Fabrication and Physical Characterization of Electrospun PVA-ZnO Fibers with Different Deposition Distance

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Abstract. PVA-ZnO composite nanofibers were successfully fabricated by electrospinning method. The effect of the deposition distance (the distance between the needle tip to the substrate) on the fiber diameter was investigated. The distance was varied from 4 cm to 20 cm and it was found out that the fiber diameter decreased as the distance increased. The fiber diameter was in the range of 156 to 251 nm with the finest fiber film was obtained for the distance of 20 cm. The presence of ZnO particles were confirmed with XRD characterization performed in which all PVA-ZnO composite samples displayed typical ZnO XRD peaks 32°, 34° and 36° that corresponded to Miller indices of (100), (002) and (101) of ZnO yet the peaks are more apparent at sample fabricated at the closer distance of 4 cm and 8 cm.

1. Introduction
Fibers producing technique such as electrospinning is of considerable interest for its ability to produce fibers with ease. The fabricated fibers can be implemented in various applications and can serve many purposes [1]. One example is its usage in wound healing and tissue engineering [2] where the fibers serve as artificial tissue that can facilitate healing process. Based on the type of liquid used, electrospinning process can be classified as melt electrospinning or solution electrospinning in which the latter is more enticing because it is capable of forming fibers with thinner diameter [3].

Four basic electrospinning parts are spinneret, syringe pump, high voltage power supply and grounded collector. Generally, electrospinning involves supplying sufficiently high voltage on needle of a solution-contained syringe, making the solution becomes electrically charged. As a result, it can be seen at the tip of the needle where the hemi-spherical shape of liquid droplet (due to surface tension) changes shape into a cone (due to repulsion forces) as the voltage becomes sufficiently high. The formation of the cone (known as Taylor cone) [4] is first studied by Geoffrey Taylor and had become essential parts of electrospinning. When the Coulombic repulsion forces exceeds the surface tension of the liquid, the liquid would be ejected in the form of jet towards the grounded collector [5].

Electrospinning is an easy-handling fabrication technique but the requirement for producing good quality fibers is dependent on three basic parameters; solution, processing and environmental. Solution parameters includes rheological properties like solution’s viscosity and conductivity whereas
environmental parameters cover external factors such as humidity and temperature. This study focuses on processing parameters, specifically the deposition distance in order to determine the best distance for fabricating PVA-ZnO (polyvinyl alcohol-zinc oxide) composite nanofibers.

2. Method
To prepare PVA-ZnO composite fibers, first 0.08139 g ZnO nanopowder was mixed with 10 wt% PVA solution. The mixing process was done at stirring speed of 300 rpm with temperature of 70 °C using Stuart’s Digital Stirrer Hotplates CD162.

![Figure 1. Figure of electrospinning setup.](image)

The mixture was stirred for one hour to ensure homogenous distribution of ZnO in liquid PVA. The solution obtained was then filled into the barrel of 10 cc/ml syringe with inner diameter of 15.8 mm. A metallic blunt needle (16 G) was connected to the syringe and then the syringe was placed on the syringe pump as depicted in Figure 1. The substrates were attached to a cylindrical grounded collector which was spun at rotational speed of 250 rotations per minute. After the setup was completed, PVA-ZnO composite deposition process was subsequently performed.

| Deposition Parameter          | Value     |
|------------------------------|-----------|
| Voltage                      | 15 kV     |
| Current                      | 400 µA    |
| Collector rotational speed   | 250 rpm   |
| Deposition rate              | 0.25 ml/h |
| Deposition time              | 1 hour    |
| Syringe inner diameter       | 15.80 mm  |
| Metal needle inner diameter  | 1.19 mm   |

Following the deposition process, drying step of the samples were performed at temperature of 80 °C for period of 10 minutes. The drying process was important to eliminate any solvent residues and
also to increase adhesion of the PVA-ZnO composite onto substrate surface. Dried fibrous composite samples were analyzed using FESEM and XRD to study their physical characteristics.

3. Results and discussion
FESEM images presented in Figure 2 are the surface morphology of the fabricated PVA-ZnO composite samples. From the images, it was conclusive that the methodology used in this study is able to produce PVA-ZnO composite film with good fibrous structure (small and no bead). This suggested that the deposition condition used such as voltage and flow rate are suitable in such way that fibers formation occur smoothly. Besides that, the polymer used has suitable molecular weight and concentration that contributes to sufficient viscosity of the PVA-ZnO solution which plays important role in electrospinning process [6].

