SEM observation. The mechanical behaviour were also studied. The stable jet electrospinning offers a possibility of producing well-aligned fiber membranes for future potential applications.

1. Introduction

Electrospinning has been widely known as a convenient tool to fabricate fiber membranes with random, aligned, woven and orthogonal structure. In the past few decades, almost all kinds of polymer were successfully electrospun for microelectronics, tissue engineering, water treatment and optics. Random oriented membranes are easily fabricated in conventional electrospinning because of the inherent bending instability of polymer jet. The bending instability makes it difficult to control the deposition of macroscopically aligned fibers and structures. Which obstruct the applications of the aligned electrospun fibers in tissue engineering with aligned structure (e.g., tendon) and other area.

A lot of methods have been reported to suppress the jet bending instability. Carnell reported in eliminating the jet whipping motion to fabricate well-aligned electrospun fibers by using an auxiliary electrode in the electrospinning setup. Zhou reported the effect of solution and electrospun parameters on the stable jet segment using poly (L-lactic acid) fibers. Results showed that well-aligned fibers formed by stable jet was attributed to the high viscoelasticity of polymer solution and low solvent dielectric constant. Another study reported by Zhang et al. showed that by adding a small amount of ultrahigh molecular weight poly (ethylene oxide) to obtain a high viscoelasticity polymer solution, parallel aligned fibers (silk, chitosan et al.) could easily be fabricated.

Polycaprolactone (PCL) is a semicrystalline biocompatible polymer. It was widely used in tissue engineering and regenerative medicine. In the present study, high viscous PCL solution is used to obtain a linear liquid jet. Well-aligned PCL fibers are fabricated by stable jet electrospinning via a collector of rotating cylinder. Conventional electrospinning and high speed drum electrospinning were used as control. Then, the morphology structure of the fiber membranes made by different electrospinning methods were explored. Tensile profile of the electrospin PCL fibrous membranes were also examined. The well-aligned multi-functional PCL fibers made by the stable jets electrospinning in this work are expected to be potential for application in microelectronics, tissue engineering and optics.
2. Materials and Methods

2.1. Materials
PCL (Mn: 80,000) was purchased from Sigma, USA. Dichloromethane (DCM), N, N-Dimethylformamide (DMF) was purchased from Aladdin, China. All of the reagents were at least of analytical grade and used as received without further purification.

2.2. Electrospinning
The electrospinning set-up was used as reported previously. PCL polymer solutions were prepared using a mix solvent of DCM: DMF. After stirring for 12 h at room temperature, the polymer solution was loaded into a syringe and extruded at a certain flow rate. A high voltage power source (Tianjin Dongwen) was applied to charge the polymer solution by connecting to the nozzle. The nozzle and a collector was adjusted to a specific distance. The fibers were collected on a rotating grounded collector with certain speed. The fibrous membranes were dried overnight under vacuum at 40°C to remove solvent residues. Table 1 provides a summary of the polymer solution and processing parameters.

Table 1 The polymer solution and processing parameters

| Method                        | DCM/DMF | Concentration | Voltage | Flow rate | Drum speed | Humidity |
|-------------------------------|---------|---------------|---------|-----------|------------|----------|
| Conventional electrospinning  | 3:1     | 22.5%         | 13kV    | 3ml/h     | ------     | 50%      |
| High speed drum electrospinning| 3:1     | 22.5%         | 13kV    | 3ml/h     | 2500rpm   | 50%      |
| Stable jet electrospinning    | 19.5:0.5| 22.5%         | 12kV    | 3ml/h     | 100rpm    | 35%      |

2.3. Characterization
The morphology of the membranes was observed by scanning electron microscopy (SEM, TM3030, HITACHI, Japan) at an accelerating voltage of 5 kV. Before observation, the samples were coated with gold using a sputter coater. Fiber diameter was obtained from the SEM photos by the Image J software. Fast Fourier transform (FFT) was used to analyse the fiber alignment from the SEM images.

For the mechanical test, the fiber membranes were cut into strips with 50 × 20 mm. The thicknesses of each samples was measured. A universal test machine (AG-I, SHIMADZU, Japan) was used at a loading speed of 1 mm/min. The loading direction was applied along the fiber alignment. Five duplicates were tested for each group.

