Fabrication of Aligned Electrospun Nanofibers by Inclined Gap Method

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ABSTRACT: A high-performance of uniaxial alignment of electrospun nanofibers was realized by introducing an inclined gap into dual collectors that consisted of two conductive strips. Because the two strips that were configured horizontally and vertically had a height difference from the inclined gap, the electrospun nanofibers were sequentially suspended across the edges of strips in a well-aligned and regularly distributed form. Some parameters, such as concentration of solution, applied voltage, and spinning distance were considered for the successful suspension and formation of the aligned electrospun fibers. The method could improve the properties of nanofiber alignment and allow for easy transfer onto other solid substrates or devices. The alignment technique used polycaprolactone, which resulted in continuous and well-aligned nanofibers with diameters ranging from 500 to 700 nm. Furthermore, it is suggested that repetitive transfer be used to achieve a higher density of aligned nanofiber arrays. This would enlarge the applicability of nanofibers, especially for the tissue engineering field. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 1800–1807, 2011

Key words: electrospinning; inclined gap method; aligned nanofiber; repetitive transfer

INTRODUCTION

Recently, the use of one-dimensional nanoscale structures, such as nanorods, nanotubes, nanowires, and nanofibers, has been increasing for their specific potential applications.[1] Electrospinning is a simple and versatile process that can produce nanofibers in diameters ranging from micrometers to nanometers. This technique uses electrostatic force from a high voltage, where the most typical form of as-spun fibers is a randomly configured nonwoven mat.[2–4] As for being suitable materials, these nanofibrous mats have a wide range of applications, such as filter media, clothing material, composite reinforcement, sensors, drug delivery system, and tissue engineered scaffolds.[5] Meanwhile, the current interest in the electrospinning methods has been concentrated on other forms of nanofibers, especially uniaxially oriented arrays of nanofibers, to expand their applications.

There have been several proposals on how to fabricate the aligned nanofibers from various angles. There have been two kinds of techniques where well-aligned and highly ordered architectures could be realized. One method has the rotating object used as collector.[6–9] For this method, a cylindrical mandrel,[6,7] a thin disk with a sharp edge,[8] and a spaced wire drum[9] were used as the rotating grounded collectors. The nanofibers from the sharp edge of the disk in these methods were reported as providing better alignment than the other methods. However, it was not easy to collect a wide area of aligned nanofiber arrays because of the geometrical limitation of the disk collector. On the other hand, the techniques of the other methods can fabricate the aligned nanofibers by using static and separated conductive electrodes, which is known as the gap method.[10–14] When the two pieces of parallel electrodes are placed with a gap, the electric field lines adjacent to the electrodes are split into each edge of the electrodes. Thus, electrospun jets are stretched and aligned across the gap by the electrostatic field profile and the repulsive force caused by the residual charge of the nanofibers.[10]

The purpose of this study was to improve the alignment quality of the electrospinning nanofibers at the base of the gap methods. A simple reconfiguration was used between the separate electrodes. Compared with the planar configuration of the electrodes in the previous gap methods, the suggested collector used included an inclined gap determined by the placement of a horizontal and a vertical conductive strip with their mutual height difference. Because of the height difference, a suspension of the electrospun nanofiber occurred in turn at the edge of the lower strip after it occurred at the upper strip. Thus, continuous and well-aligned fiber arrays could

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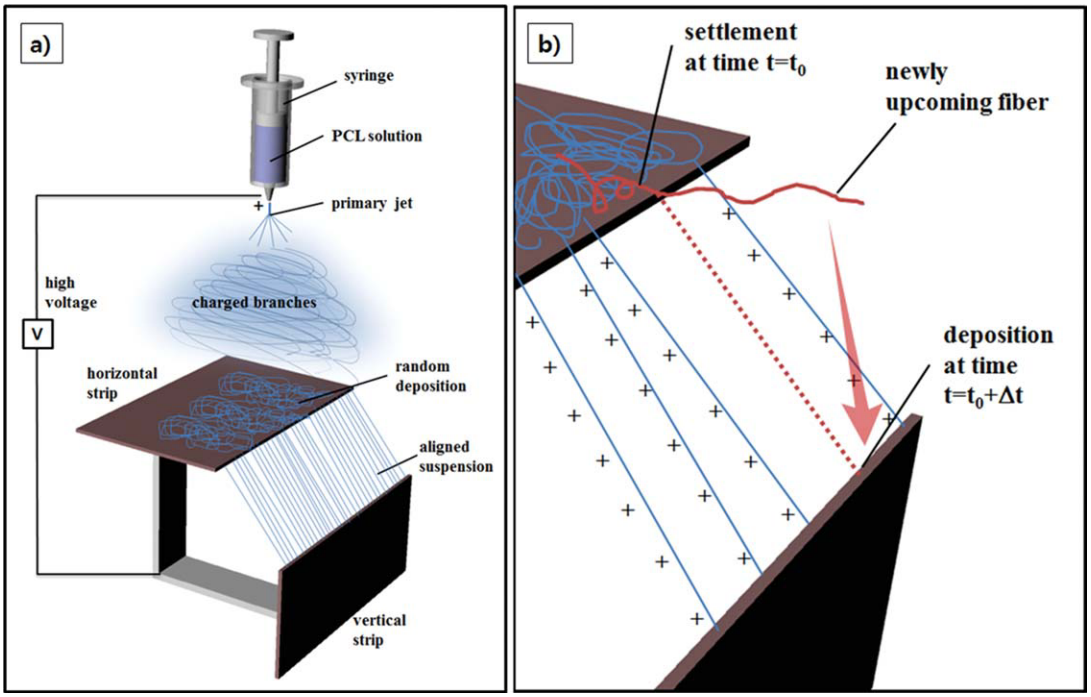

