Practical use of nanofiber made by electro-spinning process

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Abstract

The problem of the nanofiber preparation technique that used the electro-spinning method was studied. It has been understood that the electro-spinning and the electro-spray are fundamentally the same. However, the condition that Taylor cone is formed to the nozzle was different in the electro-spinning and the electro-spray. The correlation of the distance of the nozzle and interelectrode and the voltages was not clear. The multi nozzle for industrialization had a lot of problems. The efficiency of multi nozzle is 50-55% regardless of the number of the nozzle.

Keywords: Electrospinning,Nanofiber, multi nozzle, PLA, PET, Collagen

1. Introduction

When a high voltage was applied to a thin needlepoint, the phenomenon of discharged electricity happening was known since the 19th century. These are detailed to Kawamoto[1-3] and Umezu's papers. To analyze the electrostatic phenomenon, we should compare the experience with the FEM simulation. It is not easy to confirm the phenomenon by the experience because the electric field can be looking. The current begins to flow between the needle (0.3-0.5mm in the diameter) and plate electrodes when the voltage on the needlepoint edge exceeds 4KV. This is a start of the corona discharge. In addition, the spark discharge happens when stepping up the voltage. The spark discharge happens under applied voltage 6.8KV (20 A in current) when the distance between the needlepoint edge and the plate electrode is 5mm. The FEM computation result is almost corresponding to the experimental data. However, if the polarity on the needlepoint edge is subtracted, the current becomes the order of 100 A. This is because the speed of the negative air ion in the gas is about four times faster than that of the plus ion. The spark discharge happens earlier when the charge of the minus is applied to the needlepoint. Therefore, the needlepoint is made a plus pole in a usual electro-spinning.

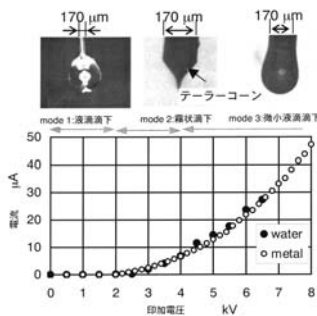## 2. Corona discharge and Taylor cone

Fig.1 Observation of nozzle by Kawamoto[2-3]. Taylor cone is made from model 2. Solution is water.

When applied voltage is low, the shape of the droplet in the nozzle is decided by the electrostatic force, the weight of the droplet, the surface tension, and hydraulic pressure. The working electrostatic force in the droplet is proportional to the second power of applied voltage. The tailor cone is formed to the electrode point with first stage (2-4kV) of the corona discharge, and fogged droplet of several ten micrometers is sprayed from the point widely. This is water, and the viscosity is 1.0cps. In the Figure 2, it is a glycerin and the viscosity is 1499cps. When the viscosity of solution is high, the spray phenomenon that happens repeatedly with about 0.2msec is observed as a spinning.

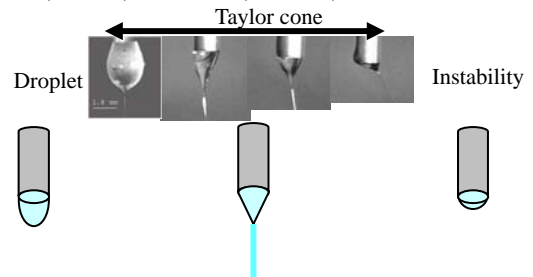mode1(0〜5kV)　　mode2(5〜20kV)　　mode3(20〜100kV)

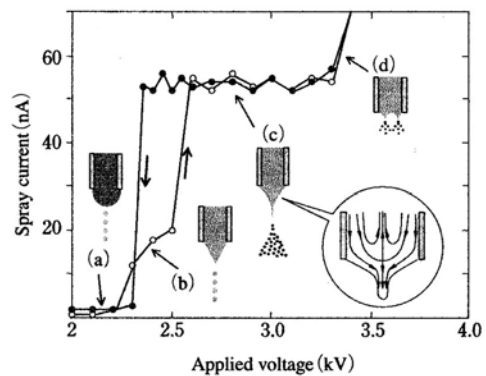Fig.2 Electro-spinning from polymer solution and glycerin.

