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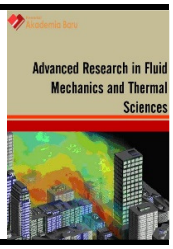

The Effects of Different Carbonization Temperatures on the Properties of Electrospun Carbon Nanofibre from Polyacrylonitrile (PAN) Precursor

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ABSTRACT

Carbon nanofibres produced from carbonization of polyacrylonitrile (PAN) precursor have been given much attention due to their superior properties. However, there is limited information available on the effects of carbonization temperature on the properties of the carbon nanofibres. This study investigates the effects of different carbonization temperature on physical, chemical and electrical properties of the carbon nanofibres. Polyacrylonitrile (PAN) precursor nanofibres were prepared using electrospinning technique. The characterization of the electrospun carbon nanofibre was carried out using scanning electron microscopy (SEM), Image J software, Fourier transform infrared spectroscopy (FTIR), and four-point probe methods. The results suggest that by increasing the carbonization temperature, thinner carbon fibres were produced due to the extended elimination of other functional groups. This is evidenced by flatter FTIR curves produced by samples with higher carbonization temperatures. In addition, the electrical conductivity improved by increasing carbonization temperature. The results presented in this study would provide useful information for the development of new conductive nano materials.

1. Introduction

In recent decades, carbon nanofibres produced using electrospinning method has been given much interest due to their superior characteristics such as high surface area, lightweight, high electrical and thermal conductivity as well as high mechanical strength [1-3]. One of the popular methods used to fabricate high quality carbon nanofibres is through pyrolysis of polyacrylonitrile (PAN) precursor. Previous studies have reported the potential applications of PAN based carbon nanofibres such as in sensors, supercapacitors, and filtration system applications [4,5].

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Electrospinning method are normally selected due to its simplicity and versatility of the process to produce nanofibres in the range of tenth nanometers to several micrometers [6,7]. A fundamental setup of electrospinning consists of a polymer solution or melt supply, a high voltage power supply, a spinneret tip, and a grounded collector as shown in Figure 1. A high voltage potential is connected to the spinneret tip causing electrostatic repulsions within the polymer. When the repulsive forces overcome the surface tension of the polymer droplet, jets of fibres are ejected towards the grounded collector [6]. The fibres are stretched and solvent evaporation takes place along the journey to the collector [8]. The nanofibres produced are normally straight, randomly orientated, and could be over several kilometres in length [9,10]. Pyrolysis of PAN involves oxidation or stabilization of the fibres, followed by carbonization process. An appropriate selection of stabilization and carbonization process is significant to obtain high quality carbon nanofibres. The typical temperature used for stabilization process of PAN electrospun nanofibres is between 200^{o}C to 300 ^{o}C under air atmosphere [11]. Stabilization process is carried out to eliminate non-carbon elements, which in turn will change the physical and chemical properties of the nanofibres [12]. Carbonization process allows the carbon to self-arrange, creating a "ladder" structure that formed through cyclization of nitrile group [11]. Typically, carbonization process is carried out at temperatures between 800 ^{o}C to 1400 ^{o}C in an inert atmosphere such as nitrogen or argon gasses. Throughout the process, non-carbon elements are removed as volatiles to produce carbon fibres with a yield of about 50% of the mass of the original PAN. It is thought that if carbonization duration and temperature are increased, the molar fraction as well as the electrical conductivity of the produced carbon nanofibres would also increase [13].

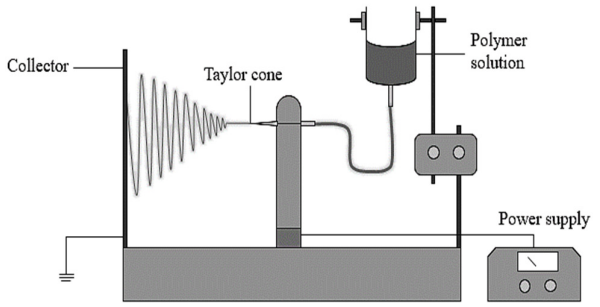

Fig. 1. A schematic diagram of electrospinning process setup

2. Methodology

Polyacrylonitrile (PAN) with an average molecular weight of 124,000-130,000 g/mol was purchased from Sigma-Aldrich. N, N-Dimethylformamide (DMF) also purchased from Sigma-Aldrich was used as the solvent. The precursor solution was prepared by dissolving 10 wt% of PAN in DMF solvent. The mixture of PAN/DMF was mixed using a magnetic stirrer model C-MAG HS7 (Ika Works Malaysia) at room temperature for about 24 hours. Throughout electrospinning process, the high voltage was set at 10 kV whereas the distance between the spinneret to the collector was set at 20 cm. The electrospinning machine used was Electrospinz Model ES1a (Electrospinz Ltd., New Zealand). The electrospinning process was performed at room temperature. Aluminium foils were fixed onto the grounded plate collector to collect fibres.

