THE EFFECT OF FLOW RATE, CONCENTRATION, AND VOLTAGE ON DIAMETER OF PAN PRECURSOR FIBER BY ELECTROSPINNING TECHNIQUE

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ABSTRACT

In the present study, electrospun PAN precursor fiber is processed under various parameters including the applied voltage, the flow rate and the concentration of the polymer that affect the diameter of PAN electrospun nanofibers. Our results demonstrate that the diameter of the fiber increases with the increase of flow rate and concentration while decreases with the increase of applied voltage. Of particular interest, we demonstrated that by monitoring the applied voltage it is possible to control the fibers morphology and bead concentration. In this paper, we studied the physical properties of PAN precursor fiber by scanning electron microscopy (SEM) and thermal gravimetric analysis (TGA). A main contribution in this study was the definition of conditions to controllably obtain fibers that are smooth and that present diameters in the range between 588 nm – 800 nm.

Keywords: Electrospinning, parameter, PAN precursor, diameter, nanofibers

Introduction

Electrospinning is a simple and direct process which can produce superfine continuous polymer fibers ranging from several micrometers to several hundred nanometers by exposing a polymer solution to an electric field [1]. The procedure is much less difficult and lower cost than any other procedures that can create nano-scale fibers. During electrospinning, a high voltage electric field, is applied to the polymer liquid resulting in ejection of a continuous jet strand from the eluting nozzle that accelerates toward the oppositely charged grounded plate collector. In the absence of any electric field the polymer droplet is held at the capillary tip by surface tension of the liquid [2]. Upon application of an electric field, as the surface tension is balanced by the electrostatic forces, the droplet elongates and develops into a cone known as a “Taylor cone”. When the strength of the electric field is sufficient to overcome the surface tension of the liquid, a fine fiber jet is ejected from the tip of the Taylor cone [3]. As the fiber jet travels through the atmosphere, the solvent evaporates and solid polymer fibers are deposited on a plate collector as a mesh or web [4].

The technique of electrospinning was first observed by Rayleigh in 1987 and investigated in detail by Zeleny in the early 1900s. However, electrospinning only surfaced as a feasible, small diameter fabrication technique in 1934 after patented by Formhals [5]. Bherdwaj and Kundu [6] patented the electrospinning process and a device that consisted of a moveable fiber-collector, such as a mandrel, to collect fibers in a stretched form. However, the distance between the jet and collector was relatively small and the fibers were unable to dry completely before reaching the collector. This resulted in the fibers sticking to each other and to the collector surface [7]. Despite the fact that electrospinning has not been broadly utilized as a part of a modern scale at present, huge advancement has been made to enhance the related equipment and processes. Kim et al. [8] acquainted an adjusted electrospinning process with enhance the mass productivity of multi-nozzle electrospinning, utilizing an auxiliary electrode for expanding the production rate of nanofibers manufacturing. Ali and Hamid [9] considered the enhancement of some electrospinning parameters, for example spinning angles, charge density, and so forth to prepare a precursor of carbon nanofibers. For some applications, it is crucial to control the arrangement of the fibers. Electrospinning fibers nonetheless, are frequently gathered in the form of randomly oriented, non-woven fabrics. Some research team have exhibited the capacity to specifically gather electrospun nanofibers as uniaxially aligned arrays by the use of rotating drum or a pair of split electrodes as the collector [10].

After much fundamental research on the basics of the electrospinning process, researchers investigated the effects of various processing variables on the structural morphology and properties of electrospun fibers [11]. They have investigated the effects of solution conditions (i.e., solution concentration, viscosity, conductivity, and surface tension) and process parameters (i.e., applied electrostatic field strength, emitting electrode polarity, nozzle diameter, and take-up speed of a rotating-drum collector) on morphological appearance and average diameter of the as-spun PAN fibers. The fabrication of the nano-size material is very complex. There are difficulties to fabricate the single carbon nano-size in term of positioning and integrating with underlying platforms. In the present contribution, Polyacrylonitrile (PAN) were electrospun into ultrafine nanofibers. PAN carbon nanofibers has been introduced as replacement for microsensors field in industry because it makes a good candidate as chemical and biosensors electrode for batteries. This project explored the best electrospinning parameters to produce nanofibers. Electrospinning process allows the control of fiber diameters as well as the characteristics of the spun fiber by using suitable innovated techniques of electrospinning. Hence, the effects of solution concentration, flow rate and applied voltage on the morphology and sizes of nanofibers were of primary concern.

