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Research on High Quality Nanofiber Electrospinning Manufacturing System:Detecting Method of Taylor-cone and Fiber diameter Control Strategy

***Abstract**. This paper designed the method to control the electrospinning process stability basing on the analysis of Taylor-cone, and built the electric field adjust method to control the fiber diameter basing on the finite element analysis, experiments results showed that the stability was improved and diameter could the adjusted in micro-nano level. ..*

***Streszczenie.** W artykule zaprezentowano metodę sterowania procesu produkcji nanowłókien bazująca na stożku Taylora i wykorzystaniu pola elektrycznego do kontroli średnicy włókna. (**Badania metody wytwarzania nanowłókien – wykorzystanie metody stożka Taylorta i elektrycznej kontroli średnicy**)*

Keywords: electrospinning; Taylor-cone; whipping movement; control; diameter.
Słowa kluczowe: nanowłókna, stożek Taylora

Introduction

Electrospinning is method to manufacture the nanofiber, which is widely used in tissue-engineered scaffolds in three-dimensional(3-D)structure which is greatly influenced by their porosity and pore size[1].In general, pore sizes created by rapid prototyping(RP) are very large for cell seeding, however, the microstructure produced by electrospinning can improve the cell adhesion, it supplies high surface area to volume ratios essential for high-efficiency cell attachment[2],the fiber diameter has great influence to the microstructure[3],several paper have confirmed that the fiber diameter has effect the cell culture to large degree[4],so this article do research on manufacturing system for high quality nanofibers and strategies to control the fiber diameter.

Since A.Formhalst raised electrospinning in 1934,this technology is focused for its unique features, and widely used in the field of filtration, nonwoven, regenerative medicine,etc[5-7].Nowadays, the nanometer fiber is more in non-woven fabric shape, fiber diameter is not controlled, it largely restricted the further development and application of electrospinning, so many domestic and foreign scholars of institutions and universities paid great attention on the fiber diameter control problem[8-10],including Taylor-Melcher leakage media theory based on fiber movement in the electric field, bead structure in the process of fiber receiving, cells culture. As a effective method, numerical simulation has been widely used in the analysis of dynamic movement12-13,many researcher used finite element to analyse the electrospinning process11.Recent research shows that, the theory of fiber diameter is the most important factors to control the size of the pore ,the pore size will increase with the fiber diameter; At the same time fiber diameter can also affect the quality of scaffold, including the surface area and the pore space; The scaffold can also affect biological growth performance, such as cell adhesion, portability and cells distribution[1]. The fiber diameter controllability is of great significance for materials degradation rate and cell survival rate in bone regeneration scaffold engineering. so the fiber the fiber production quality and diameter production control methods are of great significance.

As the exciting both fiber unpredictable and time varied diameter distribution will limit the further development of fiber manufacturing.In this paper,Taylor-cone is controlled to guarantee the stable movement;CCD,the real-time measurements of Taylor,will provide appropriate detective function and control strategies for achieving consisten and high quality diameter; experiments are presented according to that control strategies.In the experiments,the relation between the diameter and whipping is observed,through detecting the deposition morphology.Further,theoretical model of whipping fibers is built to confirm the experimental observation,analysis the relation between voltage and fiber diameter, construct the diameter control strategy.

Experiment 1

Experiment setup: Electrospinning equipment is mainly consist of three parts, the high voltage supply, the polymer solution pump, and fiber collector. Experiments were conducted on solution of PCL(Mn=80000) and the solvents, N, N-dimethyl formamide(DMF)and methylene chloride(MC),were used to fabricate the spinning solutions. The electrospinning solution was produced by mixing 80wt% MC and 20wt% DMF with 8wt% PCL. Electrospinning was conducted using a "point-plate" geometry, a high voltage power supply(0-50kv,Dongwen Tianjin) was connected to the upper point to provide different voltage between 15 and 25kv.The morphology of Taylor cone was imaged by CCD(labeled CMLN-13S2M,PointGrey Research Corporation).For each sample, the fiber diameter was measured from SEM.

