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Needleless Electrospinning of Multiple Nanofibers

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***Abstract* — To satisfy the increasing applications of the electrospun nanofibers, a novel method for the high throughput nanofibers electrospining which is called "Needleless ElectroSpinning (NES)" is presented in the article. Instead of using the conventional needle, ElectroHydroDynamics (EHD) instabilities mechanism on the electrified liquid film free surface forms the foundation of the NES process, in which, we use a metal cylindrical rotator with smooth or tipped surface as the spinneret electrode, and the production rate of nanofibers can be controlled by adjusting the length and diameter of cylindrical rotator. The main factor such as solution concentration, the diameter of cylindrical rotator, the distance between the rotator and the grounded collector and so on are investigated in our experiment. Results show that solid nanofibers with diameter of 100nm-800nm can be electrospun onto metal substrate with electrode-to-substrate distance of 10-20cm under bias of 40-70 kV. Compared with the conventional electrospinning method, the yield is expected to be increased by more than 125 times.**

Keywords — ***cylindrical rotator, electrohydrodynamics, needleless electrospinning, poly(ethylene oxide)***

I. INTRODUCTION

With the huge surface area to volume ratio, nanofibers and nanowires have the potential to significantly improve current technology. Electrospinining, which was introduced by Formhals in 1934 as the main way to produce the polymer nanofibers, has gain much attention during the last few years due to its many potential applications, such as filtration membranes, composite materials, tissue scaffolds, wound dressing, drug release systems, protective clothing and photocells[1, 2]. Unlike conventional fibre spinning methods like dry-spinning and melt-spinning, in electrospinning, a solution with the proper viscosity, conductivity, and surface tension is first fed through a spinneret. A sufficiently high voltage is applied to the solution as the critical voltage, typically more than 8kv. Electric forces imposed by a capacitor-like electric field on a droplet of polymer solution result in jetting from its tip and fibers are forced to travel towards a grounded conductor. However a single jet is issued from a single needle. This low throughput may limit the industrial use of electrospinning.

To satisfy the increasing needs for the commercial polymers, various electrospinning techniques have been investigated and developed. Multiple-nozzle arrangement was used to increase the yield [3], however, this method is technologically inconvenivent due to mutual-Coulombic interactions between different jets and high probability of clogging. Kim and his group used a cylindrical electrode connected with multiple nozzles to stabilize the initial spun jets without interruption near charged jets and obtain high production rate for electrospun nanpfibers [4]. Dosunmu et al demonstrated an innovative method of using a porous tube where an electrode was inserted into it, by applying air pressure, the solution was forced through the numerous pores on the tube spinning of numerous jets commenced and the fibres were deposited on the inner surface cylindrical collector that enclosed the porous cylindrical tube [5]. Zussman and his gorup provided a new approach employing a ferromagnetic liquid sublayer [6]. In particular, a two-layer system, with the lower layer being a ferromagnetic suspension and the upper layer a polymer solution was subjected to a normal magnetic field. As a result, steady vertical spikes of magnetic suspension perturbed the interlayer interface, as well as the free surface of the uppermost polymer layer. With the addition of normal external electric field, the perturbations of the free surface became sites of jetting directed upward.

II. EXPERIMENTS

A. The principle of NES

According to the principle of EHD, an electric field applied across the interface of the metal surface and the liquid film exerts an electrostatic pressure on the interface that will cause the fluctuations, the electrostatic pressure works against interfacial tension to generate EHD instabilities, which lead to the fast growth of one wavelength, and eventually bridges between two electrodes. EHD instabilities forms the basis for the electrospinning process where an electric potential is placed across the interface of a solution and the ground collector where the spun fibers are collected [7].

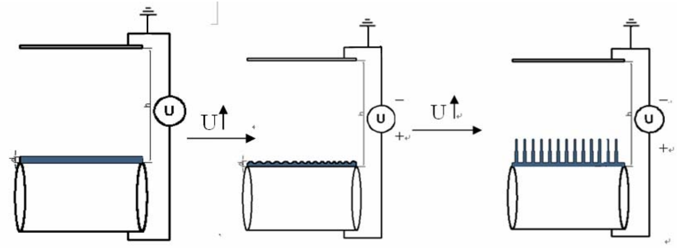

Figure 1. Depiction of the EHD instability phenomenon. An high elecric field detabilizes the polymer film amplifying undulation until they span to the grounded flat counterelectrode

Here we propose and focuse on a new method for the electrospinning of multiple nanofibers using a cylindrical rotator as the electrode in contrast to conventional needle. Figure 1 shows the principle of our new method, When a high perpendicular electric field is applied to polymer liquid film, solutions free surface wave result and numerous conical spikes stands vertically at the surface. Further increasing the electric field, the surface tension will be eventually overcome by the electrostatic force, and multiple jetting of the polymer solution began to emit toward the grounded counter-electrode.

