

Efficiency of Microwave Heating of Weakly Loaded Polymeric Nanocomposites

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ABSTRACT

Electrical and thermal conductivity of materials are typically correlated, while some applications, including thermoelectrics, require these parameters to be controlled independently. Such independent control of thermal and electromagnetic properties can be achieved by using nanocomposites. In this study, nanocomposites were produced by mixing a small amount of carbon nanofibers (CNF), carbon coated cobalt (Co), and nickel nanowires (NiNW) with paraffin, which has low thermal and almost zero electrical conductivity. The fraction of nanoinclusions in the paraffin matrix was very low (below 1%). We showed that the thermal properties of nanocomposites are essentially the same as those of pure paraffin, while electromagnetic properties are significantly different. To determine the dependence of the heating rate on filler concentration, paraffin-based samples were heated in a microwave oven. We found that the heating rate of nanocomposites made of carbon nanofibers is much greater than that of any other nanocomposites. These findings suggest that at 2.45 GHz frequency, the heating rate is mostly controlled by the electrical losses in the fillers. The theoretical model predicts that the heating rate increases linearly with the particle concentration, which is in agreement with the experimental data.

INTRODUCTION

Microwave heating can be employed for heating many materials in the 0.3-300 GHz frequency range. Microwave ovens used in everyday life is a well-known example where the ovens operate at 2.45 GHz. The major advantage of using microwaves for industrial processing is a rapid heating of the internal parts of the materials. The use of microwaves for chemically modifying textile surfaces provides significant advantages over conventional systems with regard to reducing the time and energy needs associated with conventional textile finishing. [1]

The primary mechanisms of the microwave absorption include ohmic (Joule) heating, which occurs in conductive materials; hysteresis heating, which occurs in magnetic materials; and dipolar heating which occurs in polar liquids and solids where dipoles generate heat upon rotation and friction. Adding nanoparticles to the polymer matrix or any other materials, one can rapidly heat the material to locally control a chemical reaction. [1-3]

The microwave heating processes have been extensively utilized and, currently, this method almost replaced the conventional heating/ drying systems used in industry. The advantages are as follows. For heating by convection and radiation, all heat must flow from the surface to the bulk of the material, and this heat transfer occurs through heat conduction only. As in any diffusion processes, the heat conduction cannot be intensified and the maximum temperature is always on the body surface. To avoid the surface overheating, normally the temperature of heating source cannot exceed the desired final temperature, thus the overall heating rate is restricted by that of the heating source. Another factor limiting the heating rate is the thermal diffusivity. Although the response of the surface temperature to the outside heating source could be very quick, the temperature response of the material is limited by the coefficient of thermal diffusivity: simply increasing heat flux from the boundary cannot always result in rapid heating of the whole body. With increasing heat flux, the temperature profile tends to be more nonuniform, but the temperature does not change significantly beyond a characteristic length scale associated with coefficient of thermal diffusivity.

Another advantage of microwave heating is its selective heating. In composite materials, for

example, one can choose a microwave irradiation with a given frequency guaranteeing that the EM waves would penetrate the matrix, but not the particles. That way, the embedded fillers can produce heat on demand. Therefore, one can control the rate of chemical reaction, for example, at the scale associated with the size of the inclusion. Or one can produce heat only at the given spot where the inclusions are being concentrated. The composite retains all useful mechanical and thermal properties of the original matrix material, but can be effectively heated by the microwaves.

For example, interactions of carbon nanotubes with microwaves is a subject of active ongoing research, and the mechanism of the microwave absorption by carbon nanotubes is still poorly understood. [4-6] Low thermal conductivity materials with controlled electromagnetic properties are especially important for many applications, in particular, because these materials constitute a broad class of polymeric coatings. High aspect ratio high conductivity carbon nanofibers and magnetic nanospheres allow significantly changing the microwave response of the nanocomposite using low fractions of inclusions mixed with the matrix materials. [2, 6] Since the fraction of nanoparticles in the coatings is low, the thermal properties of nanocomposites are essentially the same as those of pure polymer, while their electromagnetic properties are significantly different.