Stabilization and carbonization process were performed using a laboratory tube furnace Model TF70- 1600 equipped with nitrogen gas supply. The collected electrospun nanofibres were rolled (70mm x 70mm) and placed onto a ceramic crucible boat. Then, the crucible boat was placed into the centre heating zone of the furnace. The stabilization process was carried out at 240 ^{o}C with

heating rate of 3 °C/min and dwell time for 30 minutes in normal atmosphere. The carbonization process was initially carried out at 800°C of constant temperature with a heating rate of 5°C/min and dwell time for 30 minutes in nitrogen atmosphere. The same process was repeated for the other samples with different carbonization temperatures *i.e*. 1000°C and 1200°C. After carbonization process, the furnace was naturally cooled down to room temperature. Table 1 shows the summary of samples and the heat treatment processes.

Table 1
Summary of heat treatment process

Sample	Stabilization temperature (°C)	Carbonization temperature (°C)
NF	Not applied	Not applied
SNF	240	Not applied
CNF 1	240	800
CNF 2	240	1000
CNF 3	240	1200

Note:
1. NF – electrospun PAN nanofibres
2. SNF – stabilized nanofibres
3. CNF – carbonized nanofibers

Physical characterization of the fibres before and after pyrolysis process was carried out using a scanning electron microscopy (SEM) Model JSM-6010PLUS/LV (Jeol Ltd., Japan). The magnification of the SEM micrographs was fixed at ×5,000. The average fibre diameter was measured from SEM micrographs using ImageJ version 1.50 software (National Institutes of Health, USA). At least 100 measurements were taken from each SEM micrograph. Investigation on the change of functional group before and after stabilization and carbonization process was carried out using a Fourier transform infrared spectroscopy (FTIR) Perkin Elmer Spectrum 100 FTIR spectrometer (USA). The electrical conductivity of the carbon nanofibres was measured by using a four-point probe from Jandel Engineering Limited (UK) per ASTM F390 standard. The following equation was used to calculate the electrical conductivity [1].

$$\sigma = \frac{1}{4.5324 \times Rs \times t}(S/m) \quad (1)$$

4.5324 = correction factor
Rs = sheet resistance by four-point probe
t = thickness by digital micrometer

3. Results and Discussion

3.1 Physical Properties

Initially, the deposited PAN nanofibres appeared white in colour (Figure 2(a)). After stabilization process at 240°C with heating rate of 3°C/min, the white colour changed to brown (Figure 2(b)). Finally, after carbonization process at 800°C, 1000°C, and 1200°C with heating rate of 5°C/min, the brown colour of the nanofibres changed to black (Fiure 2(c)). The change from light to dark colour exhibits that the decomposition of other organic compounds and formation of denser structure in polymer have taken place through thermal cyclization and dehydrogenation [3]. Furthermore, the colour change also indicated that the as-spun nanofibres were altered from thermoplastic to

thermoset [14]. The black colour of after carbonization samples indicated high carbon content of the fibres. All of the materials were used without further purification.

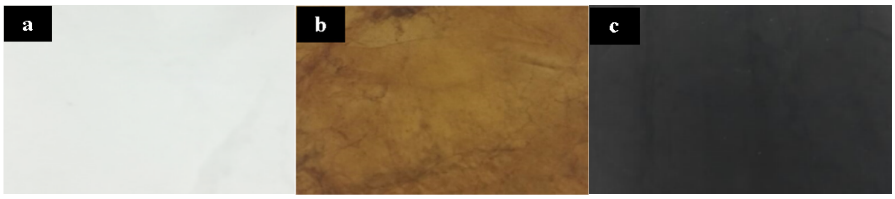

Fig. 2. The colour change of the nanofibres before and after heat treatments (a) as-spun PAN electrospun nanofibres (NF), (b) stabilized nanofibres (SNF), and (c) carbonized nanofibres (CNF)

3.2 Analysis of Surface Morphology

From SEM micrographs in Figure 3, the average diameter of the nanofibres were reduced after stabilization and carbonization processes. The average diameter of as-spun PAN nanofibres and stabilized nanofibres were 1000.10 nm and 920.70 nm, respectively. Meanwhile, the average diameter of the carbonized nanofibres at 800°C, 1000°C and 1200°C were 658.80 nm, 492.50 nm, and 352.40 nm, respectively. As shown in Fig. 3, the average diameter of as-spun PAN nanofibres was reduced about 8% after stabilization process (920.70 nm). Then, the average fibre diameter was further reduced to 34%, 51%, and 65% after carbonized at 800 °C (658.80 nm), 1000 °C (492.50 nm), and 1200 °C (352.40 nm), respectively. This finding corroborate the finding of Lee and co-workers which concluded that by increasing carbonization temperature, the average fibre diameter would also reduce [15].

