Effect of Voltage and Flow Rate Electrospinning Parameters on Polyacrylonitrile Electrospun Fibers

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Abstract. Currently, electrospinning is a very famous technique and widely used for forming polymer nanofibers. In this paper, the Polyacrylonitrile (PAN) nanofibers were prepared in concentration of 10wt% with varied processing parameters that can affect the properties of PAN fiber in term of fiber diameter and electrical conductivity was presented. Voltage of 10, 15 and 20 kV with PAN flow rate of 10, 15 and 20 ml/min were applied during processing. The electrospun PAN fibers were then undergo pyrolysis at 800°C for 30 minutes. The resultant PAN nanofibers were then analysed by SEM, XRD and four point probe test after pyrolysis process. SEM image show continuous uniform and smooth surface fibrous structure of electrospun PAN fibers with average diameter of 1.81 μm. The fiber morphology is controlled by manipulating the processing parameters of electrospinning process. The results showed that the resistance of electrospun PAN fibers decreases as the processing parameter changes by increasing the applied voltage and flow rate of electrospinning.

1. Introduction
Typically, nanofiber is processed by electrospinning into long, small diameters, and high surface area per unit volume [1]. Polyacrylonitrile fiber is also known as PAN fiber has been used in both industrial and medical applications such as precursors for the production of carbon fibers, drug deliver, wound dressing, sensor materials, and composite reinforcement [2,3]. One of the main reasons for the versatility of these fibers is due to the presence of high thermal stability at the range of 200-300°C [1]. PAN fiber has a low electrical resistivity (~1,500 μΩcm) measured along the fiber direction. Normally the electrospun PAN fiber layers will have large surface area per volume ratio with large amount of small pore sizes porosity, superior mechanical properties, and flexibility, so they are most extensively used in the electrospinning process because of their excellent properties [1]. Electrospinning which also called electrostatic fiber spinning is one of the techniques that use electrical forces to form continuous nanometer diameter fibers for natural and synthetic polymers with the help of electrostatic forces [4]. Electrospinning has been known as the most effective technique for polymer nanofibers fabrication. Various polymers especially PAN fiber have been successfully electrospun into ultrafine PAN fibers in recent years [5]. During the electrospinning process, electric forces are used for fibers formation from electrospinning solutions which are mostly in solvent solution while some were in melts form [6]. Physical and chemical properties of electrospun nanofiber can be actually controlled by manipulating electrospinning parameters either in solution (e.g., concentration, viscosity) and process (e.g., applied voltage, solution feed rate) in order to meet the requirements of a specific application [7]. The common raw material used for the synthesis of electrospun PAN fibers were Polyacrylonitrile (PAN) and N-Dimethylformamide (DMF).
2. Experiments

2.1 Materials

The solutions used in the electrospinning experiments were prepared by using Polyacrylonitrile (PAN) obtained from Sigma-Aldrich with 150000 average molecular weight without further purification. The 99.8 % N-Dimethylformamide (DMF) used was purchased from Avantor Performance Materials. The first paragraph after a heading is not indented (Bodytext style).

2.2 Methodology

This experiment has the following sections: (i) preparation of PAN polymer solution, (ii) electrospinning process of PAN polymer, (iii) measurements and characterizations, (iv) X-ray diffraction, (v) pyrolysis process of PAN polymer. The studied electrospinning parameters for this research were shown in Table 1.

2.2.1 Preparation of PAN polymer solution

PAN solutions in DMF were prepared by mixing the weighed 5g PAN powder into 45g DMF solution. The concentration of 10 wt% PAN solutions was prepared by stirring the mixture at room temperature for 24 hours prior to electrospinning.

| Voltage (kV) | Flow Rate (µL) | Tip to collector distance (cm) | Concentration (wt%) |
|-------------|----------------|-------------------------------|---------------------|
| 10          | 10             | 10                            | 10                  |
| 15          | 15             | 10                            | 10                  |
| 20          | 20             | 10                            | 10                  |

2.2.2 Electrospinning process of PAN polymer

The syringe was placed on the syringe pump which were filled with PAN solution. A medical-used needle was used as the nozzle tip for the syringe. The tip-to-collector distance was fixed at 10cm. The studied electrospinning parameters for this study are as shown in Table 1.

