Original Research Articles

Preparation and Testing the Hyperthermia Property of Electrospun Micro and Nanofibers

ABSTRACT

The hyperthermia properties of cobalt have received reasonable attention in recent years due to the advances in nanofiber production. One of its main proponents is the medical field where it is used to combat malignant cancer cells [1]. During the testing process it was observed that the cobalt solution transformed from a polymer to a ceramic after heat treatment and also the material retained more heat. This observation can lead to much greater applications. The nanofibers were produced using a process called electrospinning, which is one of the most simple and effective ways of producing such fibers and it takes advantage of the magnetic properties of cobalt. The objective of this study is to observe and verify energy conversion from electromagnetic wave to heat, observe the response of cobalt to electromagnetic waves and to give reasonable recommendations for future applications.

1. INTRODUCTION

Electrospinning is a process that produces polymer filaments using electrostatic forces and was patented in 1934 by Anton Formhals. It is a fiber-forming process aided by the application of electrostatic forces to control the production of fibers [2]. Electrospinning has emerged as a more simple and reliable method to produce nanofibers than previous conventional process as shown in Figure 1. Electrospinning is accomplished by dissolving the desired nanofiber material in a conductive liquid solvent. The fluid is then loaded in a syringe and expelled through a very fine needle. The needle itself is charged with considerable voltage (in the range of 10-30 kV) and pointed at a grounded collector surface that attracts the material. The attraction process splits the narrow stream of material into fibers that achieve a nanoscale. The fibers overlap and a thin film of material is created. The main reason the smaller nanofiber material holds together is the intermolecular forces between smaller molecular units. The overall shape of the nanofiber depends on the shape of those units [6].

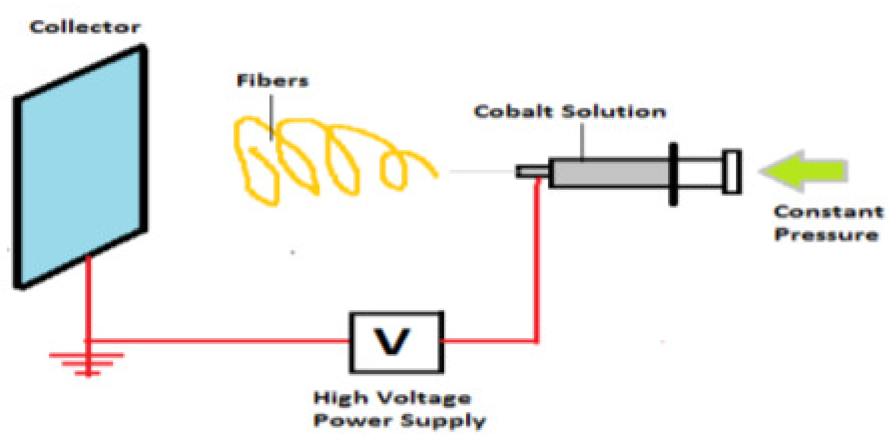

Fig. 1. Schematic of Electrospinning Process

Nanofibers can also be created by other conventional methods, such as drawing, template synthesis, phase separation, and self-assembly. Some of the differences between electrospinning and the conventional methods are listed in Table 1.

Table 1 - Comparison of Processing Techniques for Preparing Nanofibers [3]

Process	Technological Advances	Can the process be scaled?	Repeatability	Convenient to process	Control on fiber dimensions
Drawing	Laboratory	No	Yes	Yes	No
Template Synthesis	Laboratory	No	Yes	Yes	Yes
Self-Assembly	Laboratory	No	Yes	No	No
Electro-spinning	Laboratory (with potential for industrial processing)	Yes	Yes	Yes	Yes