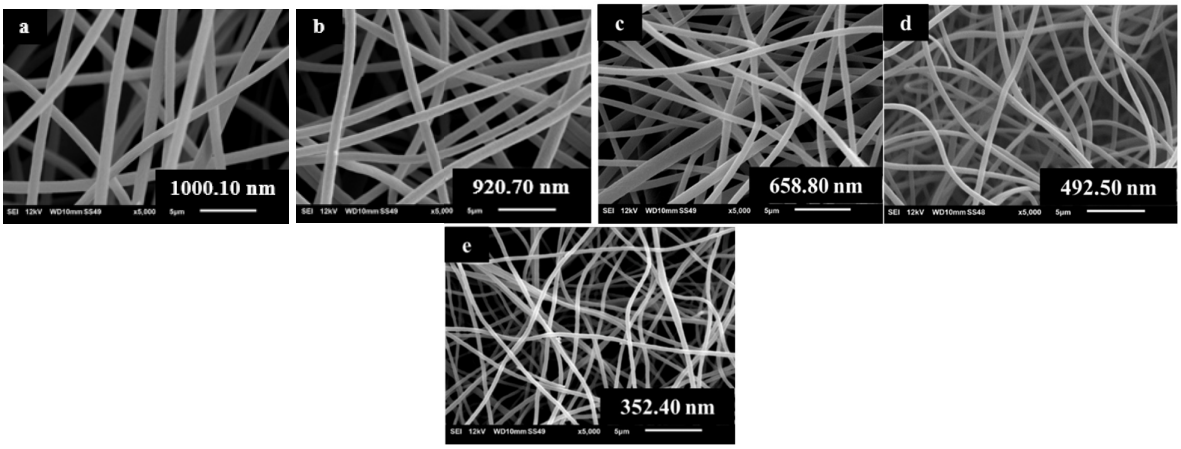

Fig. 3. SEM micrographs (×5,000 magnification) of (a) as-spun PAN nanofibres (NF), (b) stabilized nanofibres (SNF), (c) carbonized nanofibres (CNF 1) at 800°C, (d) CNF 2 at 1000 °C, (e) CNF 3 at 1200 °C

3.3 Fourier Transfrom Infrared Spectroscopy (FTIR)

FTIR spectrum transmittance of NF, SNF, and CNF at 800 °C, 1000 °C and 1200 °C, respectively are shown in Figure 4. Based on the results, it was clearly shown that there were strong and sharp peaks formed by as-spun NF. However, these peaks started to disappear after stabilization process as shown by SNF peak. Eventually, the peaks were mostly disappeared after the carbonization process

as shown by CNF peaks. From Figure 4, higher carbonization temperature produced a flatter FTIR curve. There was a huge difference between NF peak and CNF peaks. The strong peak intensity located at between 2220 cm^{-1} to 2260 cm^{-1} indicates the presence of nitrile group which (C≡N) whilst the peak intensity located at between 2850 cm^{-1} to 2960 cm^{-1}, 1440 cm^{-1} to 1460 cm^{-1}, and 1040 cm^{-1} to 1220 cm^{-1} represents the aliphatic CH group vibrations with different modes in CH and CH_2. Peak intensity at 2242 cm^{-1} was obviously reduced after stabilization process at 240 °C. This is because of the nitrile group reaction through cyclization to produce conjugated C=N and make fully aromatized cyclized ladder structures [3]. At this point, the nanofibres have become infusible and therefore cannot be melted or fused during carbonization process [16].