In this study, we first construct a simple engineering theory explaining the kinetics of nanocomposite heating. Paraffin has microwave characteristics very similar to many textile materials. Therefore, it has been chosen as a system modeling polymeric fiber-based materials. Several particulate materials were added in paraffin to study the mechanism of microwave heating. Then we analyze the thermal properties of these paraffin-based nanocomposites and find specific heat capacity, the most important thermodynamic parameter of the nanocomposite needed for microwave heating applications. We then analyze the heating efficiency of different nanocomposites. As expected, the experimental heating rate of different nanocomposites as a function of nanoparticle concentration was linearly dependent on the concentration. Thus, the use of microwaves for chemically modifying textile can be controlled by changing the concentration of nanoparticles in the polymer.

THEORY

Balance Equation

When a body is exposed to heating, the kinetics of the heat distribution in the absence of convection is described by the following energy balance equation

$$\rho C_p \frac{\partial T_p}{\partial t} - \nabla \cdot (k \nabla T_p) = \hat{P} \quad (1)$$

where ρ is the material density, C_p is its specific heat, $T_p(t, \mathbf{r})$ is the temperature at time moment t and point \mathbf{r} , k is the thermal conductivity of the body, and \hat{P} is the heating power density. The first term on the left hand side of Eq. (1) describes the energy change and the second one is responsible for the heat dissipation due to heat transfer inside the body.

The boundary conditions on the interface of two bodies state that the temperature must be a continuous function, $T_p(\mathbf{r} + 0) = T_p(\mathbf{r} - 0)$, and the flux must be also continuous:

$$k^+ \frac{\partial T_p}{\partial n} = k^- \frac{\partial T_p}{\partial n} \quad (2)$$

where k^+ and k^- are the thermal conductivities of air, $(\mathbf{r} + 0)$ and nanocomposite, $(\mathbf{r} - 0)$, respectively.

Integrating Eq. (1) over the sample volume V , we obtain

$$\int \rho C_p (T_p) \frac{\partial T_p}{\partial t} dV - k^- \int (\Delta T_p) dV = \int \hat{P} dV \quad (3)$$

where we assume that the specific heat is a function of temperature. It is convenient to transform the volume integral into an integral over the nanocomposite surface S :

$$k^- \int \Delta T_p dV = k^- \int_S \partial_n T_p dS \quad (4)$$

As seen from Eq. (2), due to the very low thermal conductivity of air, $k^+/k^- \ll 1$, the heat flux is almost zero at the body surface

$$k^- \int \Delta T_p dV = k^- \int_S \partial_n T_p dS \approx 0 \quad (5)$$

Therefore, Eq. (3) is simplified as

$$\int \rho C_p (T_p) \frac{\partial T_p}{\partial t} dV = \int \hat{P} dV \quad (6)$$

Eq. (6) can be further simplified by introducing an average temperature of the body subjected to the EM radiation, see *Figure 1* for the explanation.

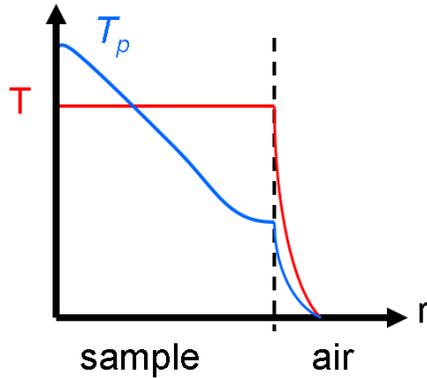


FIGURE 1. Sketch of the temperature distribution in the sample during the heating (blue). Temperature T_p can be nonuniform over the sample, but the integral characteristics of the heating process can be described by the average temperature T (red).

Introducing the average temperature, Eq. (6) takes on very simple form:

$$mC_p(T) \frac{dT}{dt} = P \quad (7)$$

Assuming a uniform distribution of the absorbed power in the sample, the temperature of the sample can be found by integration of a non-linear equation:

$$mC_p(T) dT / P = dt \quad (8)$$

In the simple case of a temperature-independent specific heat, the heating rate (slope of the temperature-time curve) is constant. For the host material, we are using paraffin, which specific heat depends on temperature (*Figure 4*). Knowing this dependence we can numerically calculate the integral

$$t = \int_{T_0}^T \frac{C_p(T)m}{P} dT \quad (9)$$

where $C_p(T)$ is the measured specific heat capacity. Embedding nanoparticles into the sample, one effectively changes the physico-chemical constants of the sample. When the concentration of nanoparticles is low and there is no contact between the nanoparticles, we can use the same heat capacity as that of pure paraffin. This statement is confirmed in a series of DSC experiments, see *Figure 4*.

