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Preparation and Testing the Hyperthermia Property of Electrospun Micro and Nanofibers

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Authors' contributions

This work was carried out in collaboration between all authors. Authors AB, CWD, JDJ, JR and MZ managed the literature searches, did experiments and wrote the first draft of the manuscript. Author LZ did the TEM work. Author YXG designed the study. All authors read and approved the final manuscript.

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ABSTRACT

The hyperthermia properties of nanomaterials have received attention in recent years due to the advances in nanofiber production. One of the main proponents is the medical field where it is used to combat malignant cancer cells. In this work we confirmed that a polymer solution containing titanium cobalt compounds as precursors can be electrospun into fibers and transformed into a ceramic oxide after heat treatment. After heat treatment the fiber size is reduced. 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°C when it is heated for 30 s. The surface temperature of the heat treated specimen increases less during the hyperthermia test as compared with that of the unheated specimen.

Keywords: Hyperthermia properties; nanomaterials; electrospinning fibers; titanium-cobalt oxide.

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1. INTRODUCTION

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]. Electrospinning is a process that produces polymer filaments using electrostatic forces. The process 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 Fig. 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 primary 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 [3].

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

The main advantages of electrospinning compared to other processes are its cost effectiveness and the reliable production of 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 within the fluid inside the syringe. The amount is dependent on different factors which can be used to obtain significantly longer nanofibers [5]. These factors include the distance from the tip of the needle to the collector, the diameter of the fluid jet near the cone, relaxation time, viscosity of the fluid, and the polymer concentration in the fluid, which is not possible through other techniques [6].

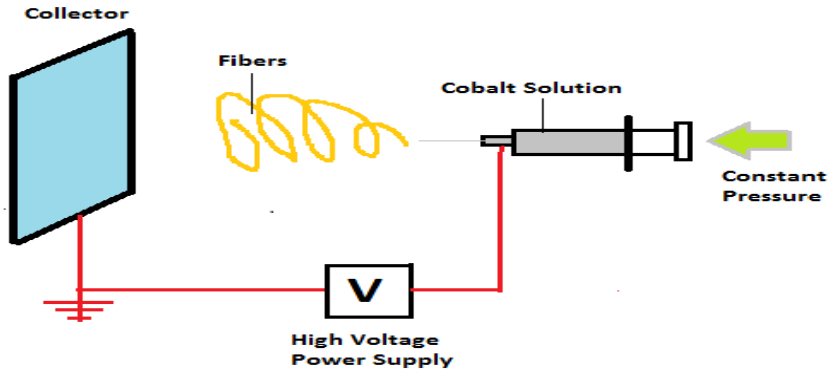


Fig. 1. Schematic of electrospinning process

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 dimension
Drawing	Laboratory	No	Yes	Yes	No
Template Synthesis	Laboratory	No	Yes	Yes	Yes
Self-assembly	Laboratory	No	Yes	No	No
Electrospinning	Laboratory with potential for industrial processing	Yes	Yes	Yes	Yes

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. PVP (Polyvinylpyrrolidone) nanofibers are commonly added to the fiber solution as a template for producing suitable nanofibers used in many 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 wear and corrosion resistance as well as keeping 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]. Hyperthermic nanofibers with simultaneous heat generation and drug release in response to an external electromagnetic field may also be made using cobalt based materials.

The objectives of this work include making a nanoparticle-containing polymer fiber and testing the hyperthermia properties. Heat treatment of the fibers will be performed to convert the polymeric fiber into a ceramic fiber. In addition, the structure of the nanofibers will be analyzed and the comparison of the behaviors of the heat treated and untreated fibers will be studied.

2. MATERIALS AND EXPERIMENTAL METHODS

The experimental part of the research began by preparing a specific composition. The composition consisted of 5 mL of ethanol (C_2H_5OH) and 0.375 g polyvinylpyrrolidone (PVP) with a molecular weight of 1,300,000. Afterwards, 0.063 g of ethanol and 0.034 g of cobalt acetate were added. The major composition in the experiment was cobalt acetate. All of the compounds were added into a beaker where they were mixed together until fully dissolved. The mixed composition was then transferred into a syringe to begin the electrospinning process. The electrospinning apparatus was already prepared and used to apply a 10 kV charge to the liquid composition. 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 approximately 10 cm from the tip of the syringe. The flow rate employed in electrospinning was set to 0.05 ml/min. 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 Figs. 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 a 900W microwave and was heated for 5, 10, 15, 20, 25, 30 seconds respectively. 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 Fig. 3(a) and was placed in a furnace as shown in Fig. 3 (b) at 500°C and was heat treated for 2 hours. After the sample was removed from the furnace of Fig. 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.