Figure 1 Schematic diagram of the used electrospinning setup for the proposed inclined gap method. (a) the setup for electrospinning; and b) the nanofiber suspended sequentially across the inclined gap. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

be fabricated. It was caused by more space and time for self-alignment as well as by more effective stretching force during the sequential suspension. We herein used the nanofiber alignment technique, i.e., an inclined gap method, using polycaprolactone (PCL), which has been widely used in the tissue engineering field. Additionally, repetitive transfer was carried out to overcome a low-density limitation caused by the residual charge of each fiber.

EXPERIMENTAL

Materials

PCL (average $M_n \sim 80{,}000$) was supplied by Aldrich (Milwaukee, WI). Methylene chloride (Junsei Chemical, Japan) and *N*,*N*-dimethyl formamide (Junsei Chemical) were used as the solvents for the spinning solutions. PCL was dissolved in a mixture of methylene chloride and dimethyl formamide (75/25 v/v) at four different concentrations (10, 14, 18, and 22 wt %). These solution systems were tested to figure out a proper condition for the spinning solution in this method.

Electrospinning setup

In electrospinning, the electrically charged jets that erupt from a Taylor cone undergo stretching and travel toward objects with lower electric potential. As the jet moves along the electric field lines, it is accompanied by solvent evaporation, which results in the formation of nanofibers on the target object. During the process of jet movement and stretching, the charged jets are influenced by the electrostatic field profile spread between the nozzle tip and the collecting target. When two conductive objects are placed at the collecting position in a parallel configuration, the electric field lines divided into two fractions can make the electrospun fibers orient themselves across the gap between the collectors.[10]

In this study, a rearrangement of two conductive strips was created by using an asymmetric configuration that included vertical and horizontal placements of the strips. Figure 1(a) shows a schematic of the suggested electrospinning setup. The collector consisted of two thin aluminum strips (0.2 mm thickness). As one was fixed horizontally at the upper position and the other was anchored vertically at the lower position, there was an inclined gap between the two strips. The inclined angle and the gap width were determined to be 45° and 30 mm, respectively.

A flat-tipped needle (0.29 mm inner diameter, stainless steel) was placed upward at a distance from the horizontal strip (80 and 160 mm) and connected to a power supply to apply high voltage from 6 to 20 kV between the needle and the collector. A 10-mL syringe with the needle was equipped on a microinfusion, and the prepared PCL solutions were extruded through the needle at a constant rate of 0.6 mL/h. Uniaxially aligned nanofibers were

