International Journal of Nanoelectronics and Materials

In Press, Accepted Manuscript – Note to user

Three-Dimensional Uniaxially Aligned Nanofibre Construct Using Secondary Electrode Assisted Gap Electrospinning

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ABSTRACT

Electrospinning is a simple, versatile, and scalable method of producing polymeric nanofibres from a solution or melt using electric charge. Due to their nanometre-scale diameters, electrospun fibres have been the subject of much study for applications that require a high surface area to volume ratio. However, challenges remain in spatially controlling the deposition of electrospun fibres due to the chaotic nature of electrospinning process. Due to the bending instability, electrospun fibres are typically deposited as random orientated fibres and furthermore, there is no control over the location where the fibres are deposited on the collector. Several techniques to control the deposition of electrospun fibres have been proposed; including the use of modified collectors and by reducing the tip-to-collector distances. Changes in solvent evaporation and the bending instability may reduce stretching of the fibre, resulting in larger diameter fibres. Recently, a new technique for controlling the deposition of electrospun fibres using charged secondary electrodes has been proposed and the results have been promising. In this study, a new approach of directly depositing uniaxially aligned nanofibres onto a holdable structure is demonstrated. The results suggest that the introduction of secondary electrodes charged with time-varying potentials could improve the alignment and distribution of fibres in gap electrospinning process. The new technique would be able to produce fibres for applications which have been previously limited by physical constraint of conventional electrospun fibres.

Keywords: aligned fibres, control deposition, electrospinning, electrospun nanofibre, nanotechnology

1. INTRODUCTION

The United States National Nanotechnology Initiative (NNI) defines nanotechnology as the understanding and control of matter at nanometre-scale for novel applications [1]. 'Nano' is a prefix in the metric system denoting one billionth of the reference unit. Thus, one nanometre means a billionth of a meter (1 nm = 1 x 10^{-9} m). Fibres are long elongated threadlike structures with a high aspect ratio i.e. ratio between longer dimension to shorter dimension. Therefore, nanofibre can be defined as ultrafine threadlike structure with a very high aspect ratio typically with a diameter in nanometre-scale.

Due to their very high aspect ratio, electrospun nanofibres have been proposed for various applications such as filtration, tissue engineering, wound dressing, drug delivery, composite reinforcement, and electronics [2,3]. To date, the main application in which random electrospun nanofibres have achieved commercial success is filtration. Electrospun nanofibres provide very high specific surface areas and small pore sizes due to the presence of fibres in nanoscale dimensions. These unique characteristics are advantageous for producing filtration media with high filtration efficiency and low pressure drop [4,5]. Furthermore, the air flow resistance and filtration efficiency can be adjusted by varying the amount of electrospun nanofibres.

In electrospinning process, polymer solution is subjected to a high potential source typically in the range of 8 kV to 30 kV [6]. When the polymer solution is charged, the repulsive forces causes a polymer jet to be ejected from the nozzle pointing towards a grounded collector. Initially, the jet travels in a straight trajectory before it buckles and continue its journey in a spiral looping motion also known as the 'bending instability' [7]. Due to the occurrence of the bending instability, electrospinning process typically produces random orientated nanofibres. However, uniaxially aligned nanofibres are sometimes favourable for certain applications [8]. One of the commonly used methods to produce aligned nanofibres is gap electrospinning. In gap electrospinning, the alignment of the fibres is highly dependent on the geometry of the collector and it is often reported in the form of two parallel gap collectors [9]. The alignment mechanism of fibres in gap electrospinning has been described previously [10]. Electrospun fibres can be considered as strings of charged elements. Upon reaching the grounded collectors, the two closest elements to the collectors would be attracted to each side of the collector creating a suspended string of fibre. The subsequent portions of the fibre then repeat the process and as a result uniaxially aligned fibres are produced between the collectors.