Fig.3 General electro spray (Wuled Lenggoro, Kikuo Okuyama)[4]

The spray becomes a multi jet to which the cone point is divided and becomes unstable in the (d) area of Fig.3[4] where the voltage is high. This is corresponding to the phenomenon that becomes unstable and irregular the spinning when the voltage is high (20kV or more). Even if it is long, the needlepoint edge and the inter-electrode distance of the electro-spray are about 10mm. It is 50-200mm in the electro-spinning, and 5 times compared with the electro-spray. The electro-spinning is 1-2kV/cm while the electro-spray is 6-8kV/cm in the condition that it can have the Taylor cone. Therefore, it is guessed that the length of electrode distance is not a control factor of the Taylor cone and the corona discharge. The relation between the diameter of the droplet and the fiber and the amount of the limit charging and the surface tension will be able to be described by the next equation[5].

$$d \propto \left(\gamma \varepsilon_0 \frac{V}{Q^2} \right)^{1/3} \qquad (1)$$

Q: Amount of charging of droplet, V: Flow velocity, ε_0: Electric constant, γ: Liquid surface tension, d: Drop size or fiber diameter
That is, when the amount of charging is larger, the fiber diameter becomes smaller. On the other hand, when the surface tension and the flow velocity of solution are larger, the fiber diameter becomes thicker. The flow of the wind in the lower direction (ion wind) is generated by the migration of the ion from the needlepoint in the voltage of 4kV or more in which the corona discharge happens. The speed is 0.7-1.2m/sec. On the other hand, the speed of the droplet sprayed from the Taylor cone is 6-11.5m/sec. Reneker[6] also measure the spinning velocity from the nozzle by the electro-spinning and it is 4.5m/sec and it almost agrees to the result by Umetzu. It is necessary to consider both the ion wind and the electrostatic force influences just under the nozzle.

When solution is sprayed from the nozzle under a high voltage, the solvent is a vaporize from the charged liquid drop. The charge density of the droplet increases and the fission of the droplet happen. It depends on coulomb repulsion powers in the droplet exceeding the surface tension. The charge density in which the divided of this droplet happens is called a Rayleigh limit. However, even if divided of this happens, the shape of the fiber is maintained in the polymeric solution. It is the electro-spinning. Divided doesn't happen because of the cohesion of polymer when the viscosity of solution rises further. Finally this nano fiber reaches the target electrode while drawing helical by the ion wind and swinging of it.
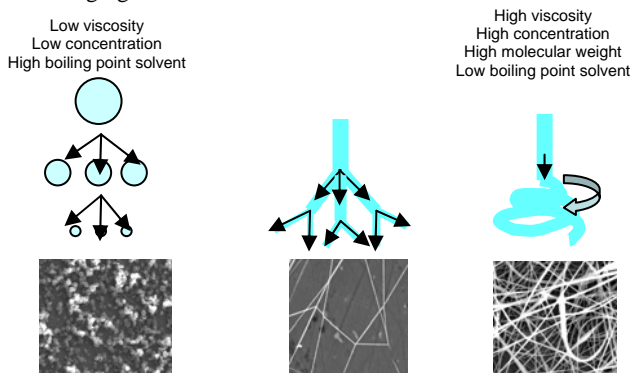

Fig. 4 Electro-spray and electro-spinning

3. Application of nanofiber to medical, sanitary and cosmetic

Fiber of nano order (10-500nm) can be easily made by the electro-spinning process, and a lot of researches that use it for medical application are done. We report on a recent nanofiber research of collagen, the polylactic acid, and PET. After acidic solution I-PC of collagen (height laboratory) had been lyophilized, it was dissolved to 2.2.2- trifluoroethanol. The polylactic acid of the L-isomer, the DL copolymer (The L-isomer: racemic isomer =70:30), and the racemic isomaer (D:L=50:50)(Aldrich) were dissolved to the mixed solvent of chloroform/DMF/acetone. PET was dissolved to the mixed solvent of HFIP. The antibacterium of PET of titanium oxide (TiO_2) 5wt% addition was done in accordance with JIS L1902. The collagen solution was made a sponge by the freeze-drying. Figure 5 shows the SEM photograph of the obtained collagen nano fiber. The mean diameter of the fiber was 200 nm. Moreover, the distribution was very narrow. Gelatin (Nitta gelatin) and peptide (Meisho) were able to be made a nano fiber by using a similar solvent.
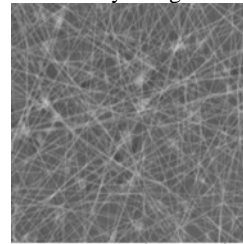