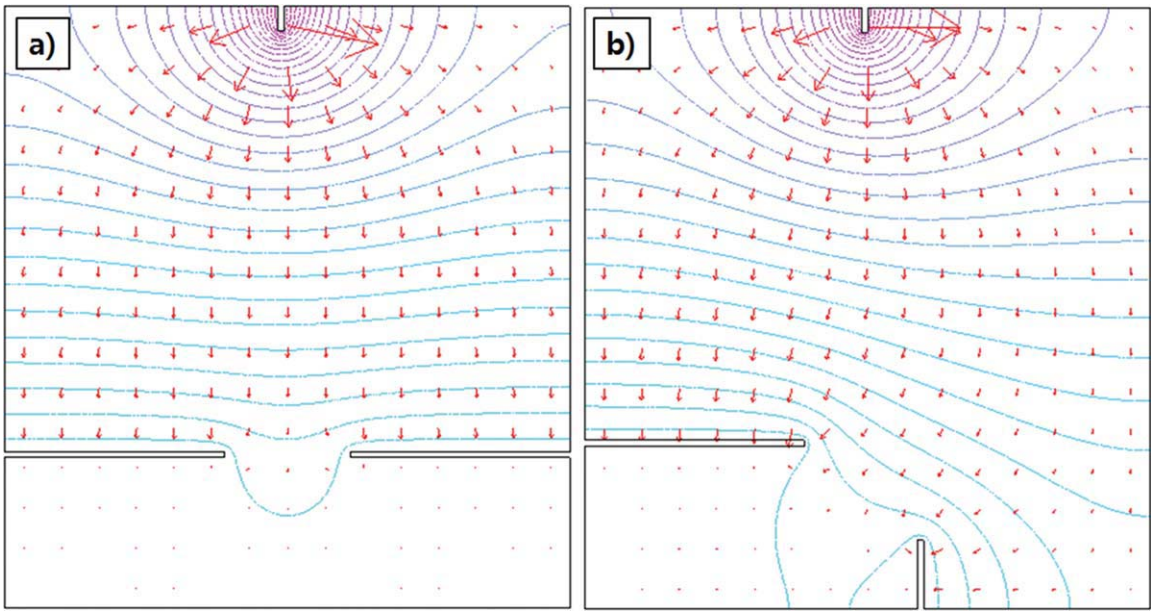

Figure 2 Calculated equipotential lines and electric field strength vectors between the needle and the collectors. (a) Symmetrical distribution of the electrostatic field in the region around the collectors with planar configuration. (b) Asymmetrical distribution of the electrostatic field because of the modified configuration of the collectors. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

suspended across both edges of the upper and lower strip and transferred onto a surface of slide glass (76×26 mm^2, 1 mm thickness). This process of collecting and transferring in sequence was repeated several times. As a result, quantitatively controlled densities of the nanofiber array were obtained depending on the number of transfers.

Characterization of aligned electrospun nanofibers

The resultant samples that were transferred with electrospun nanofibers were photographed using a scanning electron microscope (JSM-6300, JEOL) at an accelerated voltage of 10 kV after gold-sputtering onto the samples. Several images were captured by using the scanning electron microscope side by side transversely for measuring the fiber alignment. Bent, looped, and discrete fibers were excluded, and only straight fibers were analyzed. The angle distribution of each nanofiber was measured from the scanning electron microscopy (SEM) images by using ImageTool 3.0 (University of Texas Health Science Center in San Antonio, TX).

RESULTS AND DISCUSSION

Effect of inclined gap

It has been known that the influences of the electric field on the spun fiber morphology and collecting construction are extremely important.[15–18] As has been investigated previously,[10–14] separating the conducting collector by void or insulating gap allows for the self-alignment of fibers and stretching of spun jets because of the field line split toward both edges of the collectors. However, what is different here from the previous gap methods is the introduction of an inclined void gap between the two strips, where one is placed horizontally and the other is erected vertically at a lower location than the horizontal one.

To verify the effect of such an asymmetrical configuration of the strips, the distribution and shape of the electrostatic field among the needle and the collectors were simulated by using the analysis software FEMLAB 3.0. Figure 2(a,b) shows the calculated results, including the equipotential lines and electric field strength vectors in the region around the needle and the collector. As shown in Figure 2(a), when the collectors were disposed in a planar way, the lines and vectors are symmetrically distributed along a center-line from the needle tip to the middle point of the gap. In this case, the charged as-spun fibers affected by the split electrostatic force toward each edge of the collector would settle almost simultaneously at both edges of the collector. Although the two collectors were placed on the same flat [Figs. 2(a) and 3 (a)], one of the collectors was positioned endways lower than the other one, as shown in Figures 2(b) and 3(c). As we get closer to the vicinity of the collectors in this case, the shape of the equipotential line becomes asymmetric for the center-line. Additionally, the vector arrows around the horizontal collector are formed stronger than those near the vertical one. Once the charged fiber has moved through the distributed vector field, one