One of the common issues associated with gap electrospinning is that as the aligned fibres are collected between the gap electrodes, the difficulty in retrieving the fibres for further processes is problematic without damaging the delicate structure of the fibre. It is preferable to directly deposit the fibres onto a holdable structure which can then be removed from the apparatus after the deposition process. However, it is known that by putting a grounded collector in between the gap collectors will only accumulates random fibres [11]. This is because when the grounded collector is added, the electric field at the vicinity of the collector is changed and the fibres are now attracted to the substrate rather than bridging between the parallel plates.

The objective of this study was to demonstrate a new approach of directly depositing uniaxially aligned nanofibres onto a holdable structure. In achieving this goal, a thin grounded metal window was used as substrate to directly capture the fibres. A pair of secondary electrodes charged with time-varying potentials was used to alter the electric field. The hypothesis was that when the secondary electrodes are charged, the "squeezing" of the electric field would encourage fibre alignment and distribution on the substrate. A new method for fabricating a layer-by-layer three-dimensional uniaxially aligned nanofibre construct was also proposed.

2. MATERIAL AND METHODS

An aqueous solution of poly(vinyl alcohol) (PVOH) (Polyscientific, Malaysia) was prepared and used throughout the experiment. The PVOH had an average molecular weight and degree of hydrolysis (DH) of 124,000-130,000 g/mol and 86–89%. The solution was prepared by mixing PVOH powders in distilled water and stirring the mixture using a hot plate magnetic stirrer Model C-MAG HS7 (Ika Works, Malaysia) for 3 hours at 60°C. The solution concentration was adjusted until a final concentration of 8 wt.% was obtained. Measurements of weight were carried out using a four-figure balance (Mettler AE200).

A laboratory scale electrospinning machine was modified to include a pair of independently charged secondary electrodes, a magnetic substrate holder, and two grounded metal gap plates as shown in Figure 1. The secondary electrodes were made of aluminium rods measuring 50 mm long and 10 mm diameter and were positioned at both sides of the substrate holder. The secondary electrodes were placed at 80 mm from each other. A thin round stainless steel shim window was used as substrate. The substrate was 25 μm thick with 30 mm inner diameter. Two grounded metal plates were placed at 50 mm apart to create a gap similar to the concept of gap electrospinning used by Wu et al. [12].

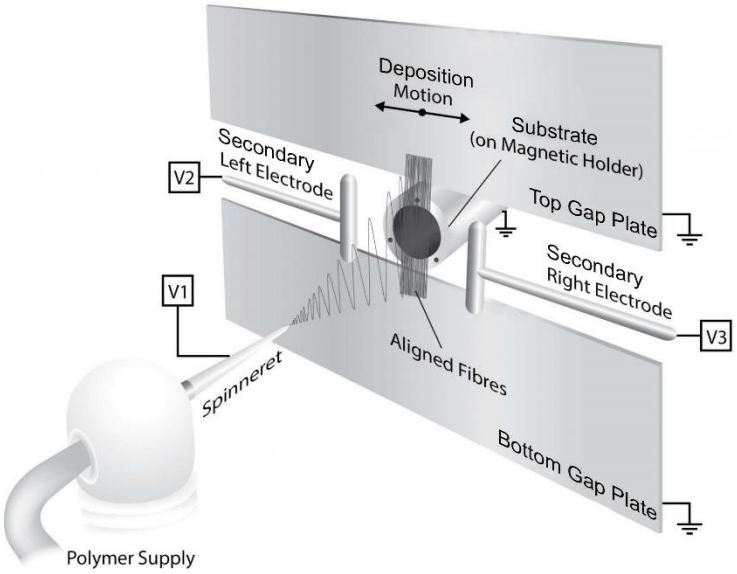

Figure 1. A schematic illustrating the introduction of secondary electrodes, substrate-holder system, and gap plates.

The polymer solution was channelled to the spinneret and was electrically connected to a DC high voltage power supply (Glassman Inc.). The electrospinning distance or the distance between the spinneret and the substrate was set at 100 mm. Two high voltage power supplies (Model 4330, EMCO Corp.) were used to independently charge the secondary electrodes. The applied potentials at the spinneret (V_1) and at the secondary electrodes (V_2 and V_3) were controlled using a LabVIEW™ program (National Instruments) with compactDAQ data acquisition platform. The applied potential at spinneret was 12 kV DC whilst two antiphase triangle wave potentials were applied at the secondary electrodes. The characteristics of the triangle wave potentials are as shown in Figure 2.