The main advantages of electrospinning compared to other processes are its cost effectiveness, and the fact that electrospinning can result in long, continuous nanofibers. Other benefits of electrospinning include good control over the nanofibers diameter by adjusting the process parameters [4]. The shape of the fibers is related to the amount of electrical charge that is carried with the fluid inside the syringe, and the amount is dependant on different factors which can be used to obtaining significantly longer nanofibers [5]. These factors include the distance from the tip to the collector, the diameter of the fluid jet near its cone, relaxation time, viscosity of the fluid, and the polymer concentration in the fluid which is not possible through other techniques [6]. Moreover, relaxation time is the amount of time it takes for the excess charge in the fluid to radially move toward the surface of the fluid in order to achieve an equilibrium state [7]. The main disadvantage of electrospinning is the instability of the jet, which can't be precisely controlled [3]. The primary components of an electrospun fiber solution can be different depending on the purpose; nevertheless, PVP (Polyvinylpyrrolidone) nanofibers are commonly added to the fiber solution as a template for producing suitable nanofibers used in various applications[8]. Standard cobalt (atomic mass 59 g/mol) has few practical applications on its own; however, it has many applications when used as an alloy material. In metallic and ceramic alloys, cobalt is used for its wear and corrosion resistance as well as keeping its strength at high temperatures. When combined with other materials such as iron, chromium, tungsten, nickel, titanium, and aluminum so called "super alloys" can be created. Sodium-Cobalt oxide has revealed a considerable potential as a thermoelectric material used in energy conversion and electronic devices [9].

2. EXPERIMENTAL PROCEDURES

The experimental part of the research began by preparing a specific composition which was researched beforehand. The composition consisted of 5 mL of ethanol (C_2H_5OH) and 0.375g (Polyvinylpyrrolidone). Afterwards, 0.063 g of ethanol and 0.034g of cobalt acetate were added. The major composition in the experiment was cobalt acetate. All of the compounds were added to a beaker where they were mixed together and stirred well. The mixed composition was then transferred into a syringe to begin the electrospinning process. The electrospinning apparatus was already setup where a 10 kV charge was applied to the liquid. The voltage applied to the composition created an electrically charged jet. The jet was ejected from the syringe to the grounded collector which was placed in the distance of approximately 10 cm from the tip of the syringe. The electrostatic repulsive forces acted against the intermolecular attractive forces of the liquid at the surface resulting in stretching the surface of the liquid to create fibers on the grounded collector.

After all of the liquid was converted to fiber filaments, the samples as shown in Figure 2(a) and (b) were collected and were ready for hyperthermia testing. The hyperthermia test measures the heat reaction when exposed to a magnetic wave. The sample was heated in a microwave for 6 different durations. Prior to placing the sample in the microwave, the temperature throughout the surface of the sample was measured using a temperature reader. After recording the unheated sample's temperature, the sample was placed in the microwave and was heated for 5, 10, 15, 20, 25, 30 seconds respectively and the temperature throughout the surface was measured after each heating process in the microwave. In order to transform the polymer to ceramic, the sample was wrapped in an aluminum foil as shown in Figure 3(a) and was placed in a furnace as shown in Figure 3 (b) at 500°C and was heat treated for 2 hours. After the sample was removed from the furnace of Figure 3(c), the sample went under hyperthermia test once again in order to compare the temperature throughout the surface before and after heat treatment. The results of both tests were then tabulated and plotted for further review.