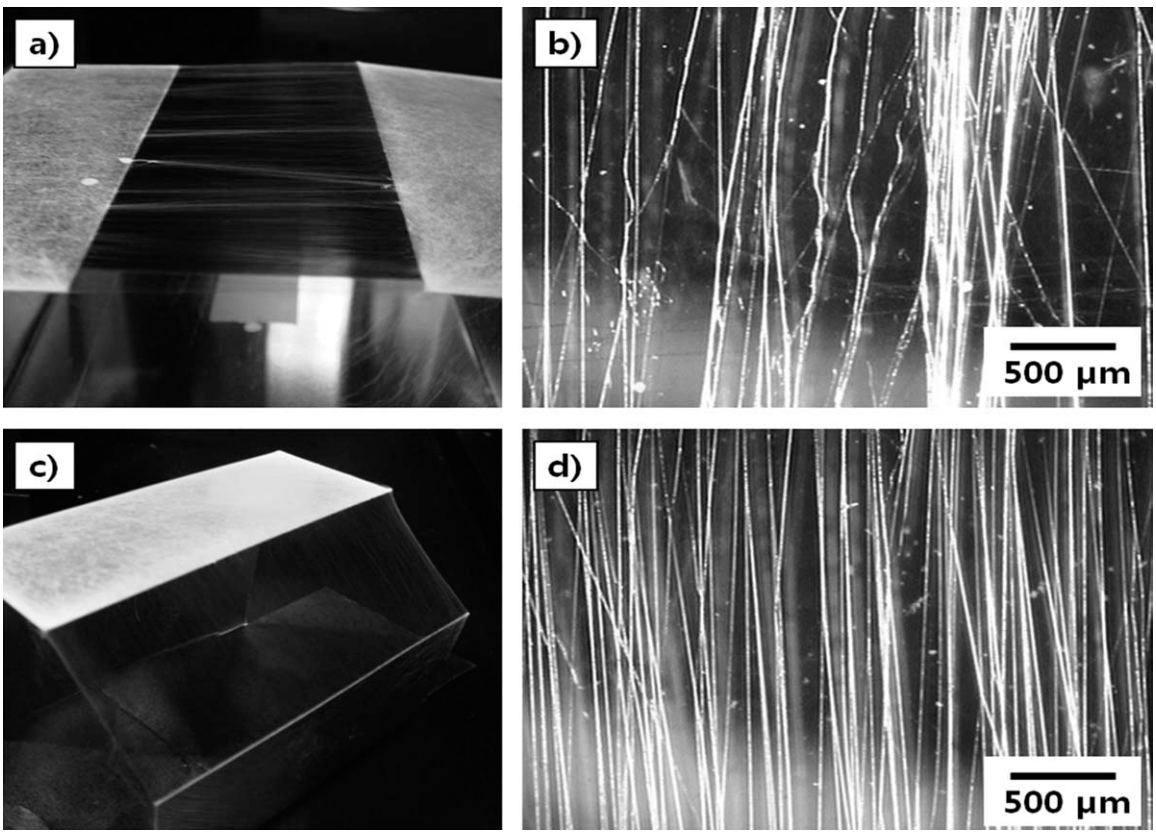

Figure 3 Photographs of the collectors with the supended nanofibers on (a) the planar gap and (c) the inclined gap. Optical micrographs of parts of the nanofiber arrays on (b) the planar gap and (d) the inclined gap.

spot of the fiber will contact and be deposited onto the edge of the horizontal collector. After the prior settlement, the fiber is stretched out toward the edge of the vertically erected collector, and a posterior deposition subsequently occurs to attain the final suspension across the gap [Fig. 1(b)]. During the process of the charged fiber suspension, the electrostatic repulsion acting between the fibers can promote parallel alignment. When the configuration of the collectors has a height difference, such as that shown in Figures 1(b) and 2(b), it can provide the suspension of the aforementioned time difference, where the alignment is expected to be further enhanced because of more time and space needed for the alignment effect by the mutual repulsion between the fibers. Figure 3 shows the experimental results on the difference between the planar gap and the inclined gap. Both the straightness of each fiber and the regularity of the fiber distribution in the case of the inclined gap [Fig. 3(c,d)] seemed to be in better conditions than the planar case [Fig. 3(a,b)]. From these results, it could be considered that the more stretch and repulsion that were caused by the sequential settlement at the edges of the inclined gap exerted a favorable influence on the fiber alignment and distribution. The electrospinning conditions included the applied voltage of 11 kV, solution concentration of 18 wt %, spinning distance of 160 mm, and spinning time of 40 s. The enlarged images of the fiber arrays were observed by an optical microscope (i-Camscope, Sometech Vision).

Figure 4 compares the accumulated fibers on the surface of the horizontal collector and the suspended fibers across the inclined gap. As shown in Figure 4(a), the fibers deposited on the upper (horizontal) collector were randomly oriented like typical electrospun fibers. In contrast, the fibers anchored at both of the edges were well aligned in a direction across the gap [Fig. 4(b)]. It is notable that the suspended nanofiber had a thinner diameter range (500 $\sim$ 700 nm) than that of the directly deposited nanofiber (1 $\sim$ 6 μm). Such a drastic difference in the fiber diameter is attributed to the aforementioned stretch effect by the action of the electrostatic forces, which is the main factor for this fiber alignment technique.

Spinning conditions for successful suspension

Throughout the electrospinning technique to obtain the aligned nanofiber arrays along the inclined gap, one of the crucial requirements was the successful suspension of the fibers onto the collector gap. More specifically, the solidity of the spun jet became important when it reached the collector for the