Experiment began, polymer was pushed to the nozzle by the pump, turn on the voltage power supply, charges collect on the surface of the polymer in the nozzle, the charges produce electrostatic repulsion against with polymer solution surface tension, and the polymer was in a state of equilibrium called “Taylor cone”, a imperative feature to study in this paper. If the value of voltage goes to a further strengthen, electrostatic force will overcome the former tension ,so that polymer solution jet which emerges from the tip of the Taylor-cone, then travels and elongates to the collect. The whole movement has two stages: Rayleigh stage and whipping stage. In the first stage, the electrically charged jet traveled for a few centimeters in a straight line, at the end of this straight segment, the fiber diameter will decrease as half of is initial value. After that, the jet will come into the instable stage, it will whip in this stage, where the fiber will decrease significantly19,this paper will focus on this stage .

Both the changing of Taylor cone shape and fiber distribution with voltage are shown in Fig.1-Fig.2.The change in the shape of Taylor cone reflects the fiber distribution. When the cone is bigger as shown in the Fig.1.(a) due to the small voltage which is not strong enough to draw the solution out of the nozzle, beads are formed as a result of salivation, it is shown in the Fig.2.(a);When the voltage is increased, the salivation phynominent is decrease as well, we can discover that in Fig.2.(b)The salivation is disappear when steady-state Taylor cone is formed in Fig.1.(c),the voltage of 20kv is the target voltage to control in order to obtain the straight and continous fiber. If the voltage is increased further, the fiber collected is not straight anymore due to the severe whipping motion,Fig.2.(d)shows that fiber begin to bend unregularly, the cooresponding cone is small, because solution is drawn out by the fiece voltage, the cone is smaller with the increase of voltage, the cone in Fig.1.(e) is so small that the solution has almost gone out of the nozzle completely, when the solution is feed again, more solution is drawn out, more bigger fiber diameter is collected as is shown in Fig.2.(e).It is visible that Taylor-cone has a great impact on the distribution of the electrospinning fiber, and influence the fiber diameter uniformity. If the Taylor -cone is controlled in a standard shape, it is possible to produce the high quality fiber with uniform diameter distribution.

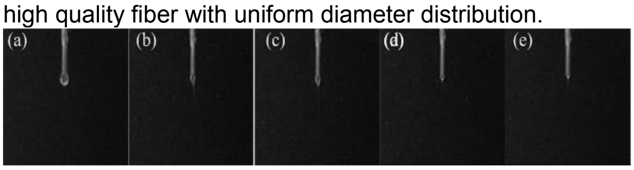

Fig.1.Taylor cone with voltage applied:(a)15kv(b)17kv(c)20kv(d)22kv(e)25kv

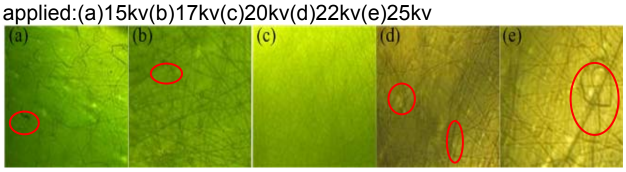

Fig.2.fiber diameter with voltage applied:(a)15kv(b)17kv(c)20kv(d)22kv(e)25kv

Experiment analysis

Standard shape of Taylor-cone is instructed in this part through theoretical analysis; the standard data will be stored in the PC in electrospinning system. As it exhibited differently with changing the voltage, the standard shape of each is accompany with varied voltage value, it is determined by the following equations (1),in which Q indicates the jet velocity driven by the voltage. The voltage will be adjusted by the computer basing on the detective result by CCD camera. The theoretical investigation Taylor cone is based on the governing electro hydrodynamic equations[10]for the mass conservation, momentum, charges conservation and for the electric potential, which are given below:

(1) $$Q = 0.0048V^{3.62}$$

where: Q –velocity, V –voltage.

(2) $$D\rho / Dt + \rho\nabla \cdot Q = 0$$

where: ρ–fluid density.

(3) $$\rho DQ / Dt = -\nabla P + \nabla \cdot \nabla(\mu Q) + qV / d$$

where: P –pressure, d –distance of the electric field, μ–electric conductivity

(4) $$Dq / Dt + \nabla \cdot (KV / d) = 0$$

where: K –charge density,

(5) $$V / d = -\nabla\Phi$$

where: Φ –electric potential,.