EXPERIMENTAL

MATERIALS

Polyacrylonitrile (PAN) (Product Number 18,131-5) with 150,000 weight average molecular weight was obtained from Sigma-Aldrich. The 99% *N,N*-Dimethylformamide (DMF) (Product Number D158,550) was purchased from Hasrat Bestari and used without purification. A predetermined amount of PAN was added to DMF at room temperature, followed by stirring using magnetic stirring apparatus for 24 h in fume chamber to obtain a homogenous polymer solution with concentration of 8 wt% (by weight), 10 wt%, or 12 wt%, to be used to obtain nanofibers using electrospinning.

ELECTROSPINNING OF PAN FIBER

The concentration of PAN in DMF was 8 wt%, 10 wt%, and 12 wt%. This concentration was varied in order to study the best electrospun PAN nanofiber diameters. Electrospinning was carried out using the electrospinning machine manufactured by the Vistech Co. Ltd (Fig. 1). The apparatus used for the electrospinning system consisted of a high voltage dc power supply (Gamma High Voltage Research, ORMON BEACH, FL), a syringe pump (New Era pump systems, Inc.), a ground electrode (an aluminium foil sheet on a stainless steel plate) and a 5 ml (Terumo) syringe with a 0.4 mm diameter tip. Each solution was loaded into a syringe and positive electrode was clipped onto the syringe needle. Solutions were electrospun horizontally onto the target. The preparation condition of the electrospinning is as follows: voltage, 10-20 kV; flow rate 5-9 µL/min and concentration 8-12 wt%. The fixed conditions were distance between nozzle targets, 8 cm and needle internal diameter, 0.4 mm. The effect of three electrospinning parameters namely the concentration of PAN solution, the flow rate of syringe pump and the applied voltage during the process on the electrospun fiber yield will be determined in this research.

Figure 1 Electrospinning machine (ESP- 1000, VT Electrospinning apparatus)

CHARACTERIZATION

The diameter and morphology of the gold-sputtered electrospun nanofibers were determined and examined with scanning electron microscopy (SEM), the measurements of about 15 random fibers were carried out to determine the average fiber diameter and distribution. SEM micrograph were analysed with SemAfore software version 4 from JEOL (Skandinaviska, Sollentuna, Sweden). The uniformity and average particle diameter were calculated wit this software. The thermal properties of the electrospun fibers were analysed by thermogravimetric analysis (TGA) at a heating rate of 10 °C/min and from 30 - 1000 °C temperature.

RESULT AND DISCUSSION

A variety series of experiments were carried out using PAN/DMF solutions as a precursor. PAN nanofibers were electrospun with different concentration, voltage and flow rate. By using 8 wt% concentration, nevertheless of the electrospinning voltage, the polymer solution slightly formed beads instead of uniform nanofibers. By increasing the concentration to 12 wt%, the morphology of nanofibers was changed from a slightly beaded fiber to a uniform fiber structure and the fiber diameter was increase slightly to 588 to 690 nm. In electrospinning, the flow rate of the polymer solution within the syringe is another important process parameter. Generally, lower flow rate is more recommended as the polymer solution will get enough time for polarization. By increasing flow rate in this work, the fiber diameter observe get thicker rather than the smooth fiber produced with lower value of flow rate. Within the electrospinning process, applied voltage is the crucial factor. However, the affection of the applied voltages on the diameter of electrospun fibers is a little controversial. By this experiment, as the voltage increase to 20 kv, the diameter of fiber diameter decrease and become narrowed.

