Carbohydrate Polymers 99 (2014) 84–90

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Thermal characterization of magnetically aligned carbonyl iron/agar composites

D. Diaz-Bleis [a], C. Vales-Pinzón [b], Y. Freile-Pelegrín [a,*], J.J. Alvarado-Gil [b]

[a] Marine Resources Department, CINVESTAV-Mérida, Antigua Carretera a Progreso Km. 6, A.P. 97310 Mérida, Yucatán, Mexico
[b] Applied Physics Department, CINVESTAV-Mérida, Antigua Carretera a Progreso Km. 6, A.P. 97310 Mérida, Yucatán, Mexico

ARTICLE INFO

Article history:
Received 6 April 2013
Received in revised form 6 July 2013
Accepted 22 July 2013
Available online 21 August 2013

Keywords:
Agar
Carbonyl iron
Composite films
Thermal diffusivity
Thermal conductivity

ABSTRACT

Composites of magnetic particles into polymeric matrices have received increasing research interest due to their capacity to respond to external magnetic or electromagnetic fields. In this study, agar from *Gelidium robustum* has been chosen as natural biocompatible polymer to build the matrix of the magnetic carbonyl iron particles (CIP) for their uses in biomedical fields. Heat transfer behavior of the CIP–agar composites containing different concentrations (5, 10, 15, 20, 25 and 30% w/w) of magnetically aligned and non-aligned CIP in the agar matrix was studied using photothermal radiometry (PTR) in the back-propagation emission configuration. The morphology of the CIP–agar composites with aligned and non-aligned CIP under magnetic field was also evaluated by scanning electron microscopy (SEM). The results revealed a dominant effect of CIP concentration over the alignment patterns induced by the magnetic field, which agrees with the behavior of the thermal diffusivity and thermal conductivity. Agar served as a perfect matrix to be used with CIP, and CIP–agar composites magnetically aligned at 20% CIP concentration can be considered as promising 'smart' material for hyperthermia treatments in the biomedical field.

1. Introduction

Polysaccharides from natural sources are often used as matrix component in composites materials (Tharanathan, 2003). Among the industrially attractive biopolymers from the marine origin, cell wall polysaccharides extracted from certain members of Rhodophyta, agar and carrageenan, are extensively used as gel-forming agents, thickeners, and stabilizers due to their low cost, biodegradability, high degree of biocompatibility, and their special rheological properties (Armisén & Galatas, 2000; Biazar et al., 2012; Freile-Pelegrıin et al., 2007; Madera-Santana, Misra, Drzal, Robledo, & Freile-Pelegrín, 2009; Madera-Santana, Robledo, Azamar, Ríos-Soberanis, & Freile-Pelegrín, 2010). Basically, agar and carrageenan are both sulphated galactans, mainly composed of alternating D-galactose and 3,6-anhydro-L-galactose and D-galactose and 3,6-anhydro-D-galactose, respectively (Usov, 1998). In particular, some properties of agar are unique and not found in other biopolymers, *i.e.* it does not require the presence of any particular ions to gel; it may to form very strong gels, and it has a uniquely large hysteresis between its gelling (35–44 °C) and melting (85–92 °C) temperatures (Armisén & Galatas, 2000).

On the other hand, composites of magnetic particles in a polymeric matrix have received increasing attention due to their capacity to respond to external magnetic or electromagnetic fields (paramagnetism) and are so-called 'smart materials' (Varga, Filipcsei, & Zrínyi, 2005). Because of their unique physical properties, magnetic polymers, in the submicrometric and nanometric size ranges, have found promising applications in the biomedical fields such as magnetic resonance imaging, DNA separation, drug delivery, cardiology and neurosurgery (Ramanujan, 2009). The application of external magnetic fields could induce heating of the magnetic particles inside the biocompatible polymeric matrix. This property can be used *in vivo* to increase the temperature of tumor tissue and destroy the pathological cells by hyperthermia, since tumor cells are more sensitive to temperature increase than healthy ones (Fukumori & Ichikawa, 2006). To successfully apply magnetic composites in biomedical fields, it is necessary to obtain polymer with magnetic particles with properties such as high and uniform superparamagnetism (collective paramagnetism of the particles where the magnetic moment of each one of them tends to align with the magnetic field), no iron leaking, and non-toxicity (Jordan, Scholz, Wust, Fahling, & Felix, 1999). Recently, iron based magnetic composite materials have stimulated increasing research enthusiasm because of its biocompatibility, high magnetic transition temperature, and high saturation magnetization. One of the most promised filling particles with high thermal conductivity are carbonyl iron particles (CIP). The CIP, together with

* Corresponding author. Tel.: +52 9999429459.
E-mail address: freile@mda.cinvestav.mx (Y. Freile-Pelegrín).