3. RESULTS AND DISCUSSION

In this section, the major results of hyperthermia testing will be presented. Table 2 lists the time vs. 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 viruses and cells to begin degradation. The data listed in Table 2 is plotted and shown in Fig. 4.

After the nanofiber specimen underwent heat treatment, the same procedure for the hyperthermia test was performed. The test results of the heat treated nanofiber specimen are shown in Table 3 and Fig. 5.

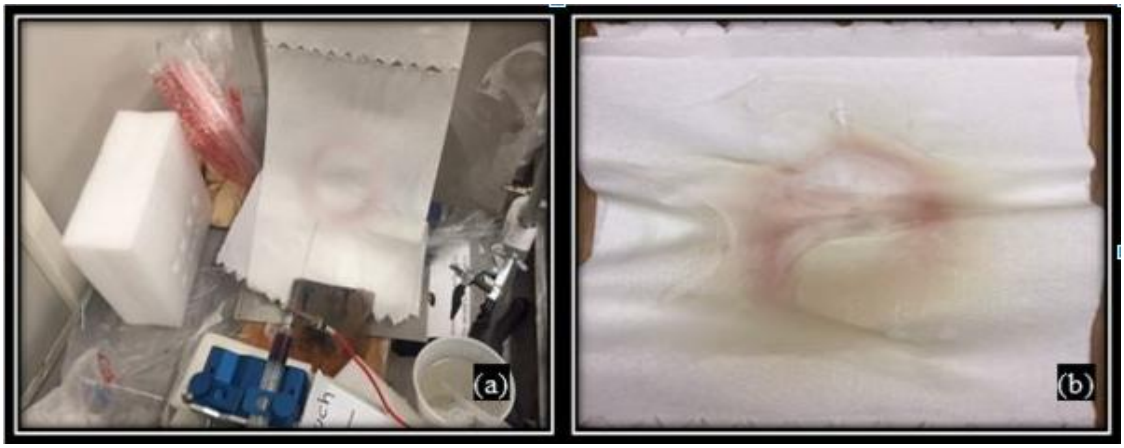


Fig. 2 (a) Electrospinning facilities, and (b) Nanofibers on the collector

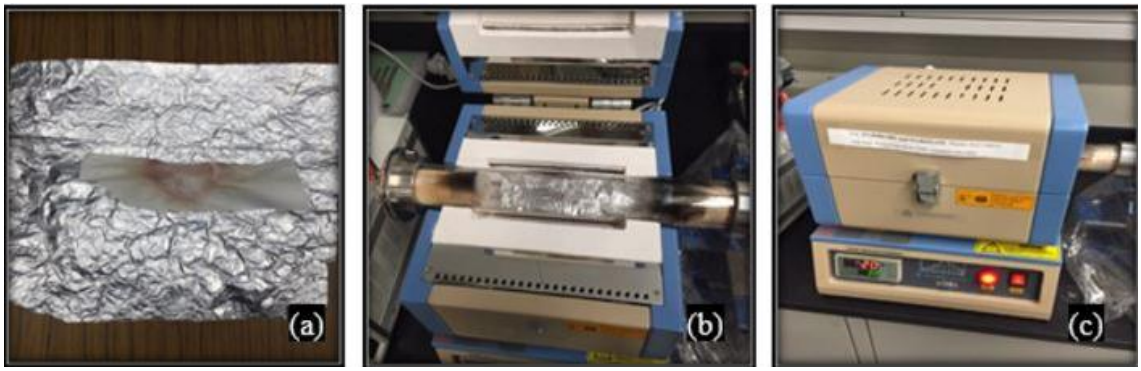


Fig. 3. Photos showing (a) Sample ready to be wrapped in aluminum foil prior to heat treatment, (b) Sample placed in a MTI tube in the furnace prior to heat treatment, (c) Heat treatment of the sample in the furnace at 500°C