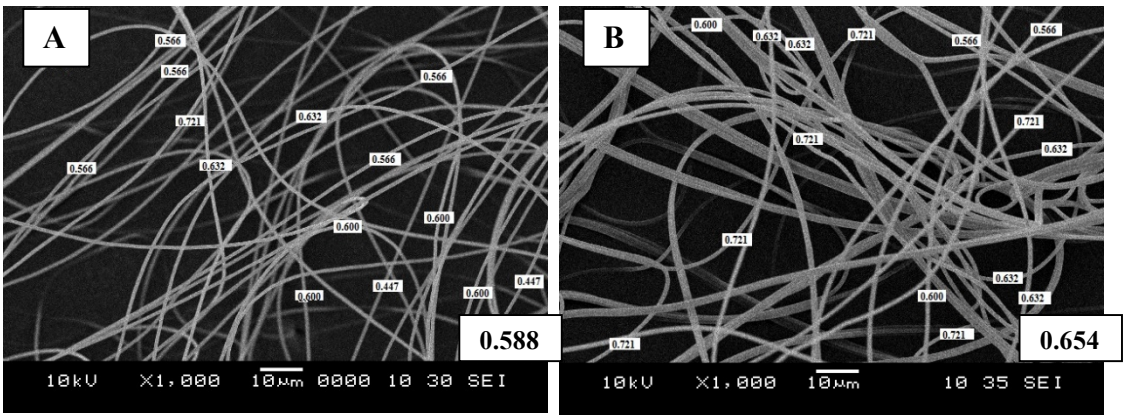
THE EFFECT OF CONCENTRATION ON THE DIAMETER OF NANOFIBERS

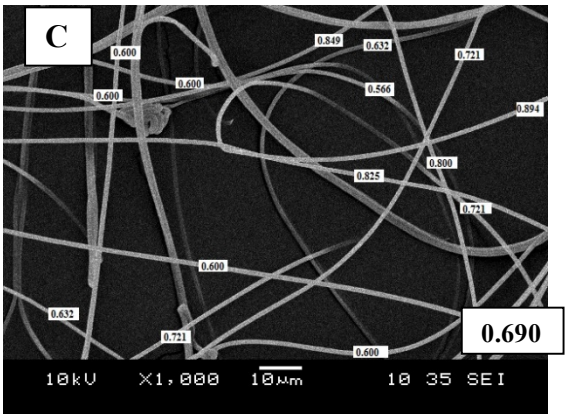
To produce uniaxially aligned nanofibers of different diameters, the electrospinning conditions that gave the best of nanofibers for 8-12 wt% concentration were experimentally obtained, these conditions are shown in Table 1. Figure 2 shows SEM images of electrospun nanofibers produced under these conditions that gave the smoothest nanofibers. For example, nanofibers with average diameter of 588 nm were obtained from 8 wt% concentration. It is noticed that the diameter of PAN nanofibers became large as the concentration increase. On the other hand, by increasing the polymer solution concentration, the fiber diameter was also gradually increased to about 690 nm. Therefore, in this experiment, the optimum solution concentration for the electrospinning process was at 8 wt% as it gives the smallest diameter. At 12 wt% which consider as high concentrations, resulting in larger fiber diameter because of the inability to maintain the flow of the solution at the tip of the needle [12] and due to their higher viscosity resistance [13].

Table 1: The Electrospinnig Conditions With Different Concentration of PAN Solution

Concentration (wt %)	Tip to target distance (cm)	Voltage (Kv)	Fiber diameter (µm)
8	8	20	0.588
10	8	20	0.654
12	8	20	0.69

Figure 2 SEM images of electrospun PAN nanofibers. Concentrations: (A) 8 wt%, (B) 10 wt%, (C) 12 wt%