The derivative equations is deprived in matlab, as is shown in Fig.3.Taylor-cone exist in different forms corresponding to different voltage value. According to the simulation results, the volume of cone will decrease with the increase of the driving force, the speed of the jet velocity rise; it leads to the drop of the cone volume. Thus Taylor-cone height could be selected as characteristic parameter, it reflect the change of cone. As is shown in Fig.4.the height's statement with the change of voltage from 15kv to25kv.When voltage is increased, more polymer solution will be driven out, so there is a smaller Taylor-cone height. In this paper, program of Taylor-cone height is stored in computer, voltage is adjusted according to computer calculation results and CCD detective results.This article instruct the high quality nanofiber electrospinning detective system basing on the recognize of the characteristic parameter of Taylor-cone, the system adjust the voltage to maintain the standard cone as the goal, aims to manufacturing high quality fibers.

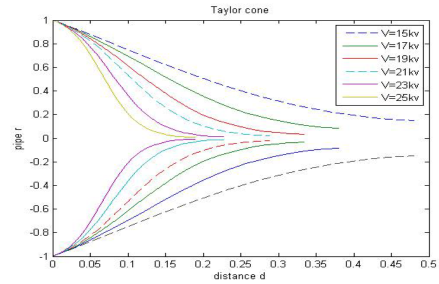

Fig.3.standard Taylor-cone figure with voltage applied ranged from 15kv to 25kv

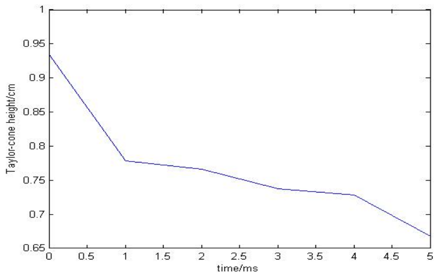

Fig.4.Taylor-cone height statement with voltage applied ranged from 15kv to 25kv

Hardware and software of the electrospinning system

Fig.5. depicts the configuration of the electrospinning system andFig.6. depicts the electrospinning hardware system. It consists of a needle as a node and a circular aluminum plate as cathode collected, a syringe with a motor and a variable DC high-voltage source. The syringe contacts the node. The positive terminal of the high voltage supply, which is capable of delivering a DC voltage of up to 50kV, is connected to the anode while its negative terminal is fixed to the ground. The cathode is covered by an aluminum foil where the nanofibers are deposited. In order to develop a close-loop electrospinning system, a real time detective camera is added, so that any changes in the electrospining process can be observed. The high voltage supply controller is made from a 16-bit digital to analog converter, a step-up transformator with a microcontroller, and an RS232 communication port, so is the syringe motor controller. Computer uses RS232 ports to send digital data. Communication between the computer and the syringe motor with the RS232 port is facilitated by RS 485 protocol. Further, the CCD device camera is used to monitor cone jet shapes at the end of the needle of the syringe, according to that, the computer will direct the high-voltage controller and

syringe motor controller, and made them cope with each other.

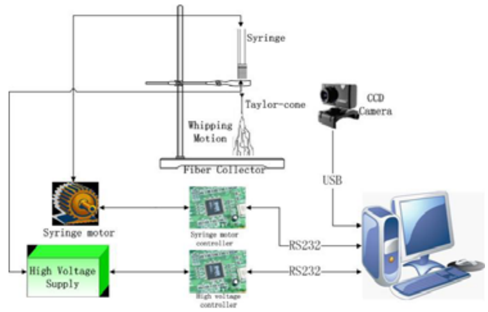

Fig.5. the configuration of the electrospinning system

Fig.6. electrospinning system hardware figure

This part of this research concentrated on process stabilization, aimed to develop a well-controlled setup to further study the effect factors of fiber diameter.The electrospinning system with closed-loop control is illustrated in Fig.1.Since the plants demands a DC high-voltage, the high-voltage actuator supply sit under a control action carried out by the PC. The feedback signal of the closed-loop control system is composed of the real time camera. In performing the control action, PC receives an input parameter of Taylor-cone height, the error between the standard value and the real value of Taylor-cone height observed by CCD will be figured out in PC.These are realized by a program saved in the computer.