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B. Materials and the NES equipment

In this letter, Poly (ethylene oxide) (PEO) were used in NES process in order to investigate the effect of process parameters, such as electrode-to-substrate distance, voltage threshold, the solution concentration, the thickness of solution coated on the upper surface of the rotator and the diameter of cylindrical rotator on NES. The concentration of PEO (Tianjin, Da Di Fine chemical Engineering Co. (Mv =300,000)) solution is from 12%wt to 18%wt PEO in wt 80 % / wt 20 % water/ethanol solvent.

The photograph of the equipment for NES of multiple nanofibers is shown in Fig.2A. There are basically three components: a metal cylindrical rotator which works as the spinneret in the traditional electrospinning, a grounded collector and a high voltage supplier which is HB-ZGZ Ⅱ (Qindao Hua Bao Electric Co. 0-120 kV). Two kind of cylindrical rotator were used in the experiment, one with smooth surface seen in Fig.2B, and the other has many tips on the surface(figure 2(C)). The polymer solutions is coated on the upper surface of cylindrical rotator, the voltage at the cylindrical collector was gradually increased to more than 20kv relative to the grounded collector and the distance between the rotator and the grounded collector can be adjusted. The grounded collector is made up of a copperplate which works as counter-electrode, two rollers and some black fabric. The black fabric was rolled by the rollers, which can be rotated so that the nanofibers electrospun by cylindrical spinneret can be deposited on the black fabric with expected uniform thickness (figure 2(D)).

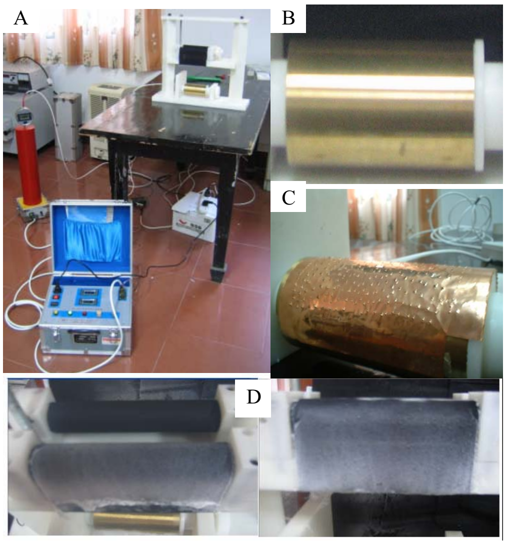

Figure 2. (A) Photograph of equipment for NES of multiple nanofibers. (B) The Smooth Surface Cylindrical Spinneret (SSCS) (C) tipped surface cylindrical spinneret (TSCS) (D) Photograph of nanofibers electrospun by NES deposited on the black fabric.

III. RESULTS

A. The Smooth Surface Cylindrical Spinneret (SSCS)

Cylindrical rotators with different diameter were used as spinneret in our experiment. Take the SSCS with diameter of 6cm for example. As the first step, PEO solution was coated on the upper surface of the cylindrical rotator, then the voltage applied at the SSCS was gradually increased to higher than 40kV relative to the grounded collector located at a distance of 15cm, some oscillation at the free surface of polymer happened and numerous conical spikes standed vertically at the surface. Further increasing the voltage to about 50kv, tens to hundreds of jets began emited from the SSCS surface at the same time, solid nanofibers with diameter of 100nm-800nm can be electrospun onto the black fabric, and the SEM photograph of nanofibers electrospun by SSCS are showen in figure 3.