3. Results and Discussion

3.1. Stable Jet Formation
In conventional electrospinning, as could be seen in Figure 1A, the polymer solution was pulled by electric forces. When the force was high than the surface tension, a polymer jet was formed. At first, there was a short straight part. Then violent whipping motions causes the jet to a bending instability segment. As the solvent evaporated, a random fiber membrane was formed when a plate collector was applied. In high speed drum electrospinning, partly the same with conventional electrospinning, when a high speed rotated drum was applied as the collector, a partially aligned fiber membrane could be obtained due to the tensile forces exerted on the polymer jet. In a typical situation, by adjusting polymer solution (solution viscosity and conductivity) and electrospinning parameter (voltage, temperature, humidity et al.), the jet bending instability is gone and a long stable linear jet up to tens of centimeters could be formed. This is named stable jet electrospinning, which were reported recently by many researchers.
Figure 1 Schematic diagrams of conventional electrospinning(A), high speed drum electrospinning(B) and stable jet electrospinning(C)

3.2. Well-aligned PCL Fiber via Stable Jet Electrospinning

The morphology of the fiber membranes made by different electrospinning methods were visualized by SEM. As shown in Figure 2, the random fiber were randomly distributed. While high speed drum electrospinning exhibited partially aligned morphology though some curved fibers could still be seen. However, by stable jet electrospinning, well-aligned fibers arranged in one direction could be seen in Figure 2C. The FFT images in Figure 2 were used to qualitatively characterized the fibers alignment (the narrower the center part area in FFT output image, the better the fiber alignment). The results were consistent with previous reports\(^4\),\(^6\). The fiber diameter of the electrospun membranes were charted in Figure 2G. The diameter of the fibers were 5.5±0.92 μm, 5.7±0.44 μm and 6.1±0.85 μm for conventional electrospinning, high speed drum electrospinning and stable jet electrospinning, respectively.

In conventional electrospinning, the random orientation might be ascribed to the severe bending instability mainly caused by the electric forces\(^10\). Thus random oriented fibers deposited on the plate collector. The deposition pattern of the random fiber can be controlled to be relatively aligned by using a high speed drum collector. The degree of alignment generally increases with increasing rotation speed. Thick aligned fiber membrane could be obtained in this way, but fiber alignment might decrease with membrane thickness because of the charge retention of previously deposited fibers\(^11\). Thus high speed drum electrospinning could produce membrane with relatively aligned fibers. Unlike the others, in stable jet electrospinning, by adjusting appropriate polymer solution and electrospinning parameter, a long stable jet with length up to several tens of centimeters was formed, which made the fabrication of well-aligned fiber easily done via a low speed drum (around 100 r/min)\(^12\).
Figure 2 Representative images of SEM by conventional electrospinning(A), high speed drum electrospinning(B) and stable jet electrospinning(C), and the Fast Fourier Transform of the corresponding images. The diameter of the fibers(G).

3.3. Mechanical properties
As shown in Figure 3, the representative stress-strain behavior of the fiber membranes made by conventional electrospinning, high speed drum electrospinning and stable jet electrospinning. As could be seen in Figure 3, the random fiber membrane presented a “soft and tough” pattern, with the lowest tensile strength of 2.02±0.13 Mpa and longest elongation at break of up to 180%. While the partially aligned fiber membrane made by high speed drum electrospinning had a higher tensile strength of 4.95±0.72 Mpa and smaller elongation at break of around 80%. The well-aligned fiber membrane made by stable jet electrospinning present a highest tensile strength of 6.12±1.23 Mpa and smallest elongation at break of around 70%. The alignment extent of the fiber might contribute to the enhancement of the mechanical properties. The higher molecular orientation of the polymer chain in the align fiber might also make contribution to the enhancement of the mechanical properties, as reported previously4, 13.

Figure 3 The Stress and Strain curve of the fiber membranes by different electrospinning methods.

4. Conclusions
In this study, well-aligned PCL fiber were successfully fabricated by stable jet electrospinning method. It is a facile method to fabricate thick well-aligned fiber membrane with conventional electrospinning
set-up. The well-aligned fiber might have potential application in microelectronics, tissue engineering and optics.

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