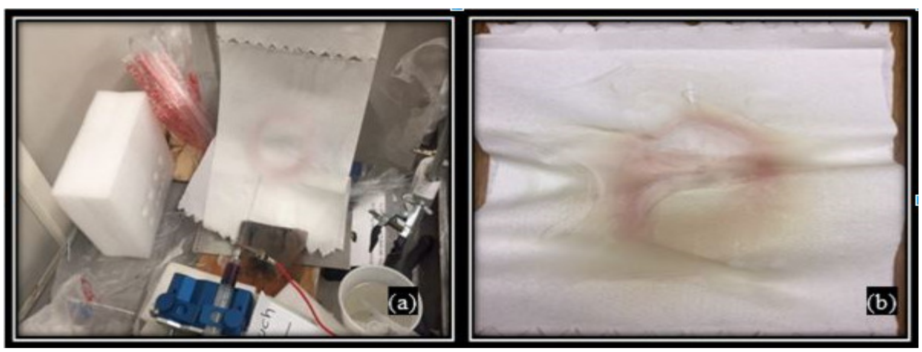

Fig2. (a) Electrospinning Process (b) Nanofibers Created on the Collector

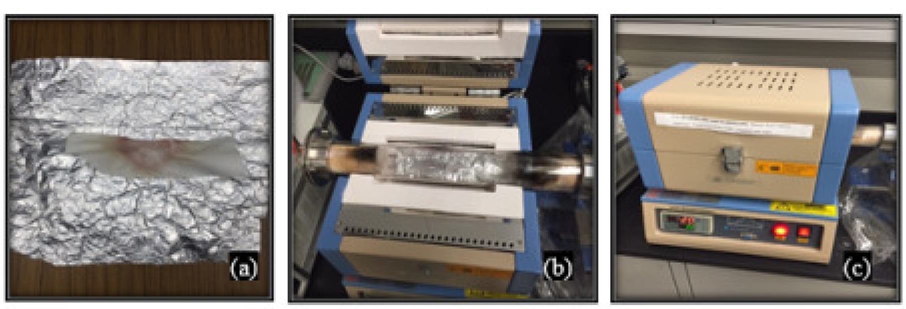

Fig 3. (a) Sample Ready to Be Wrapped in Aluminum Foil Prior to Heat Treatment
(b) Sample Placed in a Tube in the Furnace Prior to Heat Treatment
(c) Heat Treatment of the Sample in the Furnace at 500°C

3. RESULTS AND DISCUSSION

In this section, the major results of hyperthermia tests will be presented. Table 2 lists the time v.s. temperature data for the unheated samples. It can be seen that the temperature increases right after 5 s of electromagnetic wave exposure. When the time reaches 30 s, the temperature is already over 40°C, which is a typical temperature level for virus or cells to start degradation. In order to shown the results more clearly, the data as listed in Table 2 were plotted and shown in Figure 4.

Table 2. Hyperthermia Test Results before Heat Treatment

Time	Temperature (°C)					Avg. (°C)
Unheated	22.2	22.0	22.0	22.0	22.2	22.08
5	26.0	25.8	29.0	31.4	24.8	27.40
10	29.6	36.0	35.6	30.0	35.0	33.24
15	41.0	42.4	39.6	38.4	38.0	39.88
20	44.2	40.4	37.8	35.6	36.2	38.84
25	41.6	41.2	39.8	40.6	41.0	40.84
30	51.0	52.0	43.4	42.8	40.0	45.84