The program used to control the electrospinning system was described in the following chart in Fig.7.At first, the computer starts to initialize the hardware and the communication protocol. The Taylor-cone height and the voltage V are initialized. The program then asks for the standard Taylor-cone height. Next, the program reads the actual plant/process output and calculates the error and then the control signal. If the Taylor cone is higher than the standard one, voltage will be increased, otherwise, it will be decreased. This control signal subsequently activates the high-voltage actuator to provide a DC high voltage supplied to the plant. Finally, the plant gives an output voltage. The program continues the control action until any key of the key board is pressed.

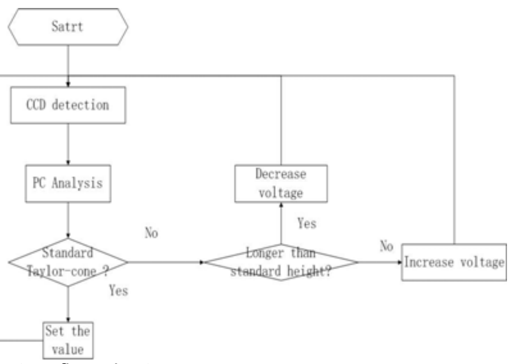

Fig.7. system flow chart

Experiment 2

Table1 shows the experiment arrangement.Electrospinning was conducted with a vertical distance of 0.15m between the electrodes,flow rate is calculated according to the equation(1) ,at various voltages of 15kv,17kv,19kv,21kv,23kv and 25kv respectively,the electrospinning time was set up to 2minutes.For each sample, the fiber diameter was measured from SEM.

Table 1. Experimental arrangement

NO.	Applied Voltage(kv)	Flow Rate (ml/min)	Collecting distance (cm)	Experiment time(sec)
1	15	0.0076	15	30
2	17	0.0101	15	30
3	19	0.0205	15	30
4	21	0.0305	15	30
5	23	0.0497	15	30
6	25	0.0608	15	30

The changes of Taylor cone shape, fiber diameter and fiber distribution with voltage are shown in Fig.4,Fig.5 and Fig.6.The shape of Taylor cone become small as the increase of the voltage, as more polymer solution will be pull out by the electrostatic force.We can see that in Fig.4(a) due to the small voltage which is not strong enough to draw the solution out of the nozzle, the volume is larger than any other Taylor-cones, more solution stored in this statement, the electrostatic repulsion is equilibrium against with the polymer surface tension; Fiber product in the condition is relatively of larger diameter comparing to those in higher voltage conditions,while whipping range is smaller comparing to higher voltage conditions. With the increase of voltage, the volume of Taylor-cone is smaller with its shorter height, as more solution is driven out by the high voltage, wherea the stable stage is shorter, whipping become fiercely, as a result, the deposition area is increasing, as is shown in Fig6,the collecting area is increased with the increase of voltage. The fiber diameter is decreased as a result of the intensed whipping stage. This trend is constant with the increase of voltage, however, when the voltage is increased further to 25kv,the fiber start to whip as soon as it is driven out of the syringe, irregularly bending lead to fiber take up almost the whole area of the collecting board. We can observe that maintain the ideal statement of Taylor cone, is a key point to obtain high quality fiber, as the collected fiber is uniform and avoiding the salivation, it is the strategies used in our system.

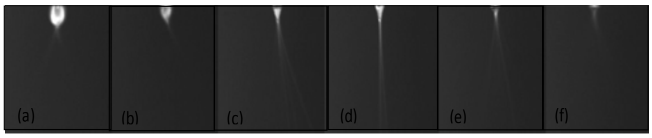

Fig.8. Experimental images of Taylor cone with voltage applied: (a)15kv (b)17kv (c)19kv (d)21kv (e)23kv (f)25kv

As we can see from the Table2 More fibers are collected as the voltage increase,the radius units of deposition area are increased, pixel points of Taylor-cone height is decrease,as the cone become smaller,the fiber diameter is decrease as the increase voltage leading to fiercer whipping.Fiber diameter is decrease as the pixel points of deposition area increase,the deposition area indicates the whipping fierce degree as well.so there is close relation between the fiber diameter and deposition area.The whipping and bending instabilities of fibers is pointed out by Reneker and Yarin11 indetail.During the jetting process,the jet body is in seize of the driving force of gravity,electric field, and surface tension, etc.