0144-8617/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2013.07.053

ferrites (Fe_2O_3), have been widely used long as the magnetic components of polymer composites in a variety of applications such as magnetorheological fluids and electromagnetic wave absorbers (Butter, Philipse, & Vroege, 2002). Carbonyl iron (Fe^0) is a unique form of elemental iron made by treating iron with carbon monoxide (CO) under heat and pressure. The resulting pentacarbonyl iron [$Fe(CO)_5$] is then decomposed under controlled conditions, yielding CO, and iron powder that is extremely pure and produced in the form of almost perfect spheres with an average particle size of 5–6 μm (Abshinova, Lopatin, Kazantseva, Vilcáková, & Sáha, 2007). CIP is superparamagnetic and non-sensitive to oxidation in water, and its toxicity has been demonstrated to be quite low (LD_{50}: 50 g/kg, Whittaker, Ali, imam, & Dunkel, 2002). Due to the high absorbing capacity of electromagnetic energy in the radio-frequency (RF) band, CIP-filled polymers are used in RF magneto-hyperthermia for heating treatment of deep-seated tumors (Abshinova, Kuritka, Kazantseva, Vilcáková, & Sáha, 2009).

Most recently, agar and carrageenan were chosen as natural polymers to build the matrix of the magnetic particles yielding promising results (Hsieh et al., 2010; Mitsumata, Kosugi, & Ouchi, 2009; Mitsumata, Honda, Kanazawa, & Kawai, 2012). In a previous study, Diaz-Bleis, Freile-Pelegrín, Vales-Pinzón, Martínez-Torres, and Alvarado-Gil (2012) prepared CIP–agar composites with a homogeneous distribution of the CIP and a suitable thermal diffusivity. In order to enhance heat transfer of the matrix, the orientation of the filling particles through a magnetic field is necessary. This induced order may increase the anisotropy of the composite and therefore, enhancement of the heat transport is expected. In this study, we evaluated the thermal behavior of composites with different concentrations of magnetically aligned CIP into an agar matrix using photothermal radiometry (PTR).

2. Materials and methods

2.1. Materials

Commercial grade agar extracted from *Gelidium robustum* supplied by AGARMEX (Mexico) with a molecular weight of 103 kDa was used as polymeric matrix. The magnetic particles were of carbonyl iron micro-sized spherical shaped and were purchased from BASF (Germany). The particles have a variable size distribution with an average radius of 2.01 μm (Fig. 1a) and form agglomerations, as is shown in a scanning electron microscope image (SEM) (Fig. 1b). Glycerol from Sigma–Aldrich (99%, GC) was used as a plasticizer. In general, the incorporation of a plasticizer into the hydrogels makes some improvements in terms of its original physical properties allowing film formation, higher elasticity and elongation at the rupture (Talja, Helen, Ross, & Jouppila, 2007). In order to produce a homogeneous blend with CIP, NaOH (Sigma–Aldrich, USA) was added to the mixture (Morris, 2006).

2.2. Preparation of CIP–agar composites

The CIP–agar composites samples were produced with and without the influence of a magnetic field. The composites were prepared using 0.15 g agar powder dissolved in 10 mL of water mixed with 0.03 g glycerol, and with 1 M sodium hydroxide to reach a pH of 10. This mixture was placed in a ball flask and heated under magnetic stirring for a 2–3 min up to100 °C for complete dissolution. The solution was poured into an Erlenmeyer flask and CIP were added. The CIP to agar mass ratios were 0, 5, 10, 15, 20, 25 and 30% w/w. The mixture was stirred during 3 min using a blade stirrer device powered by a DC electric motor. For gels with random magnetic particles the solution was poured into a Petri dish and cooled at room temperature without exposing them to magnetic fields. For gels with aligned particles, the solution was cooled at room temperature under a uniform magnetic field generated by a pair of Helmholtz coils for 20 min. The Helmholtz pair consisted of two identical circular magnetic coils that were placed symmetrically one to each side of the Petri dish along a common axis, and separated by a distance equal to the radius of the coil (Fig. 2). Each coil carried an equal electrical current flowing in the same direction that produces a magnetic field of 300 Gauss. This magnetic field induced the alignment of the particles inside the matrix, keeping their arrangement due to the gelation process. When the CIP–agar composites (with and without magnetic field) were formed, they were carefully separated from the Petri dish, placed in a plastic container, and dried in an oven for 5 h at 60 °C (Felisa, Model 294 D) in order to obtain thin films (30–35 μm). The thickness of the films was measured with a micrometer model 2118-50 (Mitutoyo, USA). These films were later used for the morphological and thermal characterization.