Fig. 5 Collagen nano fiber

As for the polylactic acid, the fiber diameter of D L-isomer was the thickest. Fiber diameter was able to be controlled by changing the concentration and the solvent. As for the weight decrease by biodegradation, the racemic isomer was the largest. It originates in the small molecular weight of the racemic isomer and its amorphous structure.
PET is used for the biomaterial. Table 1 shows the antibacterium of PET nanofiber.

Table 1 PET/TiO_2 nano fiber antibacterium test result
Viable count of 18 hours action (test specimen hit)

Sample	0 hr.	18 hr
Original	1.4×10^4	4.2×10^7
E. coli		$1.2\times10^5 1$
Yellow grape bacterium		3.8×10^5
Salmonella		1.1×10^5

The titanium oxide used here is a type to modify the surface so as not to cause the degradation of PET. It has been understood to suppress breeding of the bacterium though this doesn't show a positive antibacterium. Therefore, the antibacterial effect is expected to be exerted without giving the living body harm by using this PET nano fiber for the biomaterial.
Moreover, the nano fiber was electro-spun on the stick (10mm) of high speed rotary (3000rpm) for the artificial vessel making. The nano fiber oriented in the direction of the circumference though they were the interlocking three dimensions. It kept enough strength.
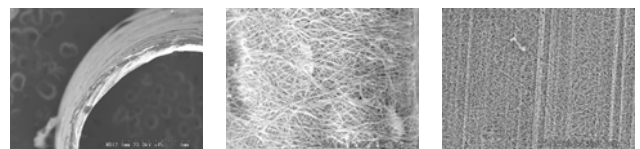
(a)General view   (b) Section   (c) Surface
Fig. 6 Artificial blood vessel model that consists of nanofiber made with high speed rotary electro-spinning device

4. Problem to industrialization

Present production capacity by the electro-spinning is presumed to be 20m/min. The amounts of the exhalation from one spray nozzle (spinneret) are 0.02 ml/min on the average. In 10wt% of the polymer concentration, the amount of polymer from one spray is 0.002g/min. A lot of problems for the improved productivity exist; Shape of nozzle, nozzle arrangement, nozzle washing, solvent elimination from nanofiber and the atmosphere, thickness controls of nonwoven etc.

4.1 Nozzle washing
Taylor cone in the point of the nozzle solidifies at once in the spray from the polymer solution that uses chloroform with a fast vapor rate as a solvent. Therefore, it is necessary to use the mixed solvent. It is unnecessary for water and DMF that the vapor rate of the solvent is slow. However, the nanofiber might adhere to the point of the nozzle when it is made for a long time. This is because the nanofiber sprayed in the air once is attracted to the nozzle side again. We are wiping the nozzle dirt off periodically by the Kim wipe wrapped around the insulation stick. Some devices move the nozzle head to the washing wiping off part, and removes dirt rubbing the nozzle there. However, it is difficult to move the entire nozzle because there are a lot of numbers of the nozzle in the industrialization device. Therefore, there are a method of wiping the entire nozzle with the washing tool and a method of removing dirt by spraying air on the nozzle etc. periodically. The nozzle comes not to be blocked easily even if the amount of the supply of solution is increased and the droplet in the nozzle is dropped periodically as a dripping. However, solution is considerably lost. Moreover, the nozzle arrangement that the droplet doesn't drop on the target is needed in this case. There is little report and challenges of the future.