EM Source P

In our experimental set-up, two heating sources can be present and have to be included into the heating power P : the (parasitic) infrared radiation from the walls of the microwave oven P_{IR} and the heating owing to the microwave radiation P_{MW} . In the latter, we distinguish two heating mechanisms induced by the microwave radiation: “electric” and “magnetic”. The electric heating occurs in the mixtures of nonmagnetic conductive materials and paraffin, which mainly interact with the electric field. The magnetic heating is induced by magnetic nanoparticles. A combination of these mechanisms is an attractive way to optimize the heating efficiency of polymeric nanocomposites.

We are in position to derive the EM losses. Assuming that the sample does not change its density during the heating process, the first law of thermodynamics for a unit volume is written as $dU = dQ + dW$, where U is the internal energy, Q is the heat added to the sample from outside, and W is the EM work done on the system. As shown in Eq. (4) through Eq. (6), the heat exchange with air can be neglected, hence $dQ=0$. The differential EM work is given by [7] $dW = \mathbf{H} d\mathbf{B} + \mathbf{E} d\mathbf{D}$, where \mathbf{H} is the magnetic field, \mathbf{B} is the induction, \mathbf{E} is the electric field and \mathbf{D} is the displacement vector. The constitutive equations for \mathbf{D} and \mathbf{B} vectors can be written in the form $\mathbf{D} = \epsilon_0 \epsilon(\omega) \mathbf{E}$ and $\mathbf{B} = \mu_0 \mu(\omega) \mathbf{H}$, where $\epsilon_0 = 8.85 \times 10^{-12}$ F/m is the permittivity of free space, $\mu_0 = 4\pi \times 10^{-7}$ T \times m/A is the permeability of free space, $\epsilon = \epsilon' + i\epsilon''$ is the complex-valued dielectric function, and $\mu = \mu' + i\mu''$ is the complex-valued permeability, both are functions of cyclic frequency $f = \omega/2\pi$ of the EM wave. The fields are collinear hence the scalar products are reduced to the products of the field magnitudes. Since electric and magnetic contributions have similar forms, it is sufficient to find the dissipation power for electric wave.

In EM wave, the magnitude of electric field changes periodically, $\mathbf{E} = E_0 \cos(\omega t) = \text{Re} \{ E_0 e^{i\omega t} \}$. The magnitude of the displacement vector is written as $\mathbf{D} = \text{Re} \{ (\epsilon' + i\epsilon'') E_0 e^{i\omega t} \} = \text{Re} \{ (\epsilon' + i\epsilon'') E_0 (\cos(\omega t) + i\sin(\omega t)) \} = E_0 (\epsilon' \cos(\omega t) - \epsilon'' \sin(\omega t))$. This field has the in-phase component proportional to ϵ' and out-of-phase component proportional to ϵ'' . The change of the internal energy per unit volume over one cycle is written as

$$\Delta U = \varepsilon_0 \int_0^{2\pi/\omega} E dD = -\omega \varepsilon_0 \varepsilon'' E_0^2 \int_0^{2\pi/\omega} \cos^2(\omega t) dt \quad (10)$$

$$= -\pi \varepsilon_0 \varepsilon'' E_0^2$$

multiplying this result by f , we obtain the volumetric power dissipation as

$$P_{MW} = -\Delta U f = \pi f \varepsilon_0 \varepsilon'' E_0^2 \quad (11)$$

For a dilute dispersion with the volume fraction of inclusions p , assuming that a single EM wave interacts only with a single nanoparticle, the dielectric function is expressed as [7]

$$\varepsilon''(\omega) = \varepsilon_p'' + p \varepsilon_m''(\omega) \quad (12)$$

where ε_p'' is the imaginary part of the dielectric function of the polymeric carrier (paraffin) and ε_m'' depends on the properties of inclusions. Conducting nanofibers change the dielectric permittivity of the nanocomposite and therefore induce the electric heating due to currents. Eq. (11) and Eq. (12) predict that the heating power should depend linearly on the particle concentration. This theoretical prediction needs to be validated for each dispersion, because long microwaves are able to interact with many nanoparticles simultaneously, and the scattering effect might change the linear dependence.