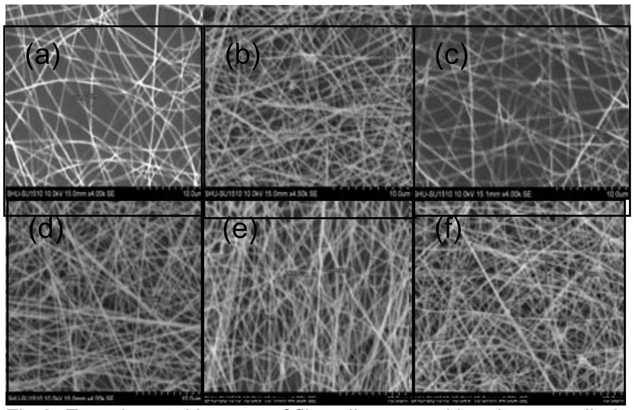

Fig.9. Experimental images of fiber diameter with voltage applied: (a)15kv (b)17kv (c)19kv (d)21kv (e)23kv (f)25kv

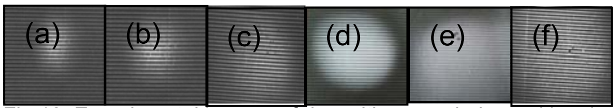

Fig.10. Experimental images of deposition morphology with voltage applied: (a)15kv (b)17kv (c)19kv (d) 21kv (e) 23kv (f)25kv

Table 2. Experiment2 results

NO.	Voltage(kv)	Deposition area(radius units)	Taylor-cone height(pixel points)	Fiber diameter(nm)
1	15	6	107	290
2	17	9	74	252
3	19	11	61	232
4	21	14	56	220
5	23	15	38	190
6	25	16	17	175

Analysis and discussion

The focus here is to study the influence of electrostactic force on the fiber path and predict the whipping motion and its effect to the fiber diameter. The path of the fibers can be controlled by understanding the forces acting on them; these forces control the movement from the source to the target. Theoretical calculations are made to determine the size of the fibers that could be controlled by electrostatic force during the flight of the fibers from the source to the target. This paper adopts viscoelastic beads model11 to describe the jet path, as fiber is consisted of slender particles, any sections of fibers are relative to other parts in terms of the bending, elongation, rotating. The whole jet can be viewed as a number of beads those stick together, it leads the movement of each fiber segment. the voltage applied on each bead is figured out by the field analysis results the value is shown in Fig.8.what Fig.9 show is the simulation results of whipping motion, the calculate process are the following:

According to the numerical solution method, the sticky beads method is as follows

1. At t = 0, jet includes two beads, bead 1 and bead 2. Set the distance to be H/100,000. Other initial conditions, including stress,beads velocity and acceleration all set to be 0.

2. for a given time t, solve the numerical equations. Solve all relevant variables of beads , including stress,location, length of the stretch distance.

3. calculate the value of time of next step according to the above results

4. set last bead head out is i= n. When the beads spray the distance long enough, adding new beads i = n + 1, calculate the voltage according to the electric field analysis in Fig.8,and apply the value to the bead.

5. Circulate the process from second step to the fourth step until get the position of all beads.When the jets stretch to collect board, the calculation reaches it terminated.

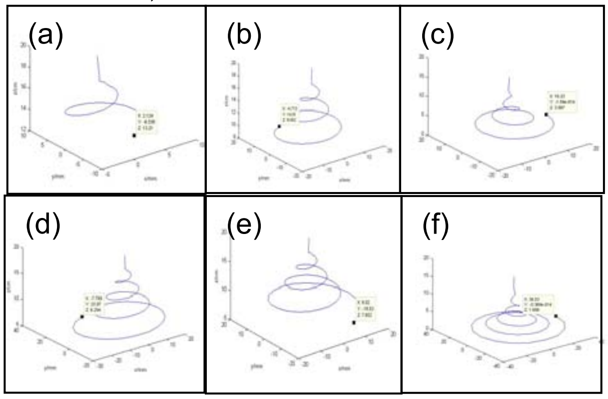

Fig.10 Electrospinning whipping plots with voltage applied: (a)15kv (b)17kv (c)19kv (d)21kv (e)23kv (f)25kv