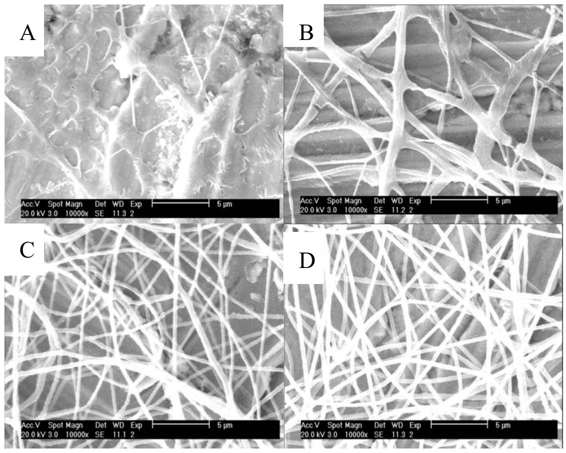

Figure 3. Scanning electron micrographs of the electrospun nanofibers, which were deposited on grounded collector (The nanofiber diameter range: 100nm-800nm) A, solution: 12%wt PEO, voltage threshold: 49KV; B, solution: 13.5%wt PEO, voltage threshold: 52KV; C, solution: 15%wt PEO, voltage threshold: 57KV; D, solution: 18%wt PEO, voltage threshold: 63KV.

One of the most significant parameters influencing the fiber diameter in the NES is the solution viscosity. A higher viscosity results in a larger fiber diameter [8,9,10]. However, when a solid polymer is dissolved in a solvent, the solution viscosity is proportional to the polymer concentration. Thus, the higher the polymer concentration the larger the resulting nanofiber diameters will be. On the other hand, liquid film and droplet are formed when the viscosity is too low. Experiments show that the concentration between 12%wt and 18%wt was suitable for NES. Outside this range, either only few fibers could be obtained from a even higher concentration or the jet broke up to droplets due to too low viscosity. In our experiments, 12%wt PEO solution (figure 3(A)) is compared with 13.5%wt solution (figure 3(B)), 15%wt solution (figure 3(C)) and 18%wt solution (figure 3(D)), the electrode-to-substrate distance is set at 15cm, and the threshold voltage are 49kv(12%wt), 52kv(13.5%wt), 57kv(15%wt) and 63kv(18%wt) respectively. From figure 3, we can find that for 13.5%wt or lower, same defects exit, such as film and thicker fiber with diameter of several microns. With the concentration increased, the nanofibers with diameter of 100nm-800nm can be deposited on the black fabric.

To assess the effect of the electrode-to-substrate distance on the voltage threshold and the diameter of nanofibers, the gap between the SSCS and the grounded collector was narrowed from 20 to 10 cm in 2.5 cm steps, keeping all other parameters constant. The voltage threshold distribution of cylindrical rotator shown in figure 4 clearly demonstrated that with the increasing of electrode-to-substrate distance, the voltage threshold become higher. However, no obvious difference in the fiber morphology was found in spite the average fiber diameters decreased slightly with the increasing electrode-to-substrate distance.

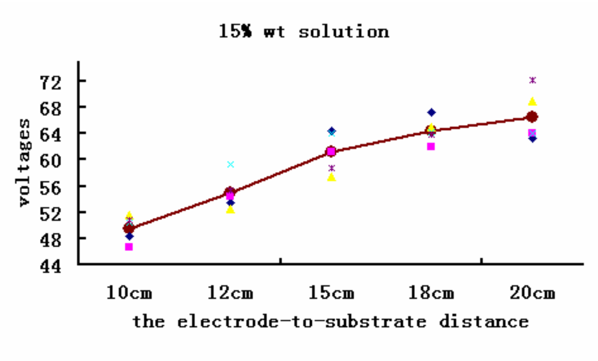

Figure 4. The voltage threshold distribution with different distance between the SSCS and the grounded collector. (The diameter of cylindrical rotator: 6cm)

To analyze the electric field in NES, ANSYS 8.0 was used, which is a commercial software providing electromagnetic analysis using finite element method. The analysis results showed that under the same voltage and same electrode-to-substrate distance, the intensity of electric field on the surface of SSCS with the diameter of 4cm (figure 5A) is much larger than the diameter of 6cm (figure 5B). in other word, if keeping all other parameters constant, the larger the diameter of SSCS, the higher the threshold voltage needed. This conclusion was also supproted by experimental results showed in figure 6.

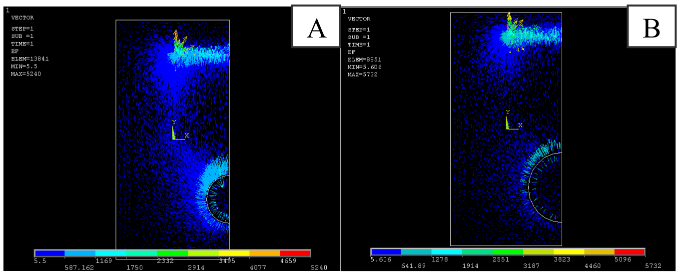

Figure 5 The intensity of electric field distribution between the SSCS and counter-electrode. (A) Voltage: 50KV, distance: 10cm, diameter of SSCS: 4cm. ;(B) voltage: 50KV, distance: 10cm, diameter of SSCS: 6cm.