In the presence of magnetic inclusions, one needs to introduce magnetic losses

$$P_{MW} = -\Delta U f = \pi f \mu_0 \mu'' H_0^2 \quad (13)$$

The imaginary part of the composite's permeability, μ'' , that is responsible for the losses, has the same form Eq. (12), i.e. it is proportional to the nanoparticle concentration. [7] In the microwave region, magnetic nanoparticles show the ferromagnetic resonance. Therefore, the heating rate is expected to increase in the vicinity of the resonance. [8]

EXPERIMENTAL

Experimental measurements of microwave absorption by paraffin-based nanocomposite materials were conducted with carbon nanofiber (CNF), carbon coated cobalt (Co), and nickel nanowire (NiNW) composites.

Nanocomposites Preparation

Four types of composites were used in this study: carbon nanofibers (diameter: 90 ± 5 nm, PR-24-XT-

LHT, Pyrograf), carbon coated cobalt nanospheres (< 50 nm, Aldrich), mixtures of nanofibers and cobalt, and nickel nanowires. Nickel nanowires were prepared by our group using template electrochemical synthesis (diameter: 200 nm, length: 16 ± 3 μ m). [9] Nanocomposites were prepared using the following procedure: Paraplast® (compound of purified paraffin and plastic polymers) pellets were mixed with aforementioned materials in the given weight proportion, then the mixture was placed in a heated ($>$ melting point of paraffin: 56°C) sonicator. After the paraffin has been melted and produced regularly dispersed mixture, the heater was turned off and the obtained nanocomposites were slowly cooled while sonicator was still operating in order to prevent the sedimentation of nanoparticles. It should be noticed that ethanol was used to disperse the cobalt nanospheres and nickel nanowires before mixing with paraffin, which allowed obtaining a more uniform nanocomposite sample. The produced nanocomposite samples (Figure 2) had a disk-like shape with a diameter of approximately 4 cm and a thickness of about 0.5 cm. The morphological surface structure of carbon nanofibers and nickel nanowires were examined with a Hitachi Field Emission scanning electron microscope (FESEM-Hitachi 4800), and shown in Figure 3.

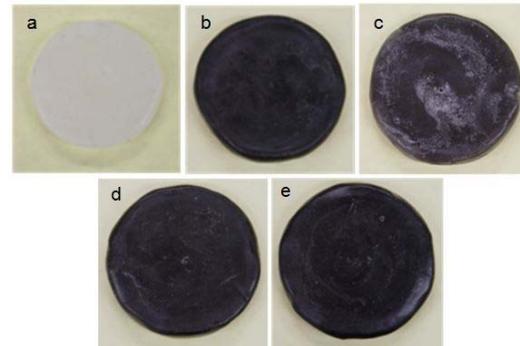


FIGURE 2. Samples used in microwave heating experiments: (a) pure paraffin, (b) 0.3 wt% carbon nanofibers in paraffin, (c) 0.3 wt% nickel nanowires in paraffin, (d) 0.3 wt% carbon coated cobalt nanospheres in paraffin, and (e) 0.3 wt% carbon nanofiber/cobalt (1/1) in paraffin.

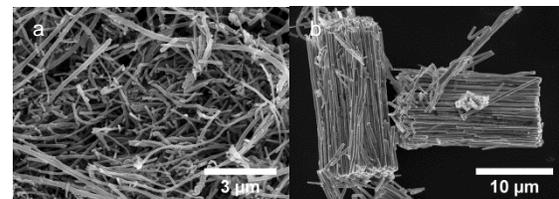


FIGURE 3. Micrographs of (a) carbon nanofibers obtained from Pyrograf, and (b) Nickel nanowires produced in our group. [9]

Microwave Heating

The nanocomposite sample was heated for a given time in a 0.9 kW microwave oven, operating at 2.45 GHz. To reduce the heat exchange between the sample and supporting structure, the sample was placed on a hollow thin-walled plastic cylinder. The temperature was measured in the center of the sample using K-type thermocouple (30 AWG) with NIST-traceable Omega HH506RA data logger thermometer. The sample and the microwave oven were cooled down to room temperature before and after each experiment. The initial temperature (T_i) and final temperature (T_f) were recorded, and expressed by temperature increment ($\Delta T = T_f - T_i$). The temperature increment of each sample was examined twice, and the variation was $\pm 0.3^\circ\text{C}$.

