Establishment of Nanofiber Preparation Technique by Electrospinning

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Abstract : We examined the applicable developments of the electrospinning device and the conditions for producing nanofiber on some polymers within the range of lab-scale to manufacturing. It is understood that the use of multi-nozzle heads is more effective than increasing the flow rate. The solution concentration is an important factor for the control of the fiber diameter of the nanofiber. Moreover, it has been understood the nanofiber that uses the electrospinning process is to apply it to medical, cosmetics, and sanitary goods.

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1. Introduction

Electrospinning[1-5] (referred to as the electro spray deposition method, electric field spinning method, electrostatic spinning method, and electric spinning method) is a yarn-weaving process derived from the balance of surface tension and the electrostatic force of the polymer solution. This idea was presented in 1934. Research on practical applications and industrialization is scarce, though a lot of research has been done on a laboratory-scale for nanofiber processing employing this method. In the industrialization of the nanofiber produced through the electrospinning process, currently the most feasible material is Polyvinyl alcohol (PVA), Polyethylene oxide (PEO), Polyacrylonitrile (PAN), Nylon, Polylactic acid (PLA), and Polyurethane (PU). But this spinning process is basically solution-spun, and the amount of the polymer fiber produced per nozzle is 0.01g/min or less, which is extremely low compared to the 0.15-0.5g/min derived from the melt-blowing method. Therefore, the multi-nozzle system (accumulation of the nozzle) is needed for improved productivity. We examined the applicable developments of the electrospinning device and the conditions for producing nanofiber on some polymers within the range of lab-scale to manufacturing.

2. Experimental

There are three basic kinds of electrospinning devices as follows.

1) A simple device that is constructed in the laboratory.

2) A practicable laboratory device that had a constant speed-syringe-piston movement (0.02ml/min), rotating drum, and syringe movement (transversal) systems.

3) A general-purpose laboratory device (Fig. 1) with spark measures and a solvent pumping system. These devices are electrospinning devices (an NEU nanofiber electrospinning unit) jointly developed with Kato-Tech Ltd..

A Hitachi scanning electron microscope Model S-3200N was used for the observation of fiber diameters. Fiber diameters were measured using Scion Image image-processing software (Scion Corporation). For polymer assessment, PAN (Mw : 150,000, Scientific Polymer Products, Inc) and PLA were used. The PLA (LACEA, Mitsui Chemical) of the L-isomer (H-100), the DL copolymer (H-400, H-440), and the racemic isomer (D : L=50 : 50, H-280) were dissolved into the mixed solvent of chloroform/ dimethyl formamide (DMF) /acetone. Other samples such as collagen and PET were used. After the acidic solution I-PC of collagen (Koken) had been lyophilized, it was dissolved to 2,2,2- trifluoroethanol.

Fig. 1 Nanofiber electrospinning device (Kato-Tech Co. Ltd.)

Fig. 2 Collagen nanofiber

Fig. 2 shows the SEM photograph of the obtained collagen nanofiber. PET (NEH2070, Unitika) was dissolved into the mixed solvent of hexa fluoro isopropanol (HFIP). The addition of antibacterium of PET of titanium oxide (TiO₂, Fuji Titan TA-500) 5wt% was conducted in accordance with JIS L1902. The collagen solution was derived from a sponge through freeze-drying.

3. Result and discussion

3.1 Nanofiber to medical, sanitary and cosmetic

Fiber on the order of nano-dimensions (10-500nm) can be easily made using the electrospinning process, and a lot of researches on medical applications have been conducted. The mean diameter of the collagen nanofiber was 200 nm. Moreover, the distribution was very narrow. Gelatin (Nitta gelatin) and peptide (Meisho) were also able to form nanofibers using a similar solvent.

As for the polylactic acid, the fiber diameter of the DL-isomer was the thickest. The fiber diameter was able to be controlled by changing the concentration and the solvent. As for the weight decrease by biodegradation, the racemic isomer proved to be largest. This arises from the small molecular weight of the racemic isomer and its amorphous structure. PET is used for the biomaterial. Table 1 shows the antibacterial effects of PET nanofiber. The titanium oxide used here is a type that modifies the surface so as not to cause the degradation of PET. It has been understood to suppress the breeding of bacterium though this doesn't show positive antibacterial properties. Therefore, the antibacterial effect is expected to be

Table 1 PET/TiO₂ nanofiber antibacterial test (conforms to JIS L 1902).