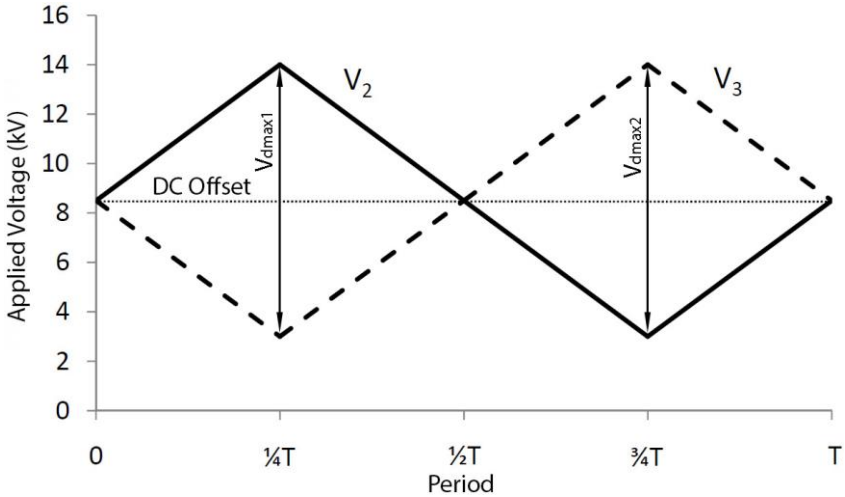

Figure 2. The applied antiphase triangle wave potentials V_2 and V_3 at the secondary electrodes as a function of period (T).

Fibre deposition process was carried out for 5 minutes for each sample. After each process, unwanted suspended fibres between the substrate and the gap plates were carefully removed. Sample collection process was repeated three times to produce triplicates of uniaxially aligned fibre samples. Samples were left overnight to remove residual solvent. Samples were then stacked

at an angle of 120˚ as shown in Figure 3. A control sample was also produced by repeating the same procedures but without using the secondary electrodes.

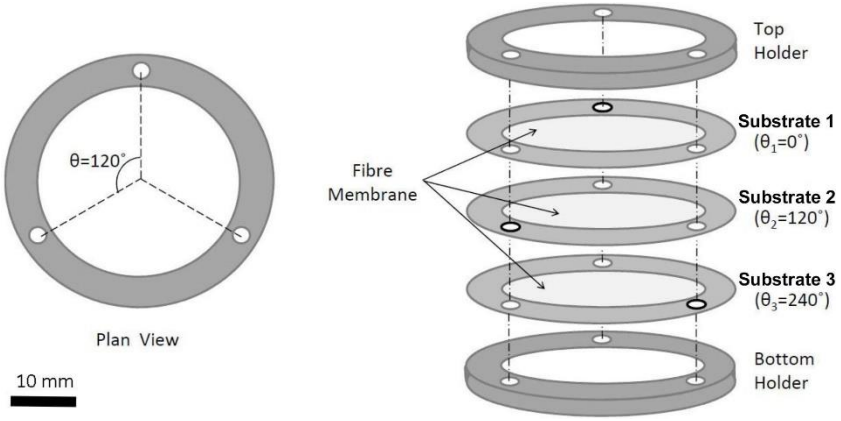

Figure 3. A schematic of the assembly of substrates to produce layer-by-layer three-dimensional uniaxially aligned nanofibre construct.

The morphology of the fibres was observed using a scanning electron microscope (SEM) (JEOL Neoscope JCM-5000, Japan). The average fibre diameter and orientation of the fibres were measured based on SEM micrograph using ImageJ software (National Institutes of Health, USA). Prior to SEM, samples were sputtered with gold for 180 seconds (Quorum Q150R, UK). A quick comparison to demonstrate the difference between test sample and control sample was also carried out by observing laser diffraction pattern using a standard green laser pointer.