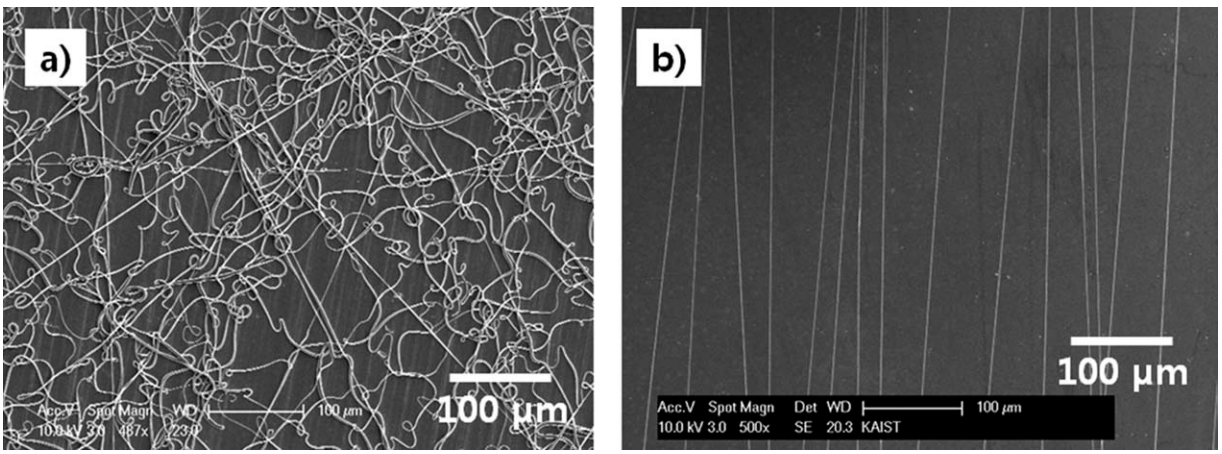

Figure 4 SEM images of (a) the randomly deposited nanofibers on the upper strip and (b) the uniaxially aligned nanofibers between the upper and lower strip edges.

suspension. As the spun jet underwent the stretching process and moved toward the collector, it was accompanied by solvent evaporation so that the liquid jet solidified. Unless the sufficient solidification has progressed, the resultant nanofiber from the jet tends to be collapsed during the suspension process because such liquid-like fiber is not sufficiently strong enough to withstand the electrostatic stretching force between the gap and the weight itself, as well as repulsive interactions with the upcoming and neighboring fibers. Considering the experimental parameters that affect the fiber condition in the typical electrospinning process, two factors for the successful suspension can be pointed out. First, the initial jet from the Taylor cone should be a relatively high concentration so that the spun fibers can hang onto the collector in a solid-like state. This is apparently related with the concentration of the material solution. The spinning distance, as well as the material parameter, from needle to collector should also be taken into account. In other words, the needle needs to be kept at a specific distance from the collector so that solvent evaporation sufficiently occurs. Although a suitable case in Figure 4(a), Figure 4(b,c) shows a worse case of less or unstable suspension because of the conditions of the low solution concentration and the short spinning distance, respectively. To figure out appropriate parameters for the successful suspension, some spinning experiments were carried out under the several conditions shown in Table I. As shown in Table I, there was no or less suspension in the conditions of 10 wt % solution concentration, regardless of the spinning distance [Fig. 5(b)]. This was attributed to insufficient solidification at the moment of suspension onto the collector, as discussed above. On the other hand, too high level of a concentration, such as the case of 22 wt %, makes the Taylor cone unable to form and the spun jets to function, even at a higher voltage. The condition of 18 wt % provided well-suspended and stable nanofibers in all the cases of short (80 mm) and long (160 mm) spinning distances. Furthermore, this condition, especially in the long spinning distance (160 mm), had a relatively wider range of applied voltage where stable formation and suspension of the nanofibers were more likely to occur than the lower concentration. Thus, from these results, subsequent studies used the conditions of 18 wt % concentration and 160 mm spinning distance. Also, using the similar parametric approach for the proper conditions of the solution concentration and the spinning distance, it can be expected that the other polymers besides the PCL may be applicable for this alignment technique.

Characterization of fiber alignment

Figure 4(b) gives a SEM image of a sectional region of the specimen on which the suspended fibers were transferred. The used conditions were as the aforementioned, including the solution concentration and

TABLE I
Electrospinning Conditions for the Successful Suspension

Solution concentration (wt %)	Spinning distance (mm)	Suspension quality	Valid range of voltage (kV)
10	80	△	–
10	160	△	–
14	80	△	–
14	160	○	13 ~ 15
18	80	○	10 ~ 14
18	160	○	8 ~ 18
22	80	×	–
22	160	×	–

(△), less or no suspension; (○), proper suspension; (×), no spinning.