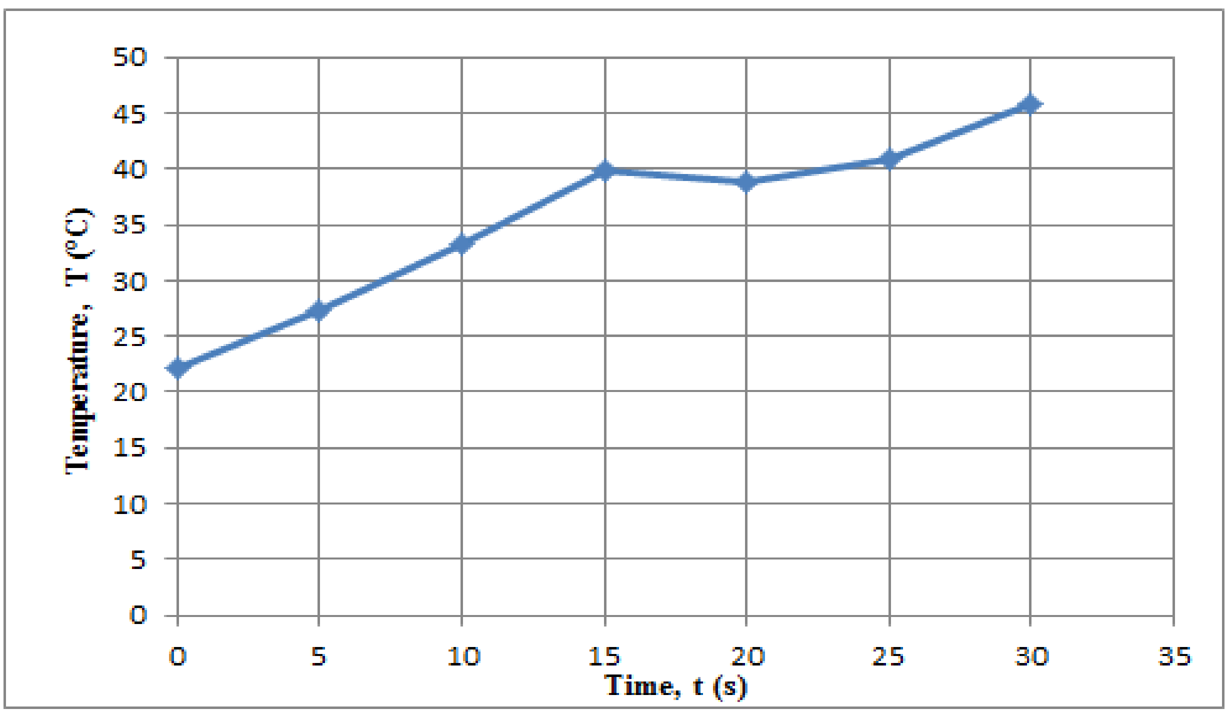

Fig 4. Average Surface Temperature at Different Heating Durations before Heat Treatment

After the nanofiber specimen underwent heat treatment, the same procedures for the hyperthermia test were adopted. The test results of the heat treated nanofiber specimen were listed in Table 3.

Table 3. Hyperthermia Test Results after Heat Treatment in Furnace at 500°C for 2 Hours

Time Sec)	Temperature (°C)					Avg. (°C)
Unheated	21.20	21.20	21.20	21.20	21.40	21.24
5	20.80	20.80	20.60	20.60	21.00	20.76
10	23.80	24.00	24.00	24.40	24.20	24.08
15	26.20	25.40	25.60	25.80	26.60	25.92
20	30.40	32.00	33.60	34.00	32.20	32.44
25	34.60	35.00	37.00	38.20	39.20	36.80
30	46.00	45.40	47.40	49.80	50.60	47.84