4.2 Removal of solvent and drying of sample
Most solvents are vaporizes at the same time as being able to do the nanofiber. However, it is deposited on the target with the solvent contained when the nanofiber is sprayed from the multi nozzle voluminously. It depends on saturating atmosphere with the solvent. The solvent doesn't remain by the rotation of the drum and the traverse of the syringe in the nanofiber in the single nozzle experimental device. However, this is an acute problem in the industrial device. The drying process of the nanofiber is necessary for industrialization. Therefore, the nozzle should do the dispersion array. Moreover, heating of solution and nozzle part, decreases in the atmosphere humidity, and the substitutions of the atmosphere gas, etc. are needed.

4.3 Making of Nano fiber nonwoven with thickness
It is difficult to make the nanofiber nonwoven with the thickness. If the charge is not removed from the nanofiber, a thick lamination cannot be obtained. Therefore, the nonwoven of the thickness 1cm cannot be made yet. It doesn't go well easily even if the removal of the surface of the nanofiber nonwoven being charged is tried by using the commercially available static eliminator. The nanofiber adheres to other places except the drum electrode of the device. And, the nanofiber adheres to another place of the nozzle and the device. Therefore, the wall thickness sample was obtained by accumulating the nonwoven. The nonwoven with such a thickness is used for the cell culture medium etc.

4.4 Production speed
The weight for unit area of the nanofiber nonwoven by the electro-spinning process is easily computable in the next expression.

$$P = \frac{g \times w \times nL}{100 \times L \times \tan(\theta / 2) \times 2 \times R} \qquad (2)$$

P(g/m^2):polymer weight for unit area, g(ml/min): amount of exhalation from the single nozzle, w(wt%):concentration of polymer solution, L: Distance between nozzle and electrode (However, a straight spray length from the nozzle is excluded), :Angle to which nanofiber scatters, R(m/min):Production speed, nL: number of nozzle in the line direction, nW: Number of nozzle in the width direction, N: total nozzle number ($N=nL \times nW$).

For example, for L=0.05m, 40° , R=20m/min, nL becomes 40 (P=0.1g/m^2) and 192(P=0.5g/m^2) and 400(P=1.0g/m^2) respectively. The number of the nozzle in the width direction is 20 in the nozzle spacing 3cm in W=0.6m. Therefore, number N of all nozzles is 800 in 0.1g/m^2, and is 3840 in 0.5g/m^2, and becomes 8000 in 1.0g/m^2. We developed the industrial electro-spinning device of 1000 numbers nozzle in which it provided with the solution supply control and the thickness control (Fig.7). The width of the coating is 0.6m. As a result, the practical application test of the filter or the surface coating is possible. We developed the laboratory test machine that corresponded to intermedius of one nozzle and an industrial device (Fig. 8). It is also possible that this device freely changes how to put it.
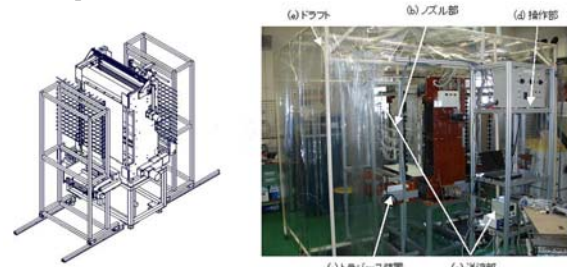

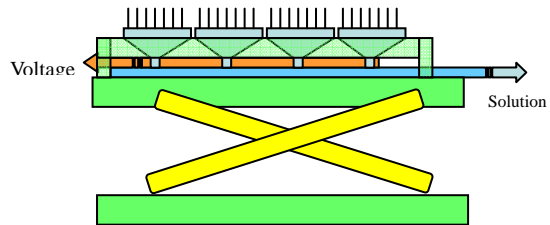Fig.7 Industrial electro-spinning device of 1000 numbers nozzle

Fig.8 Lab multi-nozzle electro spinning device

The number of the nozzle is adjustable to change the rotundate multi-nozzle. The spray from the upper part to the lower side is also possible.

5. Multi nozzle

5.1 Basic design
To evaluate the performance of the multi nozzle, the nozzle of some shape was made for trial purposes (Fig.9). It is necessary to devise the shape of the nozzle with the device used.