Table 2. Hyperthermia test results before heat treatment

Time	Temperature (°C)					Avg. (°C)
Unheated	22.2	22.0	22.0	22.0	22.2	22.1
5	26.0	25.8	29.0	31.4	24.8	27.4
10	29.6	36.0	35.6	30.0	35.0	33.2
15	41.0	42.4	39.6	38.4	38.0	39.9
20	44.2	40.4	37.8	35.6	36.2	38.8
25	41.6	41.2	39.8	40.6	41.0	40.8
30	51.0	52.0	43.4	42.8	40.0	45.8

Comparing the average surface temperature of the sample before heat treatment (shown in Table 3 and Fig. 4) and after heat treatment (shown in Table 4 and Fig. 5) in the furnace for 500°C for 2 hours reveals a slightly decreasing trend in the data. As shown in Table 2 and Table 3, the average temperature for both the unheated sample and heating durations of 5, 10, 15, 20, and 25 seconds are slightly lower than the heat treated sample. This means the thermal properties of the sample have been improved. However, for the 30 second heating duration, an unusual trend was observed. The temperature of the surface was higher on 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, the measure of the magnitude of the

induced thermoelectric voltage in response to a temperature difference across the material, was planned to be calculated. However, after the heat treatment of the sample, it was observed that the thermal properties of the material were not improved significantly. The sample was relatively weak for conducting a linear sweep test and collecting data for further analysis.

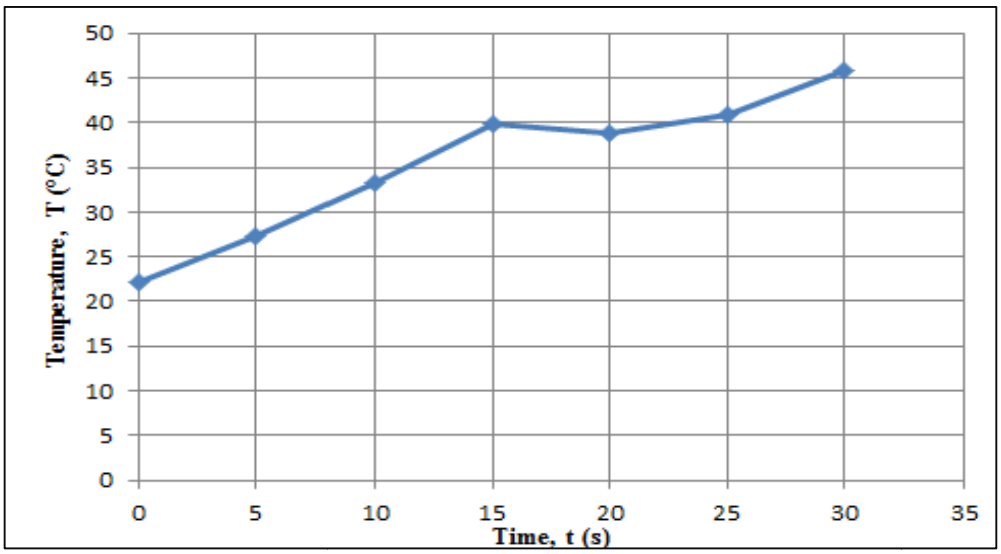


Fig. 4. Average surface temperature of the nanofibers before heat treatment

Table 3. Hyperthermia test results after heat treatment in furnace at 500°C for 2 hours

Time	Temperature (°C)					Avg. (°C)
Unheated	21.2	21.2	21.2	21.2	21.4	21.2
5	20.8	20.8	20.6	20.6	21.0	20.8
10	23.8	24.0	24.0	24.4	24.2	24.1
15	26.2	25.4	25.6	25.8	26.6	25.9
20	30.4	32.0	33.6	34.0	32.2	32.4
25	34.6	35.0	37.0	38.2	39.2	36.8
30	46.0	45.4	47.4	49.8	50.6	47.8

