Effect of solution concentration and applied voltage on electrospun polyacrylonitrile fibers

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Abstract. Electrospinning is a simple and convenient method for fabrication of polymeric nanofibers from polymeric solution. In this paper, polyacrylonitrile (PAN) fibers are fabricated from different PAN solution concentration and applied voltages by electrospinning process. The fibers were then analyzed with Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD) and four-point probe to study the effect of PAN solution concentration and applied voltage on electrospun PAN fibers in terms of fiber diameters and morphologies, crystallinity and electrical properties. SEM showed that the electrospun PAN fibers with fiber diameter ranging from 0.5 to 2.7 µm. The diameter of fibers were increased with increasing PAN concentration and voltage applied. The increasing voltage also has increased the bead formation on the fibers. The amorphous structure of electrospun PAN fibers was exhibited by XRD. Electrical conductivity of electrospun PAN fibers were increased with increasing PAN concentration but somehow reduced with increasing voltage of the electrospinning.

1 Introduction

Nanofibers are nanostructured polymer fibers with fibers diameter ranging from micrometers to nanometers [1, 2]. Electrospinning was mostly employed to fabricate nanofibers with light weight, small diameters, long lengths, large surface area per volume, high porosity and tiny pore size [3, 4]. The properties and morphologies of electrospun nanofibers are significantly being influenced by numerous electrospinning processing parameters [4]. For instance, polymer (types, molecular weight, concentration), solvent (types, vapour pressure, diffusivity in air), additives (surfactants, salts), solution properties (surface tension, viscosity, rheological behavior, relaxation time, electrical conductivity, dielectric permittivity), applied voltage, volumetric flow rate, electrospinning time, spinneret orifice diameter, distance between spinneret and collector and ambient conditions (relative humidity, temperature) [3, 4].

Based on this study, polyacrylonitrile (PAN) is chosen as a raw material to produce the nanofibers via electrospinning since PAN is the most broadly used in electrospinning because of its superior properties [5]. PAN fibers are white in colour and non-conductive. It has excellent mechanical properties and always played an important role for biomaterials due to its outstanding biocompatibility.

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PAN fibers is a copolymer which consist of first monomer of acrylonitrile and the second monomer of vinyl acetate. In addition, PAN fiber possess excellent stretching strength and also high stretching strain [6]. PAN is the most ordinary among the various precursors for fabricating carbon nanofibers. The main reasons are high carbon yield and flexibility for tailoring the structure of the finishing carbon nanofiber products and the ease of achieving the stabilized products by the formation of a ladder structure through nitrile polymerization. Apart from this, PAN nanofibers owned desired properties such as high ionic transport, low diffusion resistance, high electrolyte uptake, good compatibility with electrodes, excellent chemical, thermal, mechanical stability and long life cycle [7].

Electrospinning also known as electrostatic fiber spinning is a simple and convenient method for the fabrication of polymeric nanofibers and nanocomposites from both natural and synthetic polyemers [4, 8]. The main principle of electrospinning is to generate a charged jet of polymeric solution by applying an electric field [8]. A polymeric solution is accelerated in an electric field between a charged spinneret and a grounded collector since electrospinning is a fiber production method which uses electric force to form fibers from polymeric solution [4, 8]. When the applied electric field overcomes the surface tension of the droplet, a charged jet of polymeric solution is ejected. As the jet travels in the air, the solvent evaporates and a charged fiber is left behind which can be able to collect on a grounded collector. The jet grows longer and thinner and extends towards the grounded collector due to bending instability until it solidifies on the grounded collector [9].

Thus, electrospinning has been chosen for fabrication of nanofiber in this study. The effect of solution (in term of materials) and processing parameter via applied voltage during electrospinning on the fiber yield diameters and morphologies, crystallinity and electrical properties will be investigated.

2 Methodology

The experimental approach involved the raw materials, sample preparation, electrospinning set-up and characterization of electrospun PAN fibers. The characterization of electrospun PAN fibers were determined by using Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD) and four-point probe.

2.1 Raw materials

Polyacrylonitrile (PAN) and N, N-Dimethylformamide (DMF) are the raw materials that were used to prepare PAN solution. Polyacrylonitrile (PAN) with an average molecular weight of 150000 was purchased from Sigma-Aldrich and used without further purification. 99.8% of N, N-Dimethylformamide (DMF) was purchased from Avantor Performance Materials, was chosen as a solvent.

2.2 Sample preparation

PAN powder was dissolved in DMF to prepare PAN solution with different concentrations of 8 wt%, 10 wt% and 12 wt%. Then, the mixtures were stirred under constant magnetic stirring for 24 hours at room temperature prior electrospinning in order to obtain homogeneous solution.