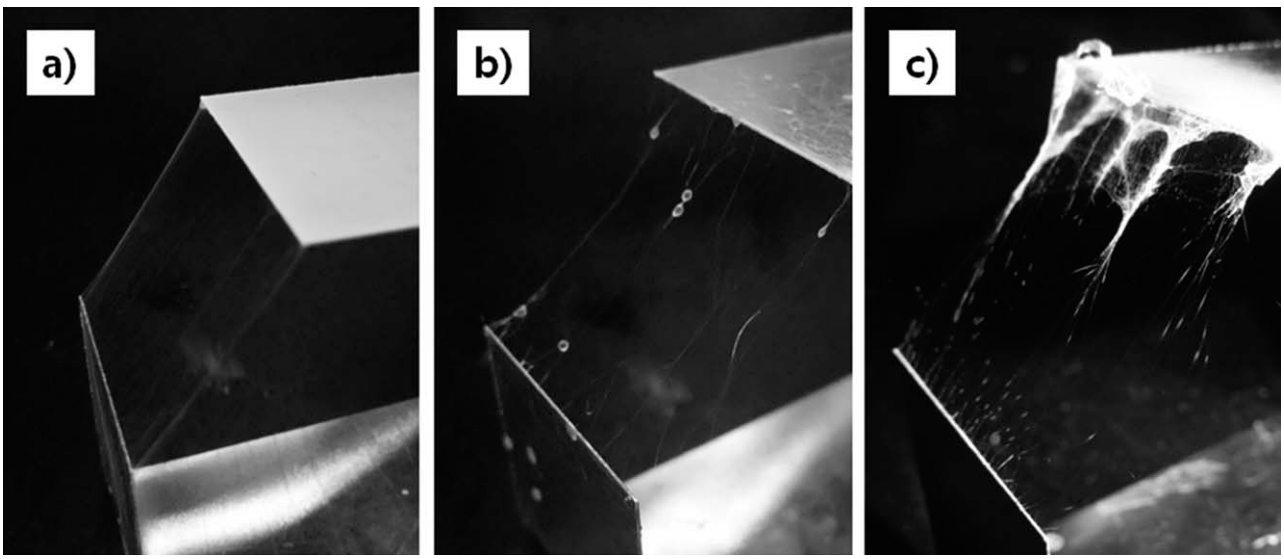

Figure 5 Photographs of (a) the successful suspension and the inappropriate suspensions because of (b) the low solution concentration (10 wt %, 160 mm distance) and (c) the short spinning distance (50 mm, 18 wt % concentration).

the spinning distance. The applied voltage and the spinning time were 11 kV and 30 s, respectively. Under these conditions, the morphologies of the most suspended fibers were uniformly well-aligned, straight, and continuous, whereas the broken or bent fibers were scarcely observed. From the serially taken SEM images, we quantified the fiber alignment by using the angles between the desired direction (perpendicular to the edge lines of two strips) and the longitudinal axes of the fibers. Totally, 510 fibers were measured from eight SEM images over an area of 18.8 $\times$ 1.60 mm^2. Figure 6 gives the resultant histogram with the angle distribution of the nanofibers. All of the processed fibers were distributed within angles ranging from -35° to 25°. It was found that more than 85% of the fibers were aligned within $\pm 10^\circ$ of the preferred direction.

To compare the corresponding results with the previous methods, we used a parameter used by Liu and co-workers.[13,19] In their studies, the parameter that was originally suggested in the research field of fiber composite was adopted to the quantitative analysis of the electrospun nanofibers made by several techniques. According to this description, the fiber orientation parameter was expressed by

$$g_p = (8(\cos^4\phi) - 3)/5$$

where

$$(\cos^4\phi) = \int_0^\pi \cos^4\phi \Psi(\phi) d\phi$$

and the fiber orientation distribution function $\Psi(\phi)$ was defined by the probability of finding a fiber between 0 and π.

$$P(0 \le \phi < \pi) = \int_0^\pi \Psi(\phi) d\phi = 1,$$

where ϕ is an inclined angle of the individual fiber from the desired direction. If all fibers were perfectly oriented uniaxially, the orientation parameter g_p would be 1. Otherwise, it would be 0 for the random nanofiber distribution. From the way of this description, it was calculated that the g_p that corresponded to the results of Figure 6 was 0.96.

There were two kinds of previous methods for electrospun nanofiber alignment, as stated above. According to an earlier investigation,[19] the orientation parameter g_p appeared up to about 0.8 in the method for rotating the drum collector. The rotating speed of the collector mainly affected the alignment property as was well known. The examples in the study included the measured parameters along the various linear

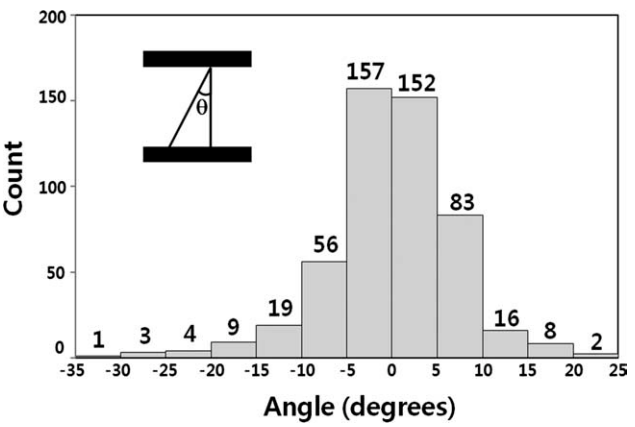

Figure 6 Histogram of distribution of the angle between the longitudinal axis of the each fiber and the expected direction.