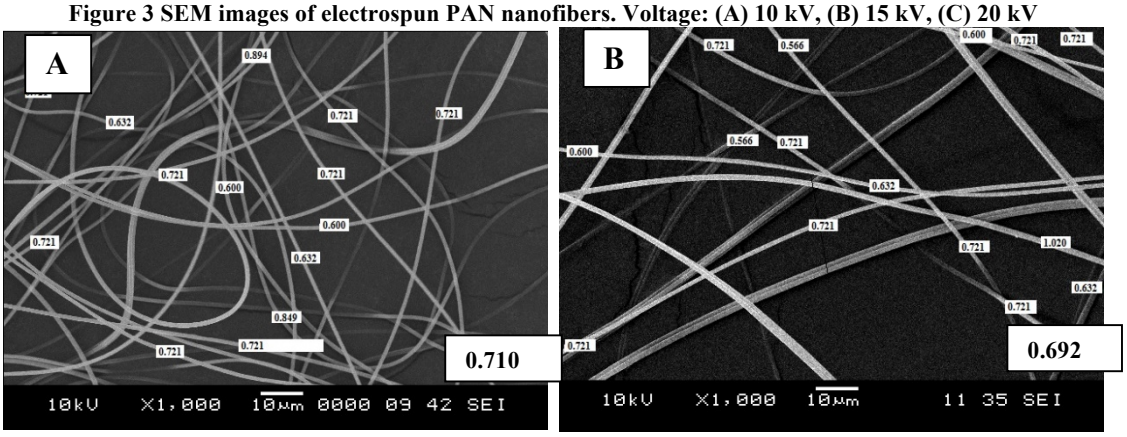


THE EFFECT OF APPLIED VOLTAGE ON THE DIAMETER OF NANOFIBERS

Within the electrospinning process, applied voltage is the crucial factor. However, the affection of the applied voltages on the diameter of electrospun fiber is a little controversional. In the electrospinning process, different results concerning the relationships between the PAN nanofibers diameters and the applied voltage were concluded. Some researchers found that the diameters of PAN nanofibers increase with increasing applied voltage. Ashraf and Hamid [14] found that the optimum charge density was 2.5kV/cm and, then further increasing the charge density would increase the fiber diameter. Fenessey and Faris [15], and by Kedem et al. [16] the fiber diameter decreased with applied voltage, which creates a stronger electric force drawing and thinning the fibers. The inconsistency might be due to the difference of the experimental conditions. Whether or not the fibers size should increase or decrease with increasing applied voltage depends very much on the ability of the system to supply the polymer solution from the reservoir to the opening of the needle as well as the viscosity.

In this experiments, the applied voltage was varied from 10 to 20 kV while the concentration and the flow rate of the solution remain constant at 8 wt% and 5 µL/min, respectively.Table 2 shows the condition of this work with different applied voltage. Electrospinning jet started forming from 8 kV, but electrostatic forces were not strong enough to form continuous jet from the tip of the syringe needle. Then, the electrospinning started from 10 kV and the jet kept continuous. Figure 3 shows images of some of the electrospun nanofibers that were spun under these conditions and their corresponding diameter in micrometer (µm) at the side of the image. It can be seen that the diameter of the fiber decreased as the voltage increase. Hence, 20 kV appeared to be the best voltage in these works and lowest diameter of fiber presented. By increasing the applied voltage during electrospinning process, will help to increase the electrostatic repulsive force on the liquid jet which ultimately favours the narrowing of fiber diameter.

Figure 3 SEM images of electrospun PAN nanofibers. Voltage: (A) 10 kV, (B) 15 kV, (C) 20 kV



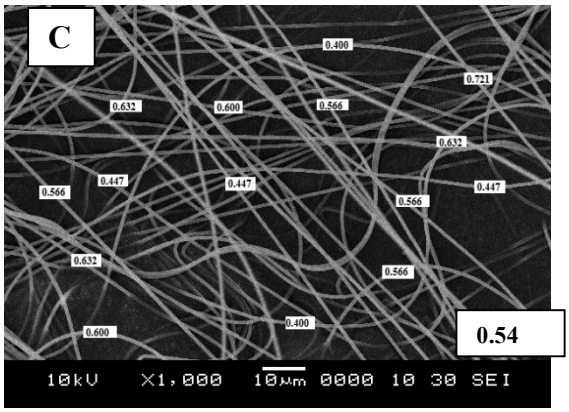


Table 2: The Electrospinnig Conditions With Different Applied Voltage

Concentration (wt %)	Flow rate (μL/min)	Voltage (Kv)	Fiber diameter (μm)
8	5	10	0.71
8	5	15	0.692
8	5	20	0.54