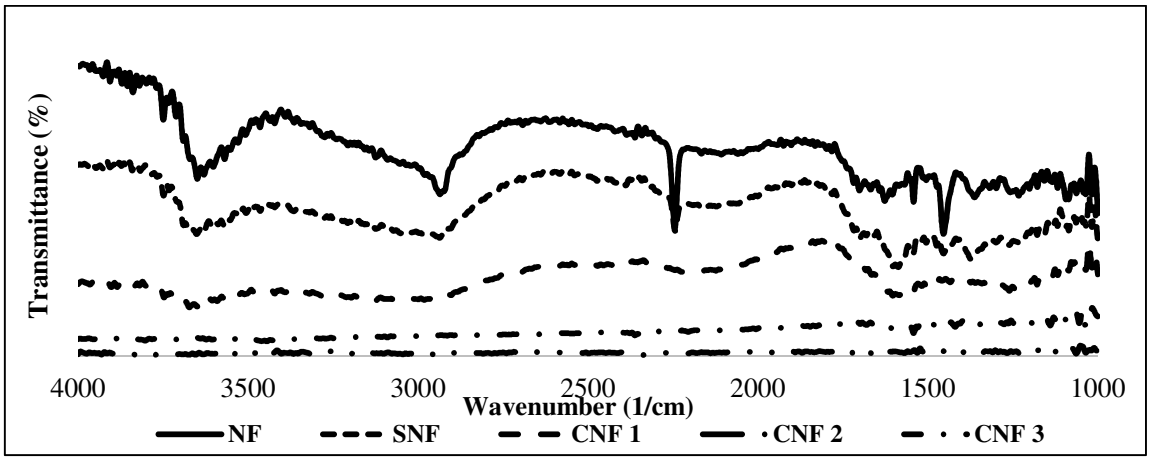

Fig. 4. FTIR spectra of electrospun nanofibre (NF), stabilized nanofibre (SNF), carbonized nanofiber (CNF 1) at 800 °C, carbonized nanofibre (CNF 2) at 1000 °C, and carbonized nanofibre (CNF 3) at 1200 °C

Based on the results, PAN electrospun nanofibres were not fully stabilized as evidenced by a small peak at 2242 cm^{-1}. To overcome the drawback, the stabilization temperature could be escalated at 280 °C [17]. This is due to the fact that higher stabilization temperature contributes to the higher reduction of organic compound. Most of the peaks were fully eliminated after carbonization process at 800 °C, 1000 °C and 1200 °C. However, full conversion of PAN polymer to carbon was not achieved due to existence of other compounds. For example, aliphatic CH group is still visible even after carbonization process for carbonized nanofibre at 800 °C. On the other hand, the FTIR results for carbonized nanofibre at 1000 °C and 1200 °C showed that other compounds have been fully eliminated. Therefore, it can be concluded that the minimum carbonization temperature of PAN electrospun nanofibres used in the present study is 1000 °C.

3.4 Four-Point Probe Method

Table 2 presents the electrical properties of the carbonized nanofibres. The conductivity of carbonized nanofibre at 800 °C, 1000 °C, and 1200 °C were 0.1337 S/m, 63.8627 S/m, and 73.1787 S/m, respectively. As the temperature of carbonization increased, the conductivity of carbon nanofibre was also increased. Theoretically, during carbonization process, the intermolecular fibres formed graphite-like structures due to disordered carbons into graphitic carbons after carbonization process [18]. Graphite is known as a good conductor due to delocalization of pi electron bond on the top and below carbon plane that allows the electron to move freely, so it can conduct electricity [19]. FTIR spectrum transmittance of NF, SNF, and CNF at 800 °C, 1000 °C and 1200 °C, respectively.

Table 2
Electrical properties of carbonized nanofibres (CNF)

Sample	Sheet resistance, (Ω)	Electrical conductivity, (S/m)
CNF 1	4.23×10^{3}	0.1337
CNF 2	11.92	63.8260
CNF 3	30.15	73.1787

4. Conclusion

In this study, carbon nanofibers were successfully fabricated through stabilization and carbonization process of electrospun PAN nanofibers using electrospinning method. The results showed that the physical, chemical, and conductivity properties of the carbon nanofibres were affected by stabilization and different carbonization temperatures. Electrospun PAN nanofibers turned from white to black colour after stabilization and carbonization process. Black colour indicates high carbon content of the nanofibers. SEM images demonstrated that the average fibre diameter was reduced from 1000.10 nm to 352.40 nm by increasing carbonization temperatures. FTIR results showed that the functional groups appeared on electrospun PAN nanofibers curve were fully eliminated after carbonization process to form carbon nanofibers. Moreover, the conductivity of the carbon nanofibres significantly improved after carbonization process. This nanoscale carbon-based material could make several noteworthy contributions to electronic applications such as for sensors and capacitors. Furthermore, this study has thrown up a number of questions that need further investigation. Further works need to be carried out and the results will be reported later.

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