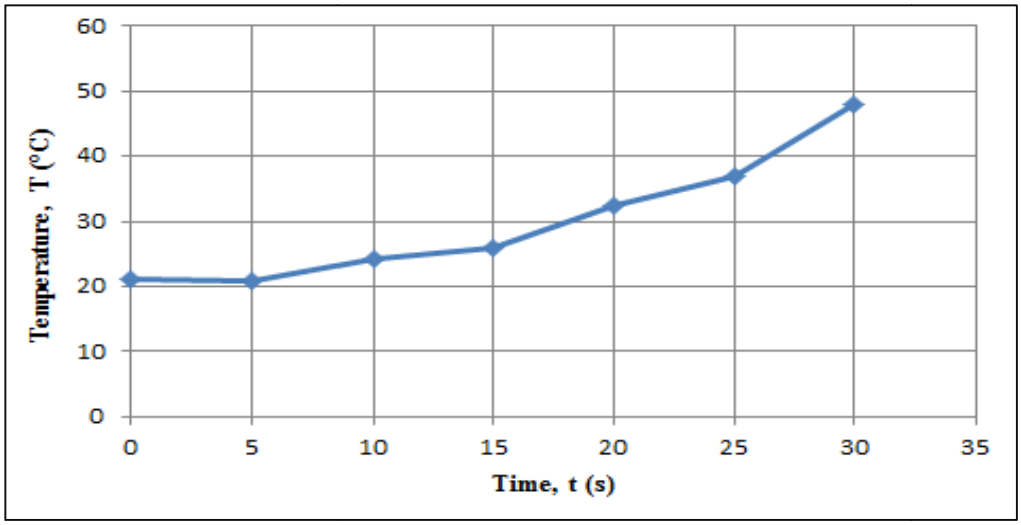


Fig. 5. Average surface temperature of the nanofibers after heat treatment

Fig. 6 demonstrates the change in microstructure of titanium cobalt after heat treatment. Before heat treatment, the titanium cobalt sample has well aligned micro and nanofibers due to the mechanical and electrical force assisted electrospinning, as shown in Fig. 6(a). The fibers have a wide range of sizes from nanometers to several micro meters. After the heat treatment a thick layer and fine layer can be seen, as shown in Fig. 6(b). The thick layer represents the carbonized substrate. The fine layer represents the electrospun fibers. Since the fibers are converted into ceramic by heating, they show better stability. They are also brittle when handled. The microstructure of the sample under study shows titanium cobalt oxide nanoparticles embedded into the heat treated nanofibers.

Fig. 7 shows the results based on the transmission electron microscopic analysis. In Fig. 7(a), the transmission electron microscope image shows the morphology of the titanium cobalt oxide nanoparticle embedded into the fiber is presented. Fig. 7(b), the selected area diffraction pattern reveals that titanium cobalt oxide nanoparticles have crystal structure.

The research work in this paper shows the preliminary results on the hyperthermia behavior of electrospun nanofibers. Electrospinning has other significant applications such as membrane filtration, catalytic processes, fibrous-sensor applications, drug delivery, and tissue engineering.

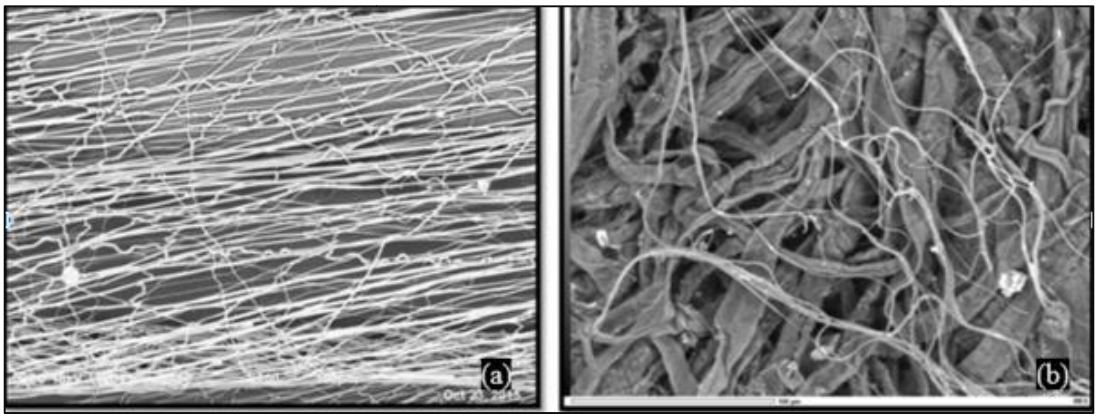
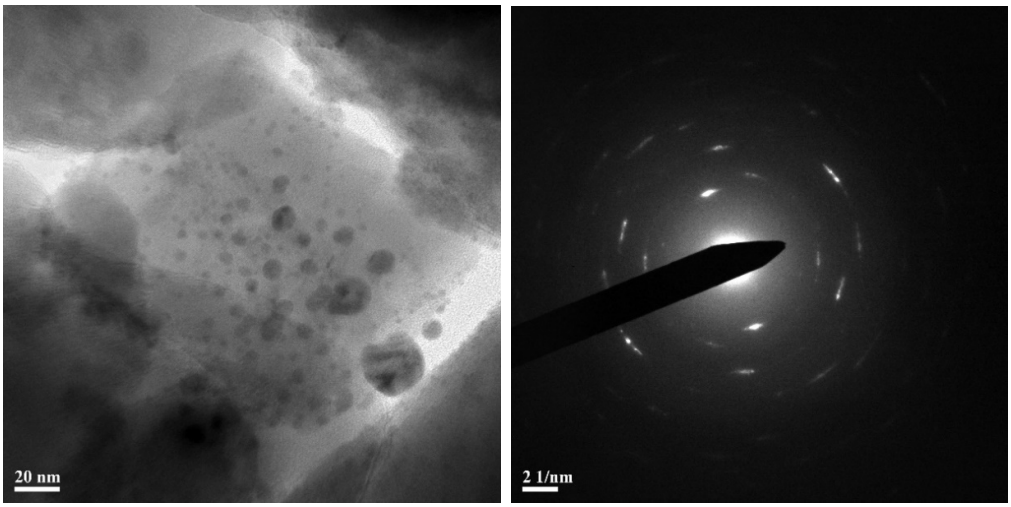