![FESEM images](image-url)
Figure 2. Figure FESEM images of PVA-ZnO composite fibers deposited with distance of (a) 4 cm (b) 8 cm (c) 12 cm (d) 16 cm and (e) 20 cm.

The distribution of the fibers throughout the substrate was homogenous but without any preferable orientation. This indicates that the deposition of stretched jet on substrate surface was random; with deposition distance plays no significant role in arrangement of the fibers. Nevertheless, the different distance used indeed has influenced some properties of composite fibers which are in term of sizes and diameter of composite fibers produced [7]. Smaller fibers are more desirable especially if the diameters in nanoscale. This is because smaller dimensions offer larger total surface area to volume (TSAV) ratio and this can be beneficial in several applications like biosensing and gas sensing [8]. Besides that, the quantum confinement effects that could be shown by nanoscale materials may offer unlimited possibilities.

In electrospinning, suitable separation gap between needle tip and collector must be applied so that optimized fiber deposition could be achieved. One of the reasons is because during the jet flight from needle to substrate on collector, fiber elongation and drying process occurs and is assisted by the whipping instability [9]. If the gap used was too close, it would decrease the jet’s flight time and this could results in failure of jet to properly stretch into fibers with small diameter. In this study, the farthest distance of 20 cm produced nanofibers with thinnest average diameter of 156.33 nm. Higher distance means longer time available for the fiber’s jet to elongate, decreasing the width of the cylindrical nanofibers [10]. The average diameters for fibrous samples with deposition distance of 4 cm, 8 cm, 12 cm and 16 cm are 251.00 nm, 222.66 nm, 211.00 nm and 192.00 nm respectively.

The diameter uniformity of produced nanofibers is also important to be studied. It is known from literatures that increasing deposition distance could lead to production of smaller fibers, and vice versa [7,11]. Interestingly, not many among the literatures discussed the effects of varying distance on diameter uniformity of fabricated fibers. This could be due to difficulty in total identification and measurement of the numerous fibers present on sample surfaces. Therefore, at the very least, this study
provides a simple data representation shown from graph in Figure 3 of the fiber’s diameters variation as the deposition distance being increased.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3}
\caption{The range of diameter of fibers produced when deposited at different distances.}
\end{figure}

It can be seen from the graph that on average, the fibers diameters indeed becoming smaller as distance between needle tip and collector becomes further apart, with the sample deposited at furthest distance of 20 cm having the fibers with smallest diameter. This is parallel with the basic theory of electrospinning and with results obtained by many researchers. However, it can be observed that the diameter of the fibers of the first sample (4 cm) differs greatly between each other, showing low fibers diameters uniformity. When distance was increased to 8 cm, the fibers diameters uniformity improves while fibers deposited at the distance of 12 cm shows best fibers diameter uniformity.

At distance longer than 12 cm (16 cm and 20 cm), the diameters of fibers becomes increasingly deviate from each other. The deviation for both 16 cm and 20 cm composite samples however still lower than sample fabricated at closer distance of 4 cm and 8 cm. This indicates that there exist an optimum distance to produce fibers with uniform diameters.

In Figure 4 below, peaks from XRD characterizations are presented. Typical ZnO major peaks were usually observed at 2-theta (2θ) of 32°, 34° and 36° that corresponds to Miller indices of (100), (002) and (101) respectively [12-13]. These peaks existed throughout all the samples, displaying presence of ZnO in the composite samples fabricated. This also means that none of the samples were amorphous although the degree of crystallinity varied as suggested by the difference in peak intensity.

Sample deposited at the shortest distance of 4 cm shows the highest peaks intensity and the intensity decreases as the distance being increased to 8 cm and 12 cm. The intensity for 16 cm and 20 cm samples however does not differs much and roughly more of the same. There are also ZnO minor peaks at 2-theta of 48°, 57°, 63° and 68° but these peaks are most apparent at the 4 cm sample and becomes more indiscernible for the subsequent samples.
Figure 4. XRD peaks obtained for the distance dependent samples.

4. Summary
The physical properties of fibers produced through electrospinning method are dependent on deposition parameters, as demonstrated from results in this experiment. One of the most significant impact of parameters variation is on the diameters of fibers produced. In this particular study, the PVA-ZnO composite fibers were found to be smaller when the deposition distance (needle-collector separation gap) were being increased. While the smallest fibers were produced using furthest deposition distance of 20 cm, the best fibers diameter uniformity is shown by the 12 cm sample.

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