3. RESULTS AND DISCUSSION

Initially, uniaxially aligned fibres were obtained bridging between the two gap plates when electrospinning was conducted without the substrate. The formation of aligned fibres was a typical phenomenon when a gap collector is used, and the reason has been explained by previous researchers [9,13]. However, when the substrate was positioned between the two gap plates, the electric field in the vicinity of the receiving end was changed, and non-aligned fibres were produced. When the secondary electrodes (V_2 and V_3) were both charged at 8.5 kV of DC potential, the "squeezing" effect of the electric field resulting from the secondary electrodes were sufficient to force the fibres to align. However, due to repulsive forces from the same charge [7,14], only a narrow band (of approximately 10 mm) of aligned fibres was produced. This narrow band of fibres was too small for any practical use.

In the authors' previous studies [15,16], it was found that the location where the aligned fibres landed on the substrate can be controlled by changing the electric field. In this study, when the secondary electrodes were charged independently using two antiphase triangle wave potentials, the deposition location was continuously moving to and fro in the direction away from the most positive electrode, expanding the coverage area of the aligned fibres. The maximum deflection of the fibres occurred when the potential difference between the secondary electrodes was at a maximum potential; i.e. V_{dmax1} or V_{dmax2} = 11 kV at t = ¼T and t = ¾T (Figure 2).

The stacking of the substrates at 120˚ angle produced a triaxial aligned nanofibre construct as shown in the macro photographic image in Figure 4. From the image, it is evidenced that a well distributed aligned fibres could be produced using this approach. A quick method to compare fibre alignment between the test sample and control sample was performed by observing laser-

induced diffraction patterns (Figure 5). The test sample using the secondary electrodes produced a six-point cross pattern denoting the triaxial alignment of the fibres (Figure 5(a)). Each of the line represents a single layer of the aligned fibres. On the other hand, the laser diffraction of the control sample showed no particular pattern indicating its random orientation (Figure 5(b)).

Figure 4. A macro photographic image showing a layer-by-layer triaxially aligned PVOH nanofibre construct.

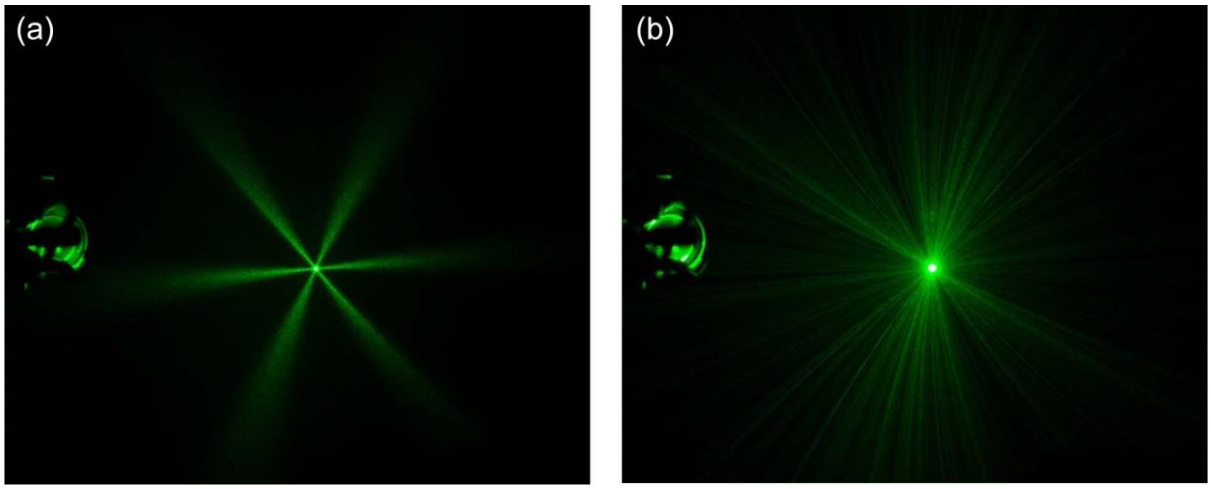

Figure 5. Photographic images showing the laser diffraction pattern of the samples exhibiting fibre orientation (a) test sample, and (b) control sample.