Fig. 6. Titanium cobalt nanofiber structures: (a) Non heat treated, (b) Heat treated



(a) **(b)**

Fig. 7. TEM image of the titanium cobalt oxide: (a) Particles distributed in the fiber, (b) Selected area diffraction pattern

According to the research conducted, electrospinning has shown the 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 electronic, optic, and sensing technologies. It has been observed that even with 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, specifically in 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. A 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) instead of carbon supports such as multiwall carbon nanotubes (MWCNT). The high porosity is necessary for nanoparticle dispersion uniformity and gas flow [12]. 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 nanostructure [9].

It is meaningful to compare the hyperthermia property of the fiber from this work with those previously reported in [13]. In [13], some other magnetic particles such as iron oxide were dealt with. From a comparison of the results, it is interesting to see that the titanium-cobalt based oxide has the similar behavior as the previously reported iron oxide in PVP fiber when considering the response time and the highest temperature reached.

Although it is challenging work to directly measure the thermal properties of the PVP nanofibers and partially carbonized nanofibers with the embedded nanoparticles, some initial modeling and simulation approaches are considered using the method as reported in [14]. It is noted that the method in [14] focuses on nanoparticles in water and/or agar gel. For a close approximation, PVP has similar physical properties as agar gel. Basically, the energy balance is used to describe the conversion from electromagnetic wave energy to the heat energy released by the nanofibers. The time-dependent temperature of the titanium-cobalt oxide nanoparticles, T, in either the PVP or partially carbonized PVP can be correlated with the converted electromagnetic wave energy of the nanoparticles as shown by Eq. (1).

$$\frac{C_p}{a}\left(\frac{dT}{dt}\right) = kf^n H^2 \quad (1)$$

Where C_p is the specific heat of the specimen; a is the concentration of the titanium-cobalt oxide nanoparticle in the nanofibers; t is the time; f is the frequency of the electromagnetic wave, k is a frequency-dependent material constant; H is the intensity of the field.

Among various parameters, the frequency f may be set by the test conditions. In the above mentioned experiments, frequency was set to f=2 GHz. It must be noted that in medical treatment of patients, f could be changed by using different modes of Magnetic Resonance Imaging (MRI) facilities. In this preliminary study, it was predicted that the temperature (T) would increase with time (t) by experimental approach. This was shown in Figs. 4 and 5. Since the specific heat of the specimen C_p is close to that of the substrate material (PVP or carbonized PVP), it is possible to find the most important parameter k associated with the hyperthermia response of the nanocomposite materials, which will be continued work in later studies.

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 oxide can be successfully spun onto a paper substrate. The size of the fiber is in the range from nanoscale to microscale. The fiber shows intensive hyperthermia behavior in the electromagnetic field. The temperature increases from 22 to 40°C when it is heated for 30 s. After heat treatment the fiber size is reduced. 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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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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