2.2.3 Measurements and Characterizations

Scanning electron microscope (SEM) were performed with JEOL JSM-6460LA. X-ray diffraction (XRD) spectra were acquired with diffractometer using Cu Kα radiation in the 2θ range 15°-60°. The resistivity were measured via four point probe test at room temperature. The formula, $R_s=KVI$ was used to calculate resistance of the electrospun PAN fibers where $R_s$, K, V, and I were the sheet resistance of electrospun PAN fiber layer, factor for shape of sample, voltage measured across the two voltage probe and current measured across the two current probe, respectively.

2.2.4 Pyrolysis process of PAN polymer

The electrospun PAN fibers were then undergo pyrolysis heat treatment. The electrospun PAN fibers were heated at 800 °C for 30 min under the rate of nitrogen flow at 0.1L/min. The heating rate for pyrolysis heat treatment was set at 5 °C/min. The electrospun PAN fibers undergo oxidation process
when the temperature is heated to the range of 200-300°C. The pyrolyzed electrospun PAN fibers will then analysed with SEM. The pyrolysis parameters studied are as showed in Table 2.

Table 2: The pyrolysis parameters applied in this experiment

| Heating time (min) | Heating temperature (°C) | Heating rate (°C/min) | Nitrogen flow rate (L/min) |
|--------------------|--------------------------|-----------------------|---------------------------|
| 30                 | 800                      | 5                     | 0.1                       |

3. Results and Discussion

The pure electrospun PAN fibers were white in colour. Electrospun PAN fibers show a continuous uniform and smooth surface fibrous structure when analysed under SEM. Figure 1 (a) shows the SEM image of electrospun PAN fibers at 10 kV, 15 μL/min before pyrolysis. The SEM image shows nonwoven thread-like structure with fiber diameter in range of 1 μm to 3 μm and an average diameter of 1.81 μm. It is a normal phenomenon obtained non-aligned nanofibers as there is no rotating drum collector used in this study. In fact, Boland et al. [8] reported that the nanofibers obtained from electrospinning can be actually aligned by using rotating drum collector with high speed. Figure 1 (b) shows SEM image of electrospun PAN fibers with 10kV, 15 μL/min after 30 min of 800°C pyrolysis. Figure 1. SEM micrographs of electrospun PAN fibers yield by 10kV at 15 μL/min (a) before pyrolysis and (b) after 800°C pyrolysis for 30min

The average diameter for electrospun PAN fibers with flow rate obtained was 3.17 μm. From the SEM image, the electrospun PAN fibers undergo slight structural changes, but overall, the morphology is remain almost the same. This also in agreement with the finding by Voepel et al [86], as they reported in their study that the electrospun PAN fibers undergo slight structural changes. The pyrolysis had fused some of the electrospun fibers which resulted in the larger fiber diameters. The overall average diameter measured of the electrospun PAN fibers before and after pyrolysis are presented in Table 3.

Figure 2 shows the XRD patterns of electrospun PAN fibers with different processing parameters. The XRD pattern of electrospun PAN fibers show the strongest diffraction peak at around 20 = 16.72° which corresponds to a planar spacing d = 5.2975Å. The electrospun PAN fibers is more on crystalline phase rather than amorphous. The crystalline peak shown was corresponding to carbon. By calculating the d-spacing for both the peaks, it is found that the d-spacing is closely to the ratio of √3:1. Hence, this
determined that the PAN chains was actually in hexagonal packing. Besides, there is a weak hill at around \(2\theta = 29.26^\circ\) which determine the amorphous structure of PAN fibers. The intensity of the peak is lower compared to the carbon peak at \(2\theta = 16.72^\circ\).