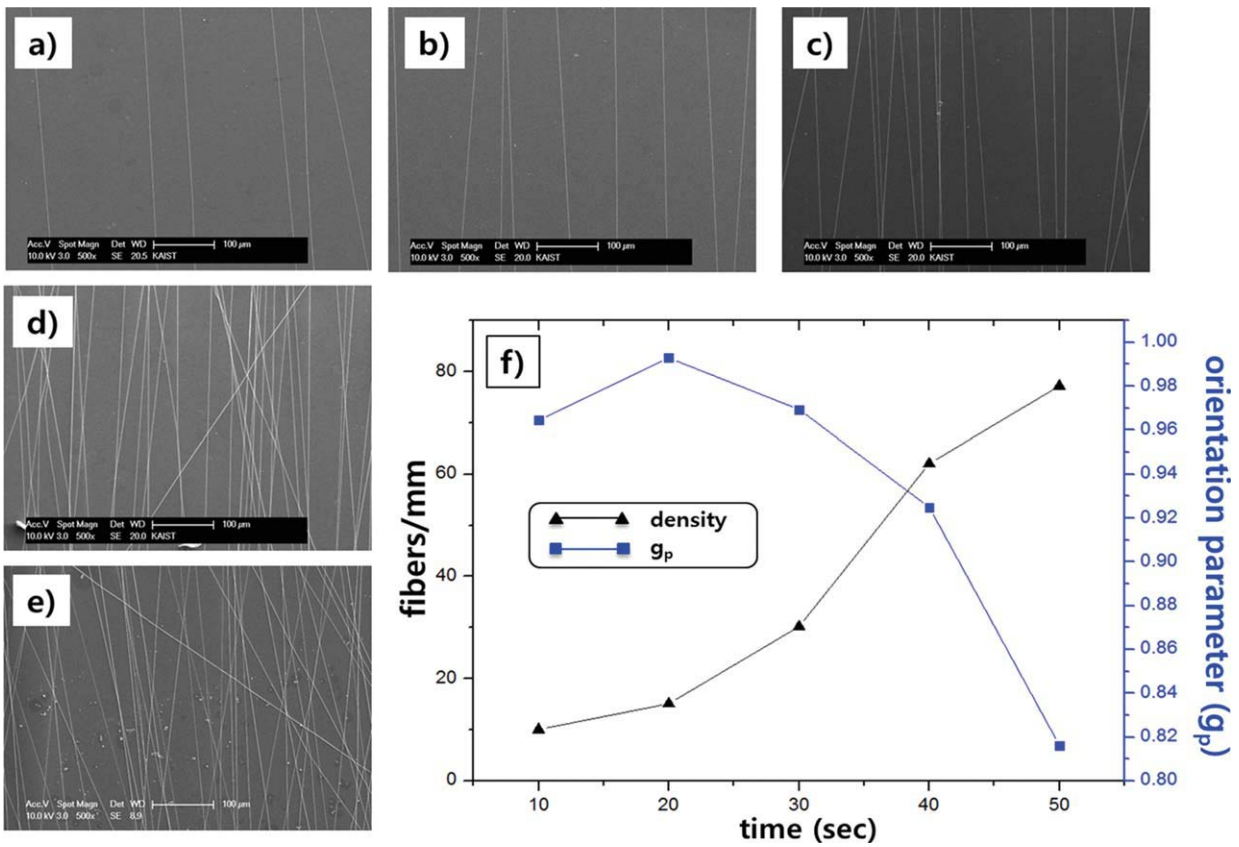

Figure 7 (a–e) SEM images of the aligned nanofiber array electrospun during different spinning times: 10, 20, 30, 40, and 50 s, respectively (the scale bars are all 100 μm). (f) Corresponding orientation parameters and values of densities. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

velocities of the drum surface, such as 0.45 for 4.19 m/s, 0.7 for 8.37 m/s, and 0.8 for 25.12 m/s. Meanwhile, another alignment technique, the gap method, which is a typical case for planar configuration of the electrodes, as shown in Figure 2(a), was mainly affected by the gap size. An increase in gap size improved the alignment quality. Along the description,[19] the parameters for experimental results approximately varied from 0.65 to 0.9 in the range of gap size (3 ~ 18 cm).

From these alignment techniques, we believe that the produced fiber array by the inclined gap method had a higher value of orientation parameter. This high-order orientation (>0.95) was similarly found under the other conditions of the applied voltage within the range from 9 to 15 kV. Furthermore, defective nanofibers, such as the looped and broken one, were observed much less.