Scanning electron micrographs of the samples showed typical solid and dry fibre characteristics of electrospun fibres Figure 6(a) and Figure 6(b). However, it is worth noting that the fibre structure in Figure 6(b) was different compared to any typical randomly orientated electrospun fibres. The SEM micrograph showed only straight fibres (no curved fibres) but were orientated at random angles. This suggests that even though without secondary electrodes, gap electrospinning still occurs across the substrate, however, the orientation of the fibres was random because of the substrate being circular. From Figure 6(c), the orientation angle of the fibres was clearly visible when using the secondary electrodes. Notable orientation of the fibres was observed denoted by the three peaks in the histogram suggesting that the majority of the fibres were aligned in approximate angles of 300˚, 0˚, and 60˚. In contrary to the test sample, the control sample which was produced without secondary electrodes produced layers of random orientated fibres (Figure 6(d)).

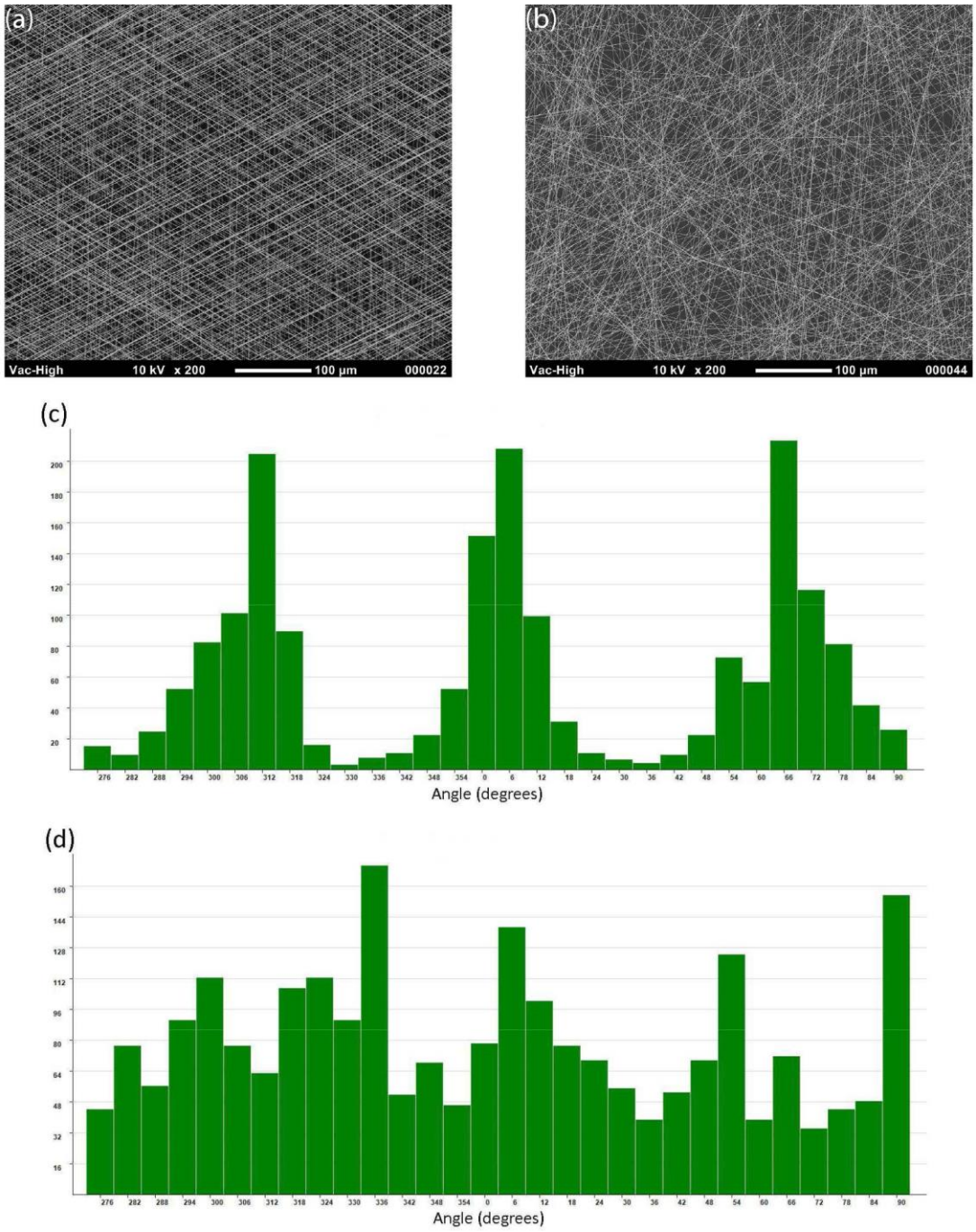

Figure 6. Scanning electron micrographs of the (a) test sample, and (b) control sample. The measured fibre orientation angle of sample (a) and (b) are shown in (c) and (d) respectively.

Based on SEM micrographs, the average fibre diameter varied between the test sample and the control sample. Thicker fibres were obtained with an average fibre diameter of 352.1 ± 83 nm (Figure 7(a)). In contrast, slightly thinner fibres were obtained with an average fibre diameter of 308.2 ± 70 nm (Figure 7(b)). The difference between the average fibre diameter values was 43.9 nm or 14.2% increase in fibre diameter. The difference is thought insignificant when considering; (a) the pixel size used (30.5 nm) when measuring in diameter using ImageJ software, and (b) the standard deviation values obtained in the calculation. The increase in fibre diameter when using secondary electrodes was expected because the introduction of the charged secondary electrodes would inevitability change the electric field which may dampen the bending instability. The effect

of the bending instability on fibre thinning process has been previously explained in previous studies [7,17].