Impedance Measurement

Impedance spectroscopy can be used to test if there is percolation in nanocomposite. The impedance of pure paraffin and nanocomposites was determined with the Impedance spectroscopy system that is built in our lab, and it can be used for the analysis of sample reaction on AC fields in 0 to 100 kHz frequency range. The system includes an Analog Devices EVAL-AD5933EB impedance converter and a HP-8757D scalar network analyzer card and uses a two-point measurement technique.

Specific Heat Capacity

The specific heat of pure paraffin and nanocomposites was determined by the Modulated Differential Scanning Calorimetry (MDSC-2920, TA Instruments). All tests were conducted in N_2 purge from 0 to 50°C at a scan rate of $5^\circ\text{C}/\text{min}$. Each sample was tested three runs and the average value was reported. The results of the measurements are shown in *Figure 4*. Pure paraffin and paraffin-based nanocomposites have essentially the same dependence of the specific heat on temperature. The heat capacity of pure paraffin and that of nanocomposites is not constant and displays a non-linearity in the range of temperatures of interest.

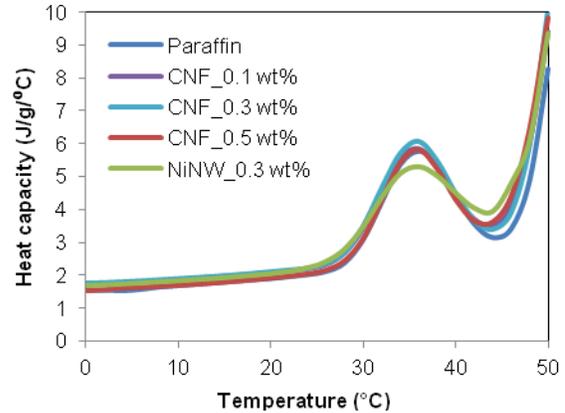


FIGURE 4. Measured heat capacity of paraffin and paraffin-based nanocomposites.

RESULTS AND DISCUSSION

Impedance

Impedance spectra of pure paraffin and nanocomposite samples that used in microwave heating experiments are shown in *Figure 5*. All samples are non-conductive in the DC field and demonstrate the same capacitance-type frequency-dependent impedance spectra, decreasing with increasing frequency. No obvious difference was detected between the spectra of pure paraffin and nanocomposites. This confirms that no percolation occurred in these samples.

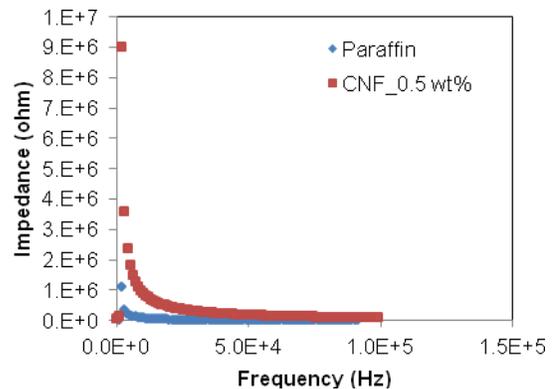


FIGURE 5. The impedance spectra of pure paraffin and nanocomposites. It demonstrates that all samples are non-conductive in this range of frequencies.

Heating Power rate (P/m)

In *Figure 6*, we demonstrate the temperature of a paraffin sample heated at the constant heating power (P/m) (calculated from Eq. (9)). In the temperature range from 0 to 25 °C, where C_p is close to constant, the temperature changes almost linearly. When the temperature crosses 30 °C, the linear dependence is replaced by a nonlinear one. As follows from Eq. (9), the time needed for heating the sample to a certain temperature depends on the input power. If the temperature dependence in a given heating experiment is known, the heating power, and the EM losses of the sample, can be calculated.

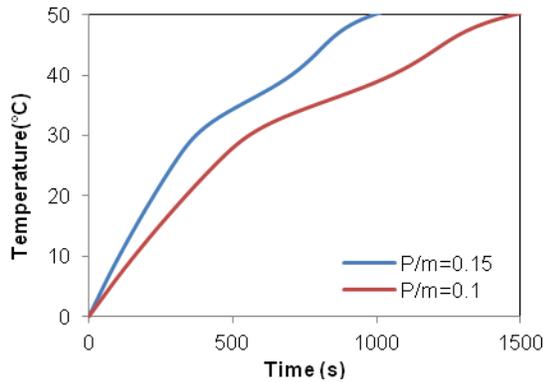


FIGURE 6. Heating of pure paraffin with a constant power ($P/m=0.1$ J/(s g), red, and $P/m=0.15$ J/(s g), blue): Temperature dependent heat capacity causes nonlinear heating.