THE EFFECT OF FLOW RATE ON THE DIAMETER OF THE NANOFIBERS

The flow rate of the polymer within the syringe is another important process parameter in electrospinning. A lower flow rate is more necessary as the solvent will get enough time for evaporation [17]. There should always be a minmum flow rate of the spinning solution. If the flow rate is very high, bead fibers with thick diameter will form rather than the smooth fiber with thin diameter owing to the short drying time prior to reaching the collector and low stretching forces.It has been observed that the fiber diameter and the pore diameter increases with an increase in the polymer flow rate in the case of polystyrene (PS) fibers and by changing the flow rate, the morphological structure can be slightly changed. Few studies have systematically investigated the relationship between solution flow rate on fiber morphology and size [18]. When the flow rate was too high, the nanofibers were unable to dry completely before reaching the collector and higher bead defects were therefore observed [19].

Figure 4 shows the SEM images of electrospun PAN nanofibers at various flow rate that are listed in Table 3. In this study, the diameters of the electrospun PAN nanofibers increase, as the flow rate decrease. This is the reason that with lower feeding rate it was desirable for evaporation of solvent to occur thus obtaining solid nanofiber. Ideally, feeding rate must match the solution removing rate from the tip. These findings suggest that in general lower feeding rates can inhibit electrospinning and high feeding rates result in beaded large diameter fibers due to unavailability of solvent to evaporate within time to reach the collector.

Figure 4 SEM images of electrospun PAN nanofibers. Flow rate: (A) 5 μL/min, (B) 7 μL/min , (C) 9 μL/min