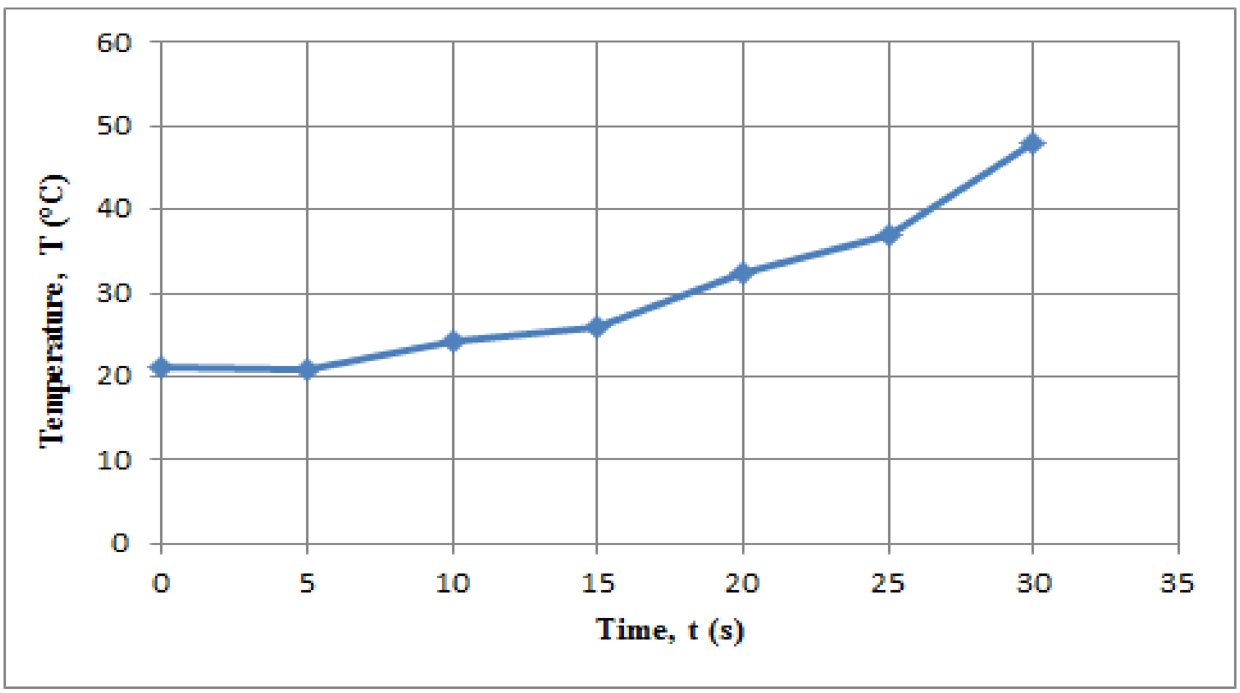

Fig 5. Average Surface Temperature at Different Heating Durations after Heat Treatment

After comparing the average surface temperature of the sample before heat treatment (shown in Table 3 and Figure 4) and after heat treatment (listed in Table 3 and illustrated by Figure 5) in the furnace for 500°C for 2 hours, a slightly decreasing trend in the data was observed. As it can be seen in the table 2 and table 3, the average temperature for unheated sample, and also at heating duration of 5, 10, 15, 20, and 25 seconds respectively, seems to be slightly lower than the heat treated sample which means the thermal properties of the sample has been improved. However, for the 30 seconds heating duration, an unusual trend was observed where the temperature of the surface was higher in the heat treated sample. The ultimate goal was to observe the change in hyperthermia properties of the heat treated material and to measure the voltage and current using the linear sweep voltammetry method. Afterwards, the Seebeck coefficient of the material which is the measure of the magnitude of the induced thermoelectric voltage in response to a temperature difference across the material. However, after the heat treatment of the sample, it was observed that the thermal properties of the material was not improved significantly, and the sample was relatively weak in order to conduct linear sweep test and collect data for further analysis.

Figure 6 demonstrates the change in microstructure of titanium cobalt after heat treatment. As it can be seen from Figure 6(a), before the heat treatment the titanium cobalt sample shows well aligned micro and nanofibers. The fibers have a wide range of size change from nanometers to several micron meters. However, it can be observed that after the heat treatment from Figure 6(b), a thick layer and fine layer can be seen. The thick layer represents the carbonized substrate. The fine layer represents the electrospun fibers. Since they are converted into ceramics by heating, they show better stability. They are also pretty brittle when handled. The microstructure of the sample under study shows titanium cobalt oxide nanoparticles embedded into the heat treated nanofibers.

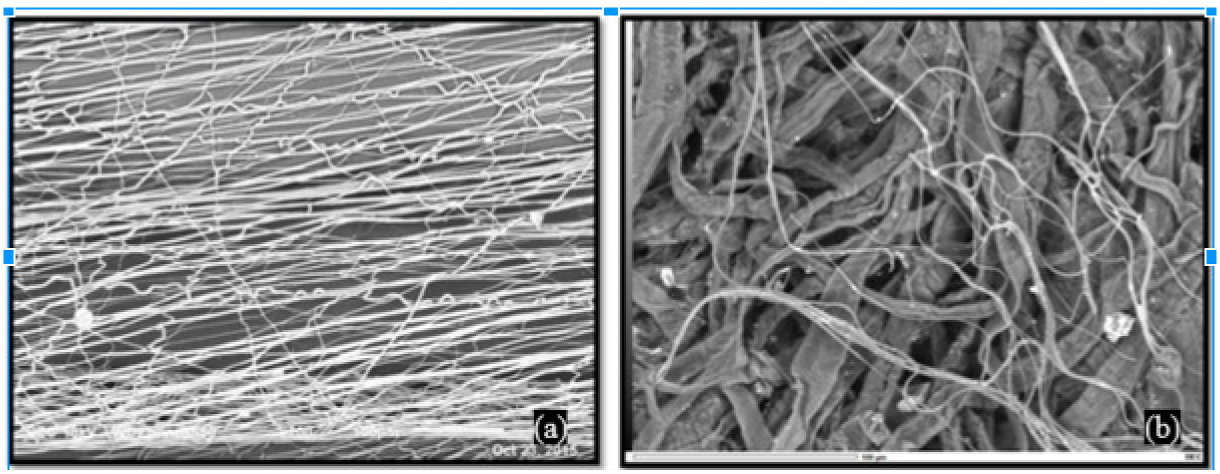

Fig 6. Titanium Cobalt Nanofiber Structures: (a) Non Heat Treated, (b) Heat Treated