Density of the aligned fiber array

Typically, in the electrospinning process, the longer the spinning time, the more increased fibers can be obtained. Therefore, a density of the spun fiber array is mainly dependent on the process time. Figure 7 shows several SEM images produced during the different collection times, as well as their corresponding densities and orientation parameters. The density was calculated as the number of nanofibers per horizontal length of 1 mm in the SEM image. As seen in Figure 7, well-aligned fiber formation was found to be present up to 30 s of spinning time. At a longer collection time of 40 and 50 s, the alignment properties of fiber arrays got worse. The loss in orientation with the denser arrays was possibly due to compulsory fiber deposition onto the previously suspended fiber array with the residual charge. The presence of charges on the collected fibers tended to keep the spacing between the fibers during the collection on the gap. The compulsory landing onto the prior fiber array within the gap can cause misaligned deposition or direct the spun fibers toward a horizontal collector rather than the gap. In our case, 30 s of collection time was selected as an optimum condition for the density of the aligned fiber array. After 30 s, the alignment property was gradually lost, although the amount of fibers was increased. The preferred collection time provided approximately 30 fibers/mm. The value came to roughly 33 μm, which was converted at average spacing between the fibers. Considering the various applications related to the aligned nanofiber mats, this low density could cause limitations if it is used as a valid structure.

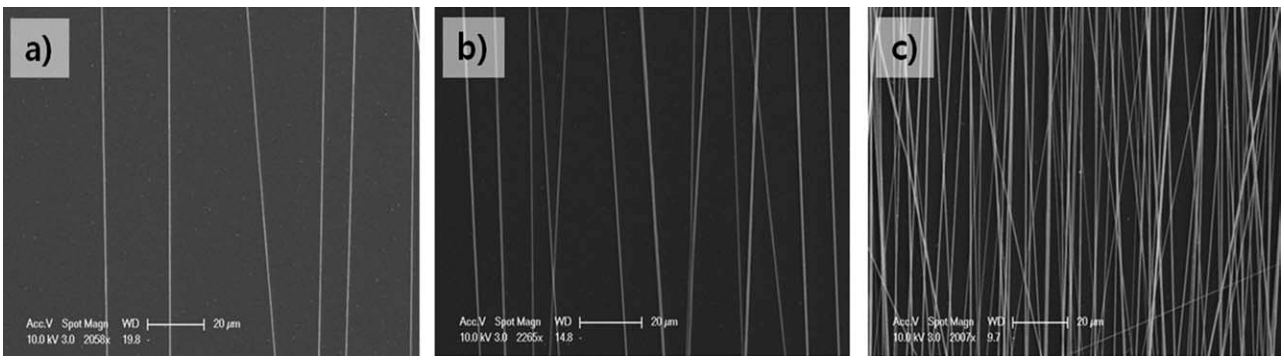

Figure 8 SEM images of the nanofiber arrays transferred repetitively; (a) one transfer, (b) three transfers, and (c) 20 transfers (the scale bars are all 20 μm).

In this study, we accomplished a higher density of the nanofiber array without having the alignment property impaired by using repetitive transfer. As shown in Figure 1, the void space within the collector frame facilitated the transfer process. After transferring the first collected array of fibers onto a glass substrate, the heap of fibers that remained on the strips was removed. The same procedure producing the aligned electrospun nanofibers on the cleaned collector was repeatedly carried out, and, thereafter, they were transferred onto the substrate with the prior fiber array. These repetitive procedures, including collection and transfer, enabled the stacked nanofiber matrix to have a more increased density. The impairment of fiber alignment, as well as destruction between the mutual mats, was not found during the repetitive process (Fig. 8). As shown in Figure 8, the average spacing between the fibers was reduced up to approximately 2 μm when the number of transfers was increased up to 20. From these results shown in Figure 8, it can be expected that a quantitative control of the density of the aligned nanofiber matrix is quite practical because the amount of nanofibers for one crop was regularly quantified to some extent and the density of the matrix could be proportional to the multiple transfers.

CONCLUSIONS

Uniaxially electrospun nanofiber mats were successfully built by a newly designed configuration of collectors, which was characterized as an inclined gap alignment technique. The calculated results of the electrostatic field and experimental results showed that the spatial composition of the collectors involving the inclined void gap could provide sufficient time and space to be self-aligned and regularly distributed, as well as the promoted stretch effect. To be stably suspended onto such a gap, adequate conditions for solution concentration and spinning distance from needle to collector were derived. The broken or the looped fibers were almost not found, and most of the fibers were aligned in a longitudinal direction of the gap. Additionally, the authors plan to study the relationship between the nanofiber array and the collector geometry such as gap width and inclined angle. Meanwhile, it was confirmed that the repetitive process of collection-to-transfer could be allowed to produce a denser matrix in a controlled manner, while the intrinsic quality of alignment was retained during the process. It is noteworthy that the fiber spacing could be reduced down to a micrometer scale or possibly less than that by the multiple transfers. The quantitatively controlled and aligned fiber mats may have great potential to be used in various applications, especially in the tissue engineering field with microenvironment or microarchitecture.

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