Fig.10 shows the numerical simulation results, jet in 3d space experiences bending, spiral and cyclization. When whipping range increase to a larger voltage, fiber diameter is decreased as a result of tensile stretching. Whipping is intensified by the electrostatic force, because the charges on fibers will repel each other, as a result the fiber begin to bend and swirl, this will lead to more fiercely whipping motion. During the whipping process, the bending motion will stretch the fiber particle, so the fiber diameter will be decreased. As the applied voltage ascend to higher value, the repel degree will be reinforced, so that fiber diameter will decrease. The diameter in simulation and experiments is shown in Fig.11.There are errors in higher voltage and lower voltage, these errors maybe related to the ignored factors in simulation. However the simulation results can reflect the experiments changing trend. The voltage could be adjust to control the fiber diameter.Fig.12 shows the scaffold made in the condition of Experiment 1,the microscopic structure was made of gelatine, the nanofiber is made of PCL, comparing the nanofiber with that made in Experiment 2,the droplet salivate phenomenon was obviously in the first experiment, however, the system in experiment has overcome the generation of this phenomenon, there was uniform fiber in the Fig.13.It is manifest that the constructed system in this paper has the ability to control the fiber diameter.

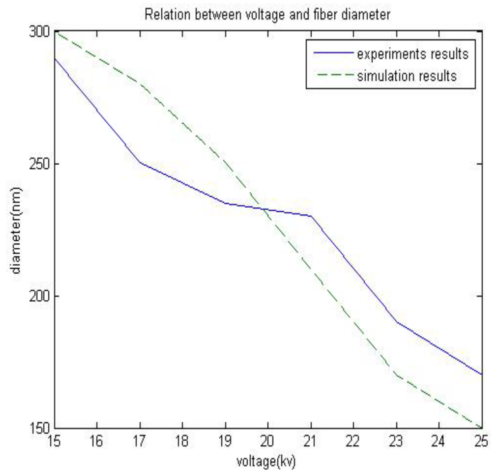

Fig.11 Relation between voltage and fiber diameter in both experiment and simulation condition

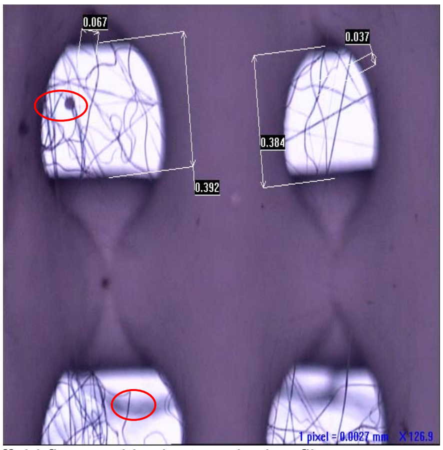

Fig.12 scaffold figure with electrospinning fiber

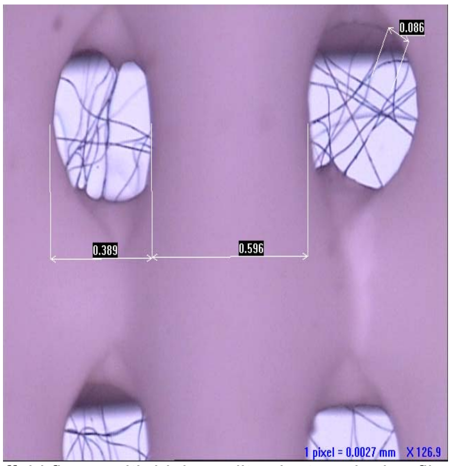

Fig.13 scaffold figure with high quality electrospinning fiber

Summary and prospect

Controlled electrospun fibers will soon bring about a revolution into the fields of nano-composites,microelectronics,due to the unique feature in terms of size and selective properties.In this paper,by applying the new electrospinning system,high qualified fibers were product,they are uniform and have less salivation.The paper proposed the following:

(1)Taylor-cone has the pentential to reflect the whipping statement of electrospinning,the suggested control system is effctively for high qualified fibers
(2)Whipping is main reason for the decreasing of the fiber diameter,as the voltage increase,diameter decrease.
(3)Taylor-cone height is an important feature parameter during the detective process of the fiber manufacturing.

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