| Processing parameters | Average diameter |
|-----------------------|-----------------|
|                        | Before pyrolysis (μm) | After pyrolysis (μm) |
| Voltage (kV) | Flow rate (μL/min) |
| 10          | 1.81             | 3.17             |
| 15          | 1.18             | 3.72             |
| 20          | 1.27             | 3.84             |

Table 3: The average electrospun PAN fibers diameters before and after pyrolysis

Figure 3 shows the XRD patterns of electrospun PAN fibers with processing parameters of 15 kV and 15 μL/min that undergoes pyrolysis at 800°C for 30 mins. The XRD pattern of electrospun PAN fibers after pyrolysis show the strongest diffraction peak at around \(2\theta = 25.68^\circ\) which corresponds to a planar spacing \(d = 3.466 \text{ Å}\). Besides that, there is a weak hill at around \(2\theta = 42.04^\circ\) which determine the amorphous structure of PAN fibers. The intensity of the peak is lower compared to first carbon peak at \(2\theta = 25.68^\circ\).

Figure 2. XRD patterns of electrospun PAN fibers that synthesized at 15kV at various flow rate

Figure 3. XRD patterns of electrospun PAN fibers at 15kV after pyrolysis at 800°C for 30 mins.

Table 4 shows that the resistance of electrospun PAN fibers before pyrolysis decreases as the processing parameter changes by increasing the applied voltage and flow rate of electrospinning. For the first sample which is electrospun PAN fibers produced with 10 kV at 10 μL/min shows the highest resistance to electrical conductivity with 512.6 Ω. The electrospun PAN fibers were then undergo a decrease in resistance when the processing parameter changes with increasing the applied voltage. The
The resistance of electrospun PAN fibers did not vary much in resistance. In other word, the conductivity of the samples are having almost the same electrical conductivity.

**Table 4:** The resistance of electrospun PAN fibers before and after pyrolysis at various processing parameters

| Processing parameters | Resistance (Ω) | Voltage (kV) | Flow rate (µL/min) | Before pyrolysis (µm) | After pyrolysis (µm) |
|-----------------------|----------------|-------------|--------------------|-----------------------|----------------------|
|                       |                |             |                    |                       |                      |
| 10                    | 512.60         |             | 10                 |                       | 468.80               |
| 15                    | 444.84         |             | 15                 |                       | 464.50               |
| 20                    | 403.23         |             | 20                 |                       | 459.19               |
| 10                    | 414.15         |             | 10                 |                       | 465.90               |
| 15                    | 412.28         |             | 15                 |                       | 462.90               |
| 20                    | 407.44         |             | 20                 |                       | 454.67               |
| 10                    | 419.32         |             | 10                 |                       | 450.80               |
| 15                    | 412.01         |             | 15                 |                       | 448.40               |
| 20                    | 410.11         |             | 20                 |                       | 445.57               |

The electrospun PAN fibers have exhibited sharp increase in resistance after pyrolysis process. The decreasing value trend of resistance when electrospinning voltage and flow rate were increased were similar to the results before fibers undergoes pyrolysis. Overall the conductivity of pyrolysed electrospun PAN fibers still consider as non-conductive fiber due to too high resistance to electrical conductivity [9].

4. **Conclusion**

In this work, the effects of processing parameters on the electrospun PAN fibers towards the morphology of PAN fibers, electrical conductivity properties and also the effect of pyrolysis on the shrinkage of fiber diameter has been explored. It was found that the properties of electrospun PAN fibers produced is strongly depending on the electrospinning processing parameters such as voltage applied and flow rate, and also the pyrolysis heating temperature. With increasing voltage applied the fiber diameter of electrospun PAN fibers increased, while increasing flow rate has resulted in decreasing fiber diameters. The pyrolysed PAN fibers show increased in fiber diameter due to the fiber diffusity and also decreased the electrical conductivity of the fibers.

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