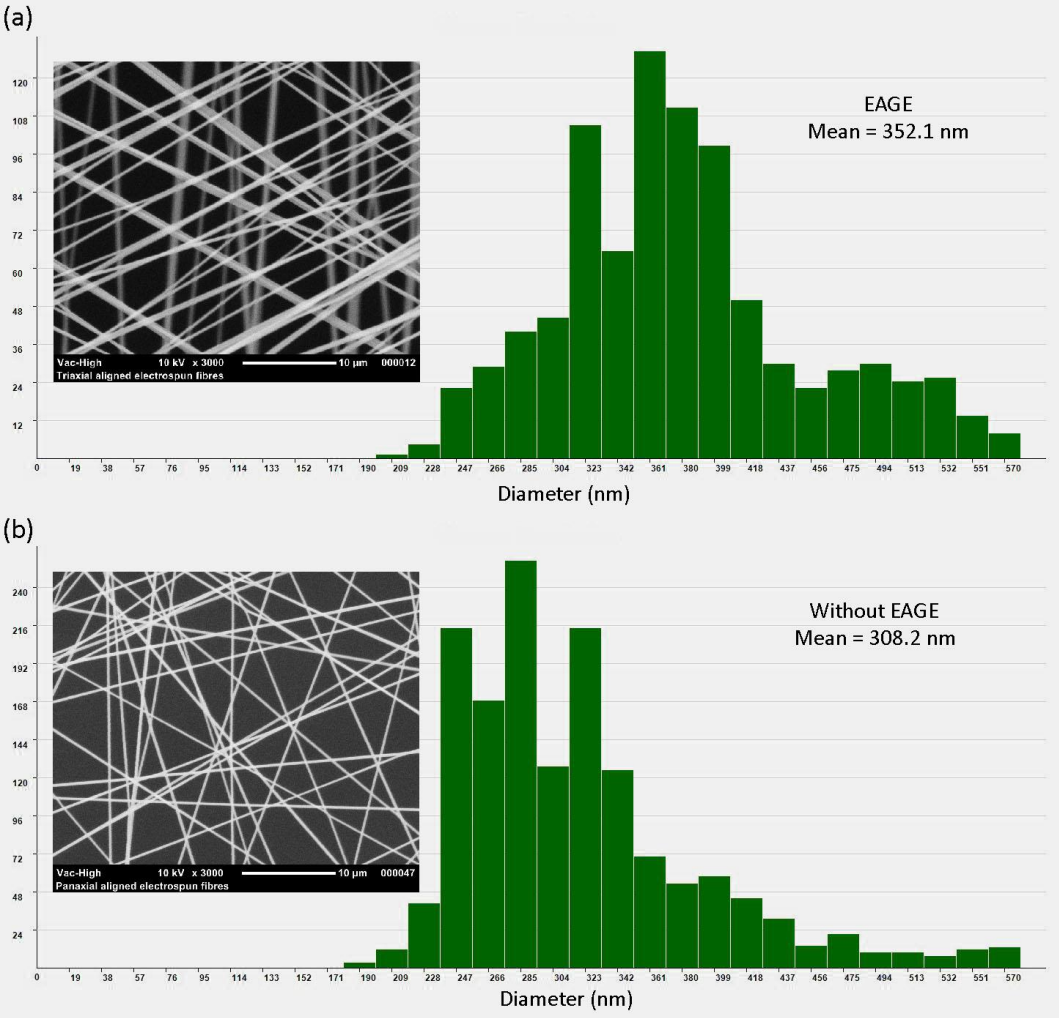

Figure 7. Average fibre diameter distribution of (a) test sample, and (b) control sample.

The results obtained from this study suggest that the introduction of secondary electrodes charged with time-varying potentials could improve the alignment and distribution of fibres in gap electrospinning process. In this case, the additional electric field imposed by the secondary electrodes improved the process in two ways. First, the electric field "squeezed" the bending instability cone forcing the fibres to flick up and down vertically before landing on the substrate. Secondly, when the secondary potentials periodically changed, the deposition area moves accordingly widening the distribution of the aligned fibres across the substrate.

This novel approach of producing aligned fibres could open up new possibility for creating complicated three-dimensional nanofibre constructs. Although the test sample demonstrated in this study has only three layers of aligned fibres, the actual possible number of layers and orientations are basically unlimited. Thicker and more complicated fibre construct can be created by increasing the number of layers at different orientations. It is therefore envisioned that this approach could be an option to extend electrospun fibres to applications which are currently limited by the geometrical constrains of the fibre constructs. Although several methods of producing layer-by-layer orientated fibres have been previously proposed [13,18,19], the approach used in this study has a major advantage in terms of ease of handling of the product.

The metal substrates with two-piece holder system allow the fibre construct to be handled easily between processes without damaging the delicate structure of the electrospun fibres. Furthermore, the method can be used to other electrospinnable polymers to suit different intended applications.