Electrospinning has recently exhibited a significant potential in various applications such as membrane filtration, catalytic processes, fibrous-sensor applications, drug delivery, and tissue engineering. According to the research conducted, electrospinning has shown limitless applications in drug delivery and tissue engineering, due to the spinnability of natural and biodegradable polymers [10]. In general, the one dimensional nanofibers have shown a great potential to be used in the electronics, optics, and sensing technologies. It has been observed that with even the same composition, one dimensional nanomaterials show distinctive properties compared to the bulk material due to nano-sized effect [11]. Electrospun nanofibers can also be used in the energy industry, and specifically in the fuel cell technology. The most important part of a fuel cell is the catalyst, which assists in the chemical reaction between Oxygen and Hydrogen. Proton exchange membrane (PEM) fuel cells use platinum nanoparticles as catalysts. However, they are not durable enough under stresses from chemical reactions in the fuel cell. One solution to this problem is to use electrospun nanowire catalysts that are more durable, have higher electrical conductivity, and better performance in general. Furthermore, catalyst particles must be uniformly scattered on support materials. The support materials should have high porosity such as electrospun polyaniline nanofibers (PANI) and should be used instead of carbon supports such as multiwall carbon nanotubes (MWCNT). The high porosity is necessary for nanoparticle dispersion uniformity and gas flow [11]. A diagram of a PEM fuel cell is shown in Figure 7. Furthermore, for thermoelectric applications, nanofibers of thermoelectric oxides will bring more chances to explore a range of intriguing properties and applications associated with their one dimensionally created nanostructures [9].

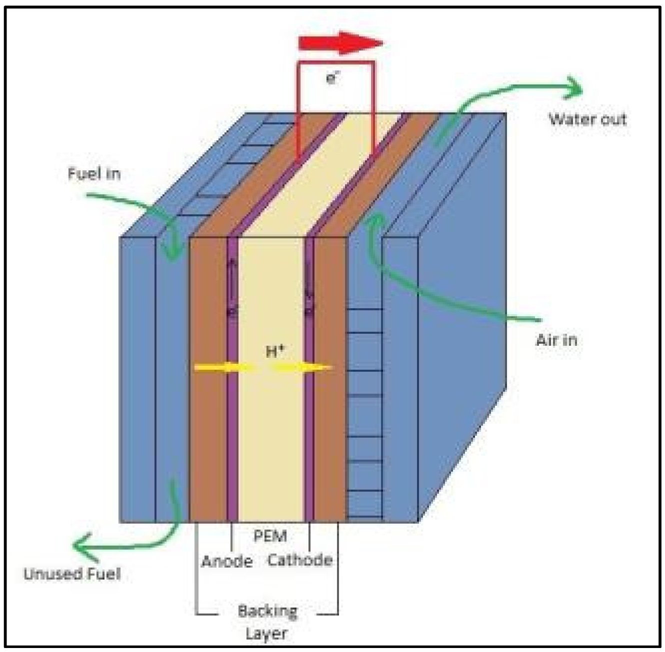

Fig. 7. PEM Fuel Cell

4. CONCLUSIONS

The study of the preparation and hyperthermia behavior characterization of electrospun fibers leads to the following conclusions:

The PVP polymer containing titanium and cobalt salt can be successfully spun onto a paper substrate. The size of the fiber is in the range from nanoscale to the microscale. The fiber shows intensive hyperthermia behavior in the electromagnetic field. The temperature increases from 22 to 40 ^{o}C when it is heated by 30 s. After heat treatment the fiber size is reduced to nanoscale.

Also found is that the surface temperature of the heated specimen increases less during the hyperthermia test as compared with that of the unheated specimen.

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