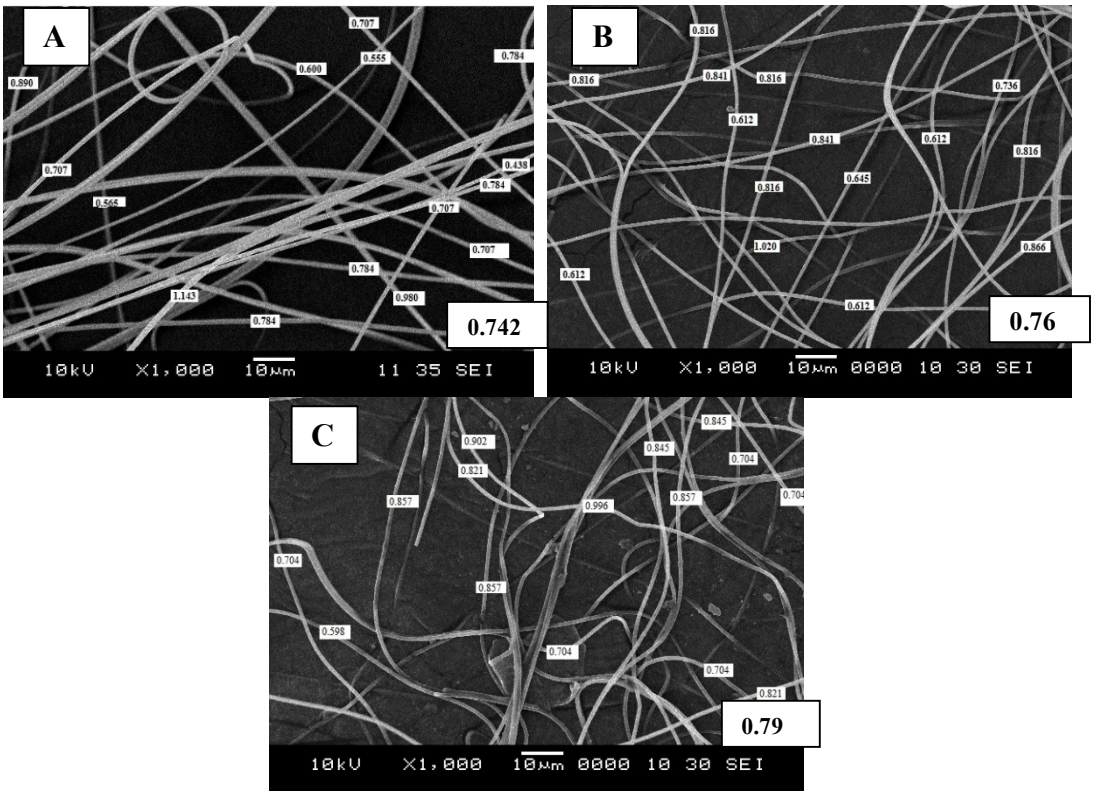


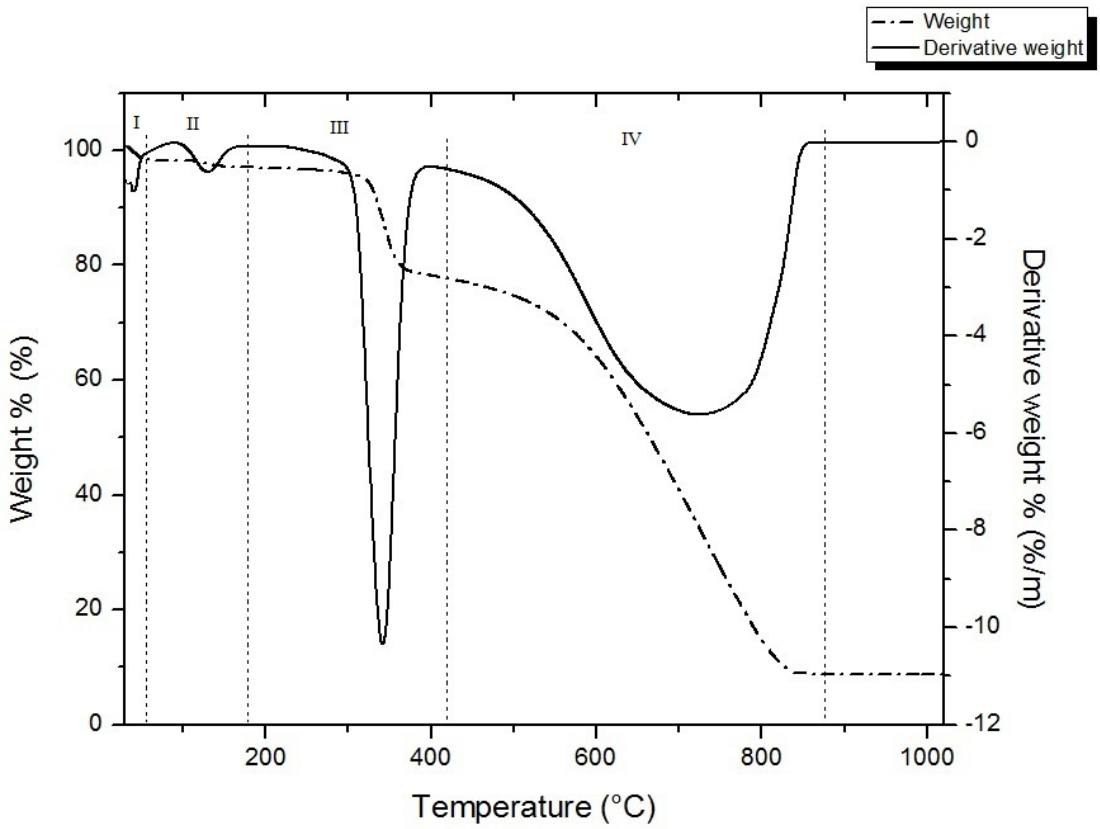
Table 3: The Electrospinnig Conditions With Different Flow Rate