Despite the promising results, there was a limitation that worth to note. Due to geometrical limitation of the experimental setup, exception has to be made on the lower limits to the applied potential. There was a minimum base potential that needed to be applied to prevent fibres from landing onto the secondary electrodes. The secondary electrodes were positioned very close to the collector (at about 15 mm) in order for the electric field to have sufficient influence to "squeeze" the deposition area. In achieving this, a minimum base potential (V_b) of +3 kV was applied to avoid fibres from landing onto the secondary electrodes.

4. CONCLUSION

A novel approach of constructing layer-by-layer aligned electrospun fibres was demonstrated by using a pair of secondary electrodes charged with time varying potentials. Initially, random fibres were produced on the substrate when no secondary electrodes were used. However, when triangle time-varying potentials were applied on the secondary electrodes, well distributed aligned fibres were produced on the substrate. The results proved the hypothesis that time varying potentials could be used to improve the alignment and distribution of aligned fibres in a gap electrospinning system. The average fibre diameter was found thicker compared to control sample; however, the difference was insignificant. The approach used in this study could potentially be used to fabricate more complicated three-dimensional fibre constructs. It would be interesting to further evaluate the approach using different type of polymer and solvent systems. This will be explored further in future works.

ACKNOWLEDGEMENTS

Special thanks to the Ministry of Education Malaysia and Universiti Teknikal Malaysia Melaka for funding this study. Thanks also to the Advanced Materials Characterization Laboratory (AMCHAL) group and Centre for Advanced Research on Energy (CARe) for their supports.

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