The yield of nanofibers electrospun by NES was found to be very large compared to the traditonal electropinning, this increased production rate is attributed to the large spinning area of SSCS, tens to hundreds of jets can emit from the free surface of SSCS, though it's difficult to estimate the exact number of jets, the yield can be calculate by weighing the nanofibers. The 6 cm diameter, 10cm length of SSCS produced nanofibers at a rate of about 2.53 g/h. Compared to the single needle which produce nanofibers at a rate of about0.02g/h, NES can lead to a 125 times enhancement of the production

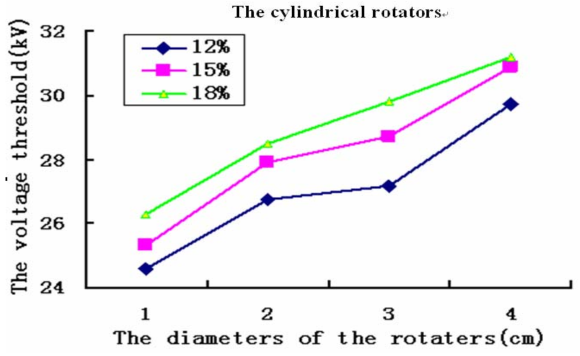

Figure 6 The voltage threshold distribution of different diameters of SSCS. The 12%wt PEO solution is compared with 15%, 18%wt PEO solution.

rate, and we also can easily change the yield by changing the diameter and length of SSCS.

In our experiment, some of jets appeared to emit first at a relative low voltage, and have much larger diameter than others, this may be due to the non-uniform thickness of polymer coated on SSCS. Result showed that the thicker the solution coated on SSCS, the lower the bias voltage needed. So to find and control the uniform and fittest thickness of solution is the main problem we will focus on at our next step.

B. Tipped Surface Cylindrical Spinneret(TSCS)

The tipped surface cylindrical spinneret (TSCS) (figure 2(C)) was also used in our equipment. Similar to the SSCS, TSCS has the same parameters discussed above in this paper, and the most advantage of TSCS is that under the same parameter, the intensity of electric field on the tip of surface is much higher than that on the smooth surface. Namely, TSCS can reduce the voltage threshold. On the other hand, as most of jets were emitted from the tips, the diameter of tips directly influence the thickness of initial jets. Figure 7 showed that less than 200nm diameter of nanofiber can be deposited on the grounded collector. But TSCS also has some default, such as the probability of clogging, the cleanout of TSCS and so on.

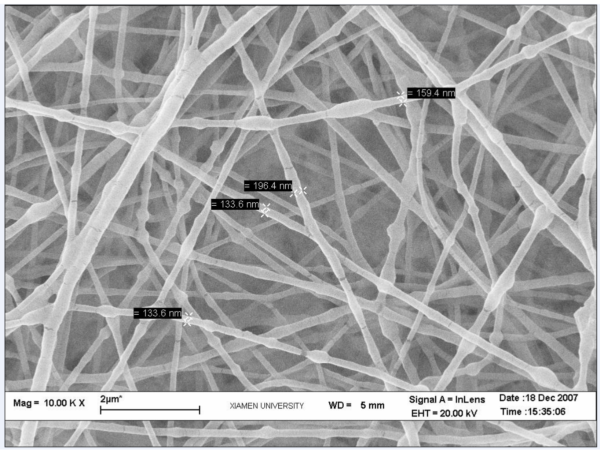

Figure 7. Scanning electron micrographs of the electrospun nanofibers electropun by TSCS

IV. CONCLUSIONS

In order to increase the yield of electrospun nanofibers, two kinds of cylindrical rotator was used as the spinneret in this work, experiment showed that tens to hundreds jets can emit from the rotator surface at the same time. Compared to the tranditional single jet electrospinning, this method can lead to more than 125 times enhancement of the yield. Another advantage of the NES is that it eliminates the high probability of clogging happened in the multiple-needles arrangement. The main effects of process parameters such as solution concentration, the diameter of spinner, the electrode-substrate distance and so on on the NES are investigated. More works will be done to improve the equipment so that it can run automatically.

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