Bacterium kind	0 hr.	18 hr.
E. coli (control, filter paper)	1.4×10^4	4.2×10^7
E. coli	1.4×10^4	1.2×10^5
Staphylococcus aureus	2.3×10^4	3.8×10^5
Salmonella	1.1×10^4	1.1×10^5

Fig. 3 Artificial blood vessel model that consists of nanofiber made with high speed rotary electrospinning device

exerted without harming living organisms using this PET nanofiber for the biomaterial.

Moreover, the nanofiber was electro-spun on the stick ($\phi 10\text{mm}$) of a high-speed rotary (3000 rpm) for the creation of artificial vessels. The nanofiber oriented toward the circumference though these were the interlocking in three dimensions and maintained sufficient strength (Fig.3).

3.2 PLA Nanofiber

Poly(lactic acid) has received attention as a resin exhibiting biodegradability. The conditions for nanofiber preparation condition while spraying it from four kinds of PLA chloroform solutions were examined. It is understood that nanofiber with PLA in concentration 8wt% can be created ; however, the distribution of the diameter of the nanofiber from the chloroform solution is wide. Moreover, the nozzle becomes blocked. These problems originate because the vapor rate of chloroform is fast. Fig. 4 shows the relation between solution concentration $c \times$ molecular weight M_w and the fiber diameter. It is understood that four kinds of PLA exhibit similar fiber diameters regardless of the structure of the polylactic acid.

3.3 Industrialization

The current production capacity through electrospinning is presumed to be 20m/min. The amounts

Fig. 4 Relation between solution concentration $c \times$ molecular weight M_w and fiber diameter

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. Many problems are encountered in an attempt to improve the production yield. The factors influencing the productivity of electrospun fibers include nozzle shape, nozzle arrangement, nozzle washing, solvent elimination from nanofiber and the atmosphere, thickness controls of nonwoven fiber.

3.3.1 Nozzle washing

The Taylor cone in the point of the nozzle solidifies instantly in spray from a polymer solution that uses chloroform with a fast-vapor rate as a solvent. Therefore, it is necessary to use a mixed solvent. This is unnecessary for water and DMF which have a slow vapor rate for the solvent. However, the nanofiber might adhere to the point of the nozzle when used at length. This is because the nanofiber sprayed in the air once is attracted back to the nozzle side again. In our apparatus, nozzle dirt was wiped off periodically with a paper wiper wrapped around the insulation stick. Some devices move the nozzle head to the area washed and wiped to remove dirt rubbing the nozzle here. However, it is difficult to move the entire nozzle due to the large number of nozzles in the industrial devices. Therefore, a method of wiping the entire nozzle with a washing tool and a method of periodically removing dirt by spraying air on the nozzle currently exist. This easily alleviates nozzle blockage even if the supply of solution is increased and the droplets periodically form to cause drips, resulting in a considerably lost of output. As yet, there is little work done on this and it will provide a challenge for future research.

3.3.2 Solvent removal and drying samples

Most solvents evaporate at the time of nanofiber formation. However, the solvent tends to deposit on the target along with the nanofibers as they are sprayed from a multi-nozzle in large volumes. This relies on saturating the atmosphere with the solvent. The solvent doesn't remain due to the rotation of the drum and the traverse of the syringe in the nanofiber in the single nozzle experimental device, but the solvent residue proves to be an acute problem in the industrial devices. A drying process for the nanofiber is necessary in industrial processing; therefore, the nozzle should form the dispersion array. Moreover, heating the solution and part of the nozzle decreases humidity in the atmosphere, and measures such as substitution of the atmospheric gas are required.

3.3.3 Making of thick Nanofiber nonwoven

It is difficult to make thick nonwoven nanofiber if

the charge is not removed from the nanofiber after it reaches the ground electrode. Nonwoven nanofiber with thickness greater than 1cm has yet been produced. The processing is difficult even if the removal of the on the surface of the nonwoven nanofiber is removed with commercially available static eliminators. The nanofiber tends to deposit on other surface than on the drum electrode of the electrospinning device. Further, the nanofiber adheres to other areas of the nozzle and the device. Therefore, a wall thickness sample was obtained with accumulated nonwoven nanofibers. These thicker nanofibers are used for applications such as cell culture media.