We numerically calculated the integral of Eq. (9) for 256 values of P/m in the range between 0 and 0.15 J/(sg). Then the theoretical temperature dependencies $T_{num}(t)$ for various heating rates were evaluated numerically by solving a nonlinear equation Eq. (9) for T . From the experiments, we know the temperature gains of the samples $T_{exp}(t_i)$ for the discrete times t_i . Comparing the measured data with the theoretically obtained curves, we can fit the experimental data using P/m as an adjustable parameter and minimizing the error

$$e = \sum_{i=1}^N [T_{exp}(t_i) - T_{num}(t_i)]^2 \quad (14)$$

for the given number of measurements, N , and finding the best matching theoretical curve.

First, the pure paraffin sample was heated in the microwave oven using 50% of its power. To extract the impact of the IR radiation from the oven walls, a reference measurement has been performed: the pure paraffin sample was covered by a foam dome,

preventing an irradiative interaction of the sample with the oven walls. By doing so, we simultaneously prohibited the convection heat transfer from the sample. No difference in the temperature curves as compared to the uncovered sample was found. We conclude that the IR radiation and convection can indeed be neglected in the model ($P=P_{MW}$ in Eq. (9)).

Next, all nanocomposites with 0.3 wt% nanoparticle concentration were heated in the microwave oven using 50% of power. The resulting thermal energy gain per unit mass was plotted in *Figure 7* and compared with that of pure paraffin. In the current configuration, we can conclude that the nickel nanowires (NiNW) in paraffin have the smallest heat production, which is almost the same with pure paraffin. However, it is obvious that the change in the heating mechanism is very significant: since paraffin has never been reported to have magnetic properties, the loss mechanism must be purely electric. Comparing carbon coated cobalts nanospheres (Co) in paraffin and its mixture with carbon nanofibers (CNF); we can also enhance the losses in the electric component of electromagnetic waves, interacting with the composite. The Co/CNF composite includes 1.5 wt% of nanospheres and nanofibers, respectively. As expected, the dissipation gain is, within the experiment accuracy, the average value of those for pure nanosphere and pure nanofiber composites.

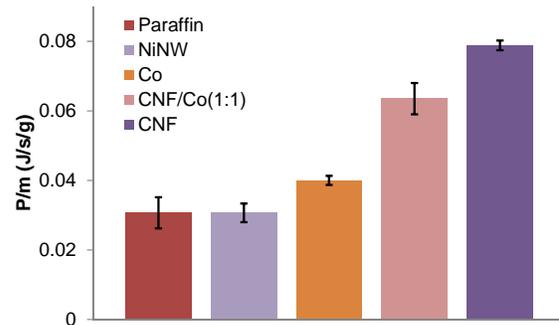


FIGURE 7. Heat gain in 0.3 wt% nanocomposites compared to pure paraffin.

In *Figure 8a*, the temperature change in CNF/paraffin and Co/paraffin nanocomposites with various concentrations is plotted against time. We started with pure paraffin, and increased the concentration gradually to 0.5 wt%. In all cases, the temperature increased almost linearly as it has been predicted by Eq. (11) and (12). We can also see that with increasing the CNF concentration, the heat energy gain is higher. The same tendency can be observed for carbon coated cobalt nanospheres (*Figure 8b*).

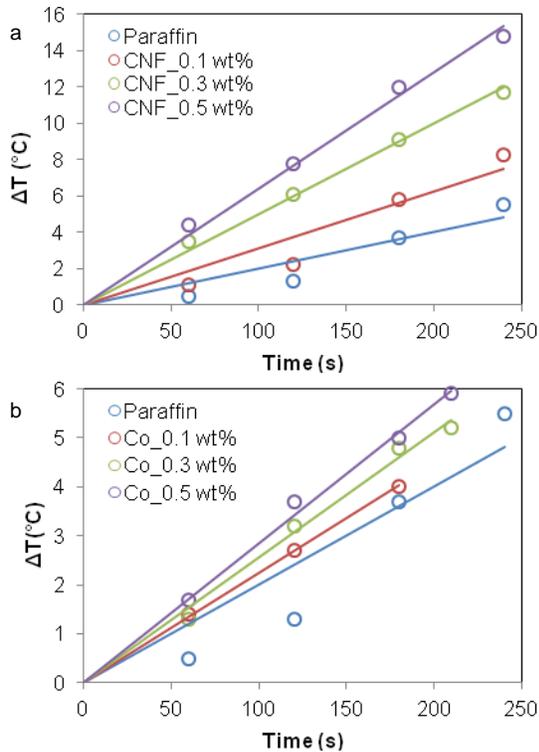


FIGURE 8. Temperature change for different (a) carbon nanofiber (CNF) and (b) carbon coated cobalt (Co) concentrations.