5ml of syringe filled with PAN solution was placed horizontally by varying the concentrations (8 wt%, 10 wt% and 12 wt%). The syringe with a spinneret nozzle of 0.6mm in diameter was held with a distance of 9cm from spinneret to collector. In this experiment, the flow rate of PAN solution is fixed at 20 µL/min. A high voltage power supply which can
generate up to 50 kV was connected to the syringe. A flat metal plate covered with aluminum foil was placed vertically serving as a grounded counter electrode. An electric field is formed between the spinneret nozzle and the grounded collector by applying voltage of 10 kV, 15 kV and 20 kV. The fibers that were charged onto the plate were then collected by using a pair of tweezers. The detailed information on electrospinning parameters of this experiment are shown in Table 1.

Table 1: The parameters of electrospinning process

| PAN solution concentration (wt %) | Applied voltage (kV) | Flow rate of PAN solution (µL/min) | Collector distance (cm) |
|----------------------------------|----------------------|-----------------------------------|-------------------------|
| 8                                | 10                   |                                   | 20                      |
| 10                               | 10, 15, 20           | 20                                | 9                       |
| 12                               | 10, 15, 20           |                                   |                         |

2.3 Characterization of electrospun PAN fibers

2.3.1 Scanning electron microscopy (SEM)

Scanning Electron Microscopy (SEM) (Model: JEOL JSM-6460LA) is employed to analyze the characterization of electrospun PAN fibers (sample). Firstly, electrospun PAN fibers were kept dried in a vacuum for 24 hours before it undergoes the characterization since the sample has to be prepared to withstand the vacuum condition and high energy electron beam. After that, the sample was placed on the sample holder and taped with double sided tape. The sample was coated with a thin gold layer by using sputter coater (Model: JFC 1600). The sample sputter-coated with gold having been prepared for viewing with an SEM. Then, high resolution images of electrospun PAN fibers surface were evaluated by an image analyzer (Sem Afore 5.0, JEOL).

2.3.2 X-Ray diffraction (XRD)

The crystalline phase and composition of electrospun PAN fibers are analyzed by using X-Ray Diffraction (XRD) (Model: XRD-6000, Shimadzu, Tokyo, Japan). The diffraction patterns were recorded using Cu Kα radiation over a 2θ range of 15° to 60°, a position-sensitive detector using a step size of 0.02° and scan rate of 10°/min. The sample holder was cleaned before put it into the chamber. The specimen was well-compacted and placed on the sample holder to obtain an optimal result. The analyzed data is then interpreted by using a software called HighScore Plus.

2.3.3 Four point probe test

The electrical conductivities of electrospun PAN fibers was measured with four-point probe. The four-point probe was typically used to measure the resistivity of sample in nanofabrication. The four equally spaced probes were linked with the sample of unknown resistivity. A high impedance current source is applied by passing a current through the two
outer probes while the voltage across the two inner probes is measured by a voltmeter to measure the sample resistivity.

3 RESULTS AND DISCUSSION

The results of the sample characterization including Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD) and Four Point Probe are discussed in the following section.

3.1 Scanning Electron Microscopy (SEM)

3.1.1 Effect of PAN Solution Concentration

Based on the Figure 1 (a) to (c), there was an increase in fiber diameter with higher polymer concentration. This statement was in agreement with the finding by Shao-Hua Wu et al. since the electrospun fibers produced were same with the conventional electrospinning results [11]. As described by Wang et al., the fiber diameter and flux of electrospun PAN nanofibers has been increased by elevating the PAN solution concentration [12]. As the concentration and viscosity of the electrospinning solution increases, the number of macromolecular chains as well as chain entanglements in the electrospinning solution also increase, while the size of Taylor cone keeps relatively constant. Therefore, the charged jet becomes thicker and longer, due to the higher viscosity resistance leading to the increase of fiber diameter [13,14]. The tendency of bead formation (marked with red circle) in Figure 1(a) were reduced when the PAN solution concentration increased as can be seen in Figure 1(b) and (c) where there are no bead was can be observed in these figures. This phenomenon is owing to the increase in the concentration that has resulting in larger fiber which then regulated the flow, thus reduced the formation of beads.

![Fig. 1: SEM images of electrospun PAN fibers at 10 kV with different PAN solution concentration (a) 8 wt%, (b) 10 wt% and (c) 12 wt% at 1k magnification](image)

3.1.2 Effect of Applied Voltage

Some researchers found that the PAN fiber diameter become larger with increasing applied voltage. The optimal charge density was 2.5 kV/cm and then further increasing the charge density would increase the diameter of electrospun PAN fibers has been reported by Ashraf and Hamid [15].
Normally, more fluid will be ejected in a jet at a higher applied voltage, thus resulting in a larger fiber diameter [16]. This statement has been agreed by Zhang and Demir et al. since they have proposed that there is more ejection of polymer when higher voltages were applied, causing the formation of fiber with larger diameter [1]. However, the higher the applied voltage, the higher the probability of bead formation. According to the Figure 2 (a) to (c), the beaded fibers (marked with red circle) were electrospun from 8 wt% of PAN solution with applied voltage increased from 10 to 20 kV. As can be seen, higher bead formation can be observed when as the applied voltage were increased. This was due to the increase the electrostatic repulsive force on the liquid jet which then increased the formation of beads on fibers.