2.3. Morphological characterization

A scanning electron microscope (SEM) with an acceleration voltage of 5 kV (JEOL model JSM7600F) was used to measure the CIP diameter and characterize the surface morphology, the dispersion, and the alignment of CIP in the agar matrix. Samples were gold-coated to raise electrical conductivity.

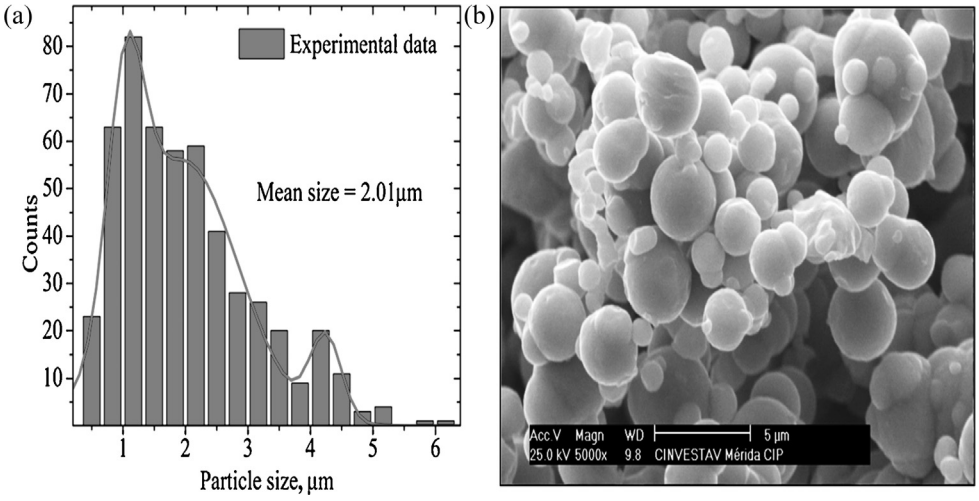

Fig. 1. (a) Size distribution and (b) scanning electron microscopy (SEM) of the carbonyl iron particles used to elaborate the composite samples.

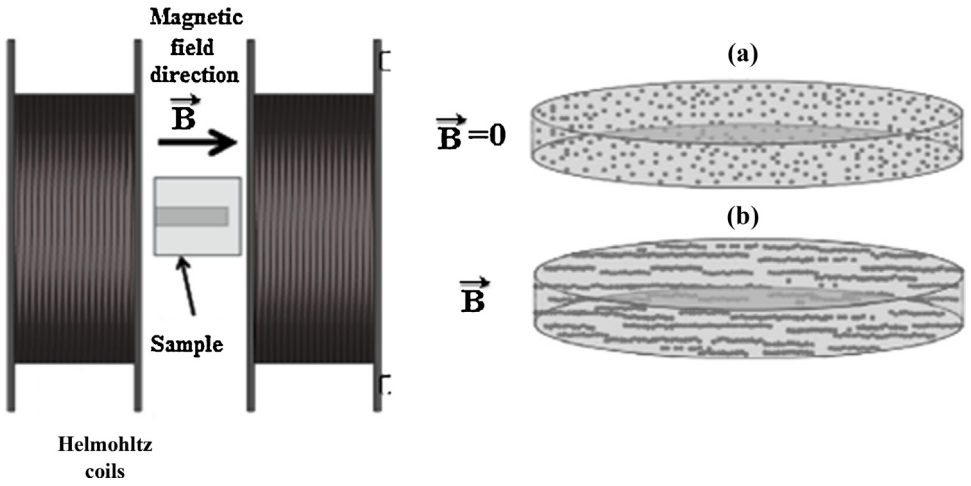

Fig. 2. Diagram of the Helmholtz coils set up used to generate a magnetic field through two different kind of prepared samples: (a) random distribution of particles, and (b) horizontal chain-like structure.

2.4. Thermal diffusivity measurements

Thermal diffusivity (α), typically measured in $mm^2\ s^{-1}$, is a crucial parameter for thermal management because it describes the rate at which heat flows through a material, and represents the ability of a surface to conduct and store thermal energy away from the surface exposed to the heat source. Thermal diffusivity is related to other well-known thermal properties in the form:

$$\alpha = \frac{k}{\rho c} \tag{1}$$

where κ is the thermal conductivity, ρ is the density and c is the specific heat of the sample at constant pressure. The importance of α as a physical quantity to be monitored is due to the fact that, in combination with other quantities as the optical absorption coefficient can be used for the complete characterization of a material (Almond & Patel, 1996).

To perform the thermal characterization of the CIP–agar composites, a photothermal radiometry (PTR) system was used (Zambrano-Arjona, Medina-Esquivel, & Alvarado-Gil, 2007). PTR is a non destructive method, operating at distance and without contact, and that do not induce geometrical or thermal changes inside the sample. It is based on the detection of the modulated thermal radiation emitted from a material surface after photothermal excitation by a modulated light source, usually a laser beam. The analysis of the PTR signal as a function of the modulation frequency leads to the thermal diffusivity (α).