The heating rate of different nanocomposites as a function of nanoparticle concentration was predicted to be linearly dependent on concentration, Eq. (11) and (12). In Figure 9, we plot the heating power of nanocomposites with different concentrations. This graph was obtained by fitting the experimental data of temperature versus time with Eq. (9) and using P/m as an adjustable parameter. This method does not involve any particular theoretical model for the analysis of microwave absorption. Thus, it can be treated as the experimental method to find the P/m dependence on nanoparticle concentrations. As expected, the experimental data fall on a linear dependence on concentration confirming that the experimental heating power can be fitted well by a straight line.

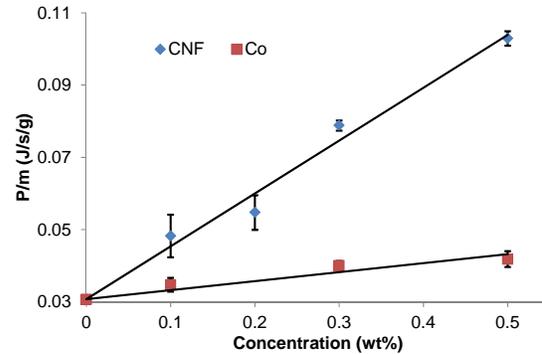


FIGURE 9. Heating rates of various nanocomposites depending on the nanoparticle concentration.

CONCLUSIONS

The microwave absorption at 2.45 GHz of pure paraffin can be significantly improved by adding a small fraction (< 1 wt%) of nanoparticles. Both carbon nanofibers and cobalt nanospheres showed better enhancement on absorption of microwave radiation comparing with pure paraffin. In addition, the heating rate increases significantly with increasing nanoparticle concentration. The dependence is nearly linear, which agrees qualitatively with the theoretical predictions. This confirms that one can control the chemical reactions by changing the concentration of nanoparticles in the polymer. An addition of nanoparticles to the fibrous materials would provide significant advantages over conventional systems with regard to reducing the time and energy required for materials heat treatment.

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REFERENCE

- [1] Hayn, R.A., et al., *Preparation of highly hydrophobic and oleophobic textile surfaces using microwave-promoted silane coupling*. Journal of Materials Science, 2011. 46(8): p. 2503-2509.
- [2] Hatton, T.A., et al., *Enhanced microwave heating of nonpolar solvents by dispersed magnetic nanoparticles*. Industrial & Engineering Chemistry Research, 1998. 37(7): p. 2701-2706.

- [3] Li, S.M., et al., *Cellulose-silver nanocomposites: Microwave-assisted synthesis, characterization, their thermal stability, and antimicrobial property*. Carbohydrate Polymers, 2011. 86(2): p. 441-447.
- [4] Vázquez, E. and M. Prato, *Carbon Nanotubes and Microwaves: Interactions, Responses, and Applications*. ACS Nano, 2009. 3(12): p. 3819-3824.
- [5] Ghasemi, A., *Remarkable influence of carbon nanotubes on microwave absorption characteristics of strontium ferrite/CNT nanocomposites*. Journal of Magnetism and Magnetic Materials, 2011. 323(23): p. 3133-3137.
- [6] Benitez, R., A. Fuentes, and K. Lozano, *Effects of microwave assisted heating of carbon nanofiber reinforced high density polyethylene*. Journal of Materials Processing Technology, 2007. 190(1-3): p. 324-331.
- [7] Landau, L.D. and E.M. Lifshitz, *Electrodynamics of continuous media*. 1960, Oxford: Pergamon. 417.
- [8] Ramprasad, R., et al., *Magnetic properties of metallic ferromagnetic nanoparticle composites*. Journal of Applied Physics, 2004. 96(1): p. 519-529.
- [9] Tokarev, A., et al., *Magnetic Nanorods for Optofluidic Applications*. AIP Conference Proceedings 2010. 1311: p. 204-209.

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