**Fig. 2:** SEM images of electrospun PAN fibers with 8 wt% of PAN solution at different applied voltage (a) 10 kV, (d) 15 kV and (g) 20 kV at 1k magnification

### 3.2 X-Ray Diffraction (XRD)

Figure 3 shows the XRD diffraction patterns of electrospun PAN fibers at 10kV with different concentrations. PAN is a semi-crystalline polymer [17]. All samples showed two equatorial peaks with a diffuse meridian peak (broad peak) that represents rather random molecular orientation. These data exhibited that the molecular arrangement in electrospun PAN fibers were mostly similar across all samples. Thus, equatorial peaks are normally found in PAN fibers. In fact, the molecules of PAN have a very short crystallization time and corresponding PAN in all the fibers mainly existed in an amorphous state with a small difference between the fibers [18, 19].

**Fig. 3:** XRD patterns of electrospun PAN fibers at 10 kV with different PAN concentration (a) 8 wt%, (b) 10 wt% and (c) 12 wt%

### 3.3 Four Point Probe Test

The electrical conductivity of electrospun PAN fibers with different parameters was shown in Table 2. The four-point probe test which is used for electrical conductivity was carried out
at room temperature demonstrated that all electrospun PAN fibers formed have different conductivity values with different parameters. Based on the Figure 4, there was an increasing trend of electrical conductivity for the electrospun PAN fibers produced at applied voltage of 10 kV with different concentrations of 8 wt%, 10 wt% and 12 wt%.

Table 2: Effect of PAN concentration and voltage of electrospinning on electrical conductivity of electrospun PAN fibers

| PAN Concentration (wt%) | Voltage (kV) | Electrical conductivity (S/mm) |
|------------------------|-------------|-------------------------------|
| 8                      | 10          | 0.00165                       |
|                        | 15          | 0.00172                       |
|                        | 20          | 0.00181                       |
| 10                     | 10          | 0.00181                       |
|                        | 15          | 0.00175                       |
|                        | 20          | 0.00174                       |
| 12                     | 10          | 0.00200                       |
|                        | 15          | 0.00180                       |
|                        | 20          | 0.00203                       |

The electrical conductivity of electrospun PAN fibers increased from 0.00165 S/mm, 0.00181 S/mm to 0.002 S/mm when the PAN solution concentration increased from 8 wt%, 10 wt%, to 12 wt% while maintaining the applied voltage at 10 kV. The electrospun PAN fibers fabricated at applied voltage of 15 kV with increasing the concentration from 8 wt%, 10 wt% to 12 wt% was showed an increase in electrical conductivity. The electrical conductivity of electrospun PAN fibers increased from 0.00172 S/mm, 0.00175 S/mm, to 0.0018 S/mm when the PAN solution concentration increased from 8 wt%, 10 wt%, to 12 wt% while maintaining the applied voltage at 15 kV. Initially, there was a decreasing trend of electrical conductivity for the electrospun PAN fibers produced at applied voltage of 20 kV with 8 wt% and 10 wt% of PAN solution concentration, then it is start to increase gradually from 10 wt% to 12 wt%. The electrical conductivity of electrospun PAN fibers decreased from 0.00181 S/mm to 0.00174 S/mm and then increasing to 0.00203 S/mm when the PAN solution concentration increased from 8 wt%, 10 wt%, to 12 wt% while maintaining the applied voltage at 20 kV. The electrical conductivity of electrospun PAN fibers did not varies much. The small increased in conductivity of the yield fibers was due to the increasing fiber diameter with increasing PAN concentration and voltage applied during electrospinning process.

![Fig. 4: The electrical conductivity of electrospun PAN fibers produced from different PAN solution concentration and applied voltages.](image)
Conclusion

In this work, the effect of PAN solution concentration and applied voltage on electrospun PAN fibers in terms of the morphologies, crystallinity and electrical properties has been explored. It was found that the properties of electrospun PAN fibers fabricated is critically depending on the electrospinning parameters such as PAN solution concentration and applied voltage. With decreasing the PAN solution concentration, the fiber diameter decreases. When applied voltage increases, there is increasing in bead formation on electrospun PAN fibers has been observed. As analyzed by XRD, all electrospun PAN fibers mainly existed in an amorphous state without any changes with increasing PAN concentration or voltages. Electrical conductivity of electrospun PAN fibers were increased with increasing PAN concentration and voltage of the electrospinning.

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