For the PTR measurements, a 1 W infrared (IR) laser diode (Thorlabs TCLDM9) was modulated at 635 nm in amplitude, at a frequency (f) using a high-power laser diode driver (Melles Griot 60DLD205). The output beam was focused directly onto the surface of the sample. The laser spot size was expanded in order to generate one-dimension thermal waves. The IR radiation from the optically excited sample surface was collected and collimated by two silver-coated, off-axis parabolical mirrors and then focused onto a liquid-nitrogen cooled HgCdTe (mercury–cadmium–telluride) detector (EG&G Judson). The heated area of the sample was at the focal point of one mirror, and the detector was at the focal point of the other mirror. The detector had an active area of 1 mm^2 and spectral width band of 2–12 μm. An antireflection-coated germanium window with a transmission bandwidth of 2–14 μm was mounted in front of the detector to block any radiation from the laser. The PTR signal was pre-amplified by a low-noise preamplifier (EG&G Judson PA300) and sent to the digital lock-in amplifier (SR830). This lock-in amplifier received and demodulated the preamplifier output, amplitude, and phase of the PTR signal, which were recorded as a function of frequency in a computer. The process of data acquisition, storage, and frequency scanning was fully automated. The experiments were performed by frequency scans from 5 Hz to 1190 Hz in the back-propagation emission configuration. In order to simplify the theoretical analysis of the experimental data, it will be assumed that most of the infrared radiation emitted by the sample comes from its surface. In our case, to produce a photothermal heating just at the sample surface, a thin plate of brass, previously immersed in H_2SO_4 to increase surface roughness, was attached to the CIP–agar films (randomly dispersed and aligned) as follows: the CIP–agar solution was poured into the Petri dish containing the brass plate. The solution completely covered the metal, and proceeded to the alignment of the magnetic particles as described before. With this procedure, the agar film was adhered to the metal without the need to use thermal paste for this purpose. In this simple configuration, a one-dimensional heat transfer with a heat source at the surface of the material can be assumed (Almond & Patel, 1996). PTR signal is proportional to the surface temperature oscillations $S(f) = K(f)T$, where $K(f)$ depends on the frequency, the sample surface emissivity averaged on the spectral bandwidth of the detector, and the Stephan–Boltzmann constant and geometrical factors (Diaz-Bleis et al., 2012). In order to eliminate the detector response, an experiment over the complete frequency range using a stainless steel 316 of 50 μm thickness was measured. Given that the thermal and optical properties of this material are known, it is possible to obtain $K(f)$. The fitting of the experimental data using $S(f)$ allows determination of the thermal diffusivity (Almond & Patel, 1996). After measuring the thermal diffusivity of the material, the thermal conductivity can be determined using Eq. (1), if the heat capacity and density of a material are known.

3. Results

The SEM images of the microstructure of CIP–agar composites at the different concentrations of CIP (5, 10, 15, 20, 25 and 30%) are shown in Figs. 3 and 4. In the absence of magnetic field the random dispersion of CIP (at 10% of concentration) in the agar matrix yields an isotropic material with uniform spatial distribution (Fig. 3). Our previous studies revealed that at higher concentrations (above 15%) CIP agglomerates were formed and CIP were encapsulated by the polysaccharide (Diaz-Bleis et al., 2012).

The arrangement of the particles induced by magnetic field and the existence of structural anisotropy characterized by uniaxially ordered filler particles were observed in the SEM images

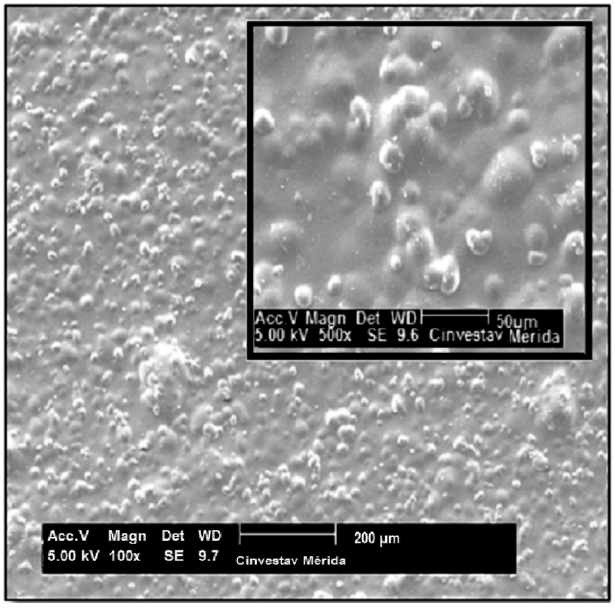

Fig