Concentration (wt %)	Flow rate (μL/min)	Voltage (Kv)	Fiber diameter (μm)
8	5	20	0.742
8	7	20	0.765
8	9	20	0.79

THERMAL PROPERTIES OF ELECTROSPUN PAN NANOFIBERS

It is necessary to acquire information about the thermal properties of precursor fibers before undergoes heat treatment in order to transform to carbon nanofibers. Figure 5 presents TGA curves of the electrospun PAN nanofibers using a heating rate of 10 °C/min in the temperature range from room temperature to 1000 °C. The thermal decomposition of raw PAN consisted of four degradation steps in the temperature ranges of 36 °C – 42 °C, 100 °C – 190 °C, 200 °C – 400 °C and 500 °C – 850 °C. During the first step, there was a slightly weight loss remarkable about 1.272% due to the release of water and followed by the solvent xylene evaporates in the second stage. The notable weight loss of electrospun PAN nanofibers start to occur at the third stage between 200 °C - 400 °C. This pure PAN nanofibers in nitrogen atmosphere undergo a main mass loss at this stage due to the cyclization and thermal degradation [20]. On the other hand, the main weight loss from 500 °C – 850 °C, that is about 69%, indicate that the PAN nanofibers are stabilized in air due to reaction with oxygen by forming ladder structure to enable them to withstand high temperature during pyrolysis process [21]. Only 8.75% was left at 850 °C, above which the weight decreases slowly with the increasing of temperature.

Figure 5 presents TGA curves of the electrospun PAN nanofibers



CONCLUSION

This study has shown that electrospun PAN nanofibers with ranging diameter from 0.55-0.79 nm were obtaineed by electropsinning of PAN/DMF solution with varying electrospinning conditions, such as solution concentration, applied voltage and flow rate. Thus, the following points emerge from the present investigation:

1. The concentration solution of PAN highly influence the properties of electrospun PAN nanofibers produced during electrospinning process. The PAN solution at 8 wt% produced smooth and small diameter of fiber in the range of 588 – 690 nm, whereas high concentration solution which is 12 wt% shows larger diameter and some of them formed bead on plate collector. As a result, electrospun PAN nanofibers produced at 8 wt% showed the highest potential candidate as a precursor to produced carbon nanofiber in further experiments.
2. The diameters of the PAN nanofibers increase as the applied voltage increase. This condition led to larger fiber diameters with lower zeta potential and lower diffusion coefficient values of dispersions containing nanofibers. Therefore, in this research the best applied voltage that produce the smallest fiber diameter of electrospun PAN was 20 kV.
3. The increasing feed rate leads to larger diametes and bead formations. Based on the result obtained, it shows that when the flow rate increase, the number of fiber diameter also increase. This is because high feeding rate will eventually result in beaded large diameter fibers due to unavailability of proper solvent evaporating time prior to reach the collector. Thus, the best flow rate that produce smallest fiber diameter in this work was 5 µL/min.

The need of the smallest fiber diameter of PAN precursor fiber in this work was regarding to its performance in sensor application. When the lower the diameter of fiber is produced, the more the contribution in electrical conductivity, which is, the smallest fiber diameter gives higher electrical conductivity. Hence, it perform better in sensor field.

In future study, it can be imply that to have further investigation and carry out experiments with different experimental parameters to obtain better properties of carbon fiber in terms the performance in sensor application. The influence of pretreatment such as stabilization and oxidation before pyrolysis process should be done in the future study that include high mechanical properties, high surface area and high electrical conductivity. The use of electrospinning method as one of the fabrication technique to produce carbon nanofibers bring more advantages in this field of research. But, conventional needle type use sometimes gives disadvantages such as it produce small scale of sample. Its take time to do it repeatedly in order to get more sample. Besides that, it always clogging at the needle (nozzle) tip and the mechanical complexity of the design make it hard to handle. Therefore, in the future, this field of research can be explore more by using electrospinning with needle-free technology.

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