3.3.4 Production speed

The areal density or weight per unit area of the nonwoven nanofiber by electro-spinning process can be computed using the following equation :

$$P = \frac{g \times w \times nL}{100 \times L \times \tan(\theta/2) \times 2 \times R} \quad (1)$$

where P (g/m²) : polymer weight for per unit area ; g (ml/min) : amount of exhalation from the single nozzle ; w (wt%) : concentration of polymer solution ; L : distance between nozzle and electrode (excluding a straight spray length from the nozzle) ; θ : angle to which nanofiber scatters ; R (m/min) : production speed ; nL : number of nozzles in the line direction ; nW : number of nozzle in the width direction ; N : total nozzle number ($N = nL \times nW$).

To illustrate further, with $L = 0.05$ m, $\theta = 40^\circ$ and $R = 20$ m/min, nL becomes 40 ($P = 0.1$ g/m²) and 192 ($P = 0.5$ g/m²) and 400 ($P = 1.0$ g/m²) respectively. The number of nozzles in the width direction is 20 with a nozzle spacing of 3cm in $W = 0.6$ m. Therefore, the number N of all nozzles is 800 in 0.1g/m², 3840 in 0.5g/m², and becomes 8000 in 1.0g/m². We developed an industrial electrospinning device with 1000 nozzles provided with a solution supply control and thickness control (Fig.5). The

Fig. 5 Industrial electrospinning device

Fig. 6 Experimental multi-nozzle electrospinning device

width of the coating is 0.6m. As a result, the practical application test of the filter or the surface coating becomes possible.

We developed a laboratory test machine that corresponded to the intermedius of a single nozzle and an industrial device (Fig. 6). It is also possible that this device can be configured according to specific needs. The number of nozzles is adjustable by changing rotundate multi-nozzles. Spray from the upper part to the lower side is also possible.

3.4 Multi nozzle

3.4.1 Basic design

To evaluate the performance of the multi-nozzle heads, nozzles of various shapes were made for trial purposes (Fig.7). It is necessary to devise the shape of the nozzle to the device used.

Fig. 7 Multi-nozzle heads of various shapes
Number of nozzle (upper part) and nozzle inner diameter size (down part)

Because of the complex interaction between solution flow in the nozzle and the electrostatic repulsion the design of the nozzles needs a great deal of care. Nozzles that arrange commercially available needles in rows can be used (Fig.8). And nozzle spacing can be arbitrarily altered (to at the least 10mm). The distance between nozzles can be freely set. Needles are disposable, and the distance between nozzles is 50mm (upper) and 20mm (under). Kim [6] analyzes the relation between the nozzle geometry and the fluid flow and states that it is necessary to devise their shape in the conic upper part of the nozzle so that the amount of the exhalation from each nozzle more readily becomes uniform. We designed a multi-

Fig. 8 Handmade multi-nozzle

Fig. 9 Several type multi nozzle

Left: Nozzle combination with an inside diameter 21G and outside diameter 27G.
Right: Arrangement of five nozzles in one line.

nozzle that was thin in the core area with a thick circumference (Fig.9).

3.4.1 Problem of multi nozzle electrospinning

There are many problems associated with multi-nozzle electrospinning. Droplets tend to bond together when the nozzle spacing is too narrow (Fig.10). And the spray exhalation is not straight enough for electrostatic repulsion in the nozzle. In addition, the exhalation from the nozzle becomes unstable because of a high voltage. Fig. 11 shows the relation between the number of multiple nozzles and the weight of the nonwoven nanofiber produced. 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 ideal amount of exhalation is equal the number of multiple nozzles. However, fluid dripping occurs when multi-nozzle arrays are used; therefore, the use of multinozzle head electrospinning is very challenging.

Fig. 10 Bonding of droplets

Fig. 11 Relation between the number of the multiple nozzles and the weight of the obtained nonwoven nanofiber. (circle & line ; experimental, dotted line ; ideal)

4. Summary

(1) To industrialize the processing of nanofiber using the electrospinning method, it is understood that the use of multi-nozzle heads is more effective than increasing the flow rate. (2) The efficiency of the multi-nozzle heads was found to be 50%, due to the electrostatic repulsion between nozzles. (3) The solution concentration is an important factor for the control of the fiber diameter of the nanofiber. By changing the solution concentration, going from particles to nanofiber became possible. (4) As for forming polylactic-acid nanofiber, a mixed solvent of solution concentration of 8wt% and a chloroform/DMF weight ratio of 8 : 2 is optimal. (5) It was possible to make artificial blood vessels with intertwined nanofiber

in three dimensions using high-speed rotation of a small diameter target drum.

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