Num. of Nozzle
Nozzle distance

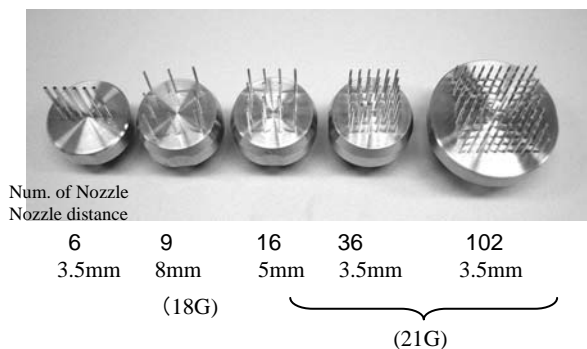| 6	9	16	36	102
3.5mm	8mm	5mm	3.5mm	3.5mm
	(18G)			

(21G)

Fig. 9 Multi nozzle of various shapes

The distance between nozzles (lower side) and number of nozzle (upper part)

Because a solution flow in the nozzle and the electrostatic repulsion between nozzles relate complexly each other, the nozzle design is not easy. Nozzles that arrange commercially needles to the row can be used. This can arbitrarily change the nozzle spacing (the least 10mm).
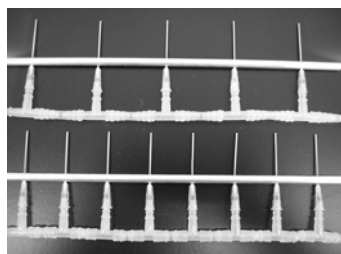

Fig.10 Handmade multi nozzle

The distance between nozzles can be freely set. The needle is disposable. The distance between nozzles is 50mm (upper) and 20mm (under).
Kim[7] analyzed the relation between the nozzle geometry and the fluid flow. It is necessary to devise shape in the conic upper part of the nozzle so that the amount of the exhalation from each nozzle may become uniform. We designed a multi nozzle that was thin in the core part and thick in the circumference part.
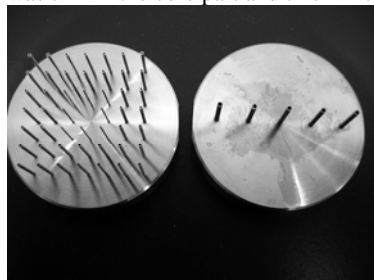

Fig.11 Several type multi nozzle

Left: combine nozzle of inside diameter 21G and outside diameter 27G
Right: arrange five numbers of nozzle in line

5.2 Problem of multi nozzle
Many problems exist in the multi nozzle. The droplet bonds mutually when the nozzle spacing is narrow. It is not sprayed straight for electrostatic repulsion in the nozzle. In addition, the exhalation from the nozzle becomes unstable because of a high

voltage. Figure 13 showed the relation between the number of the multi nozzle and the weight of the obtained nanofiber nonwoven. The vertical axis is weight of the nanofiber sprayed on surface ($0.047m^2$) of the target drum in one minute. White circle is a

measurement result, and dotted line is a multiple of the number of the nozzles. The exhalation efficiency is 0.5-0.55 regardless of the number of the nozzle. It is a ratio of a theoretical value and an actual value. The amount of the exhalation of the ideal is sure to become the number of the multi nozzle. However, the fluid dripping happens when making it like that. Therefore, the multi nozzle is very difficult.
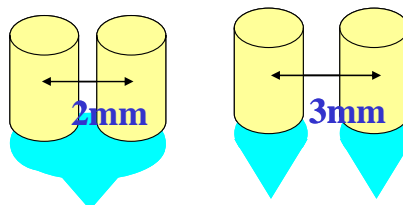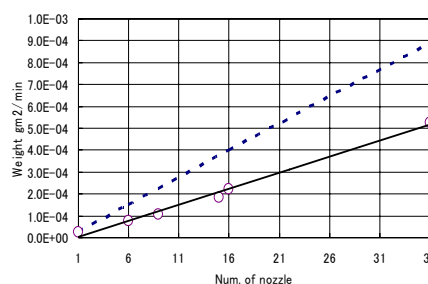

Fig. 12 Bonding of droplet

Fig.13 Relation between the number of the multi nozzle and the weight of the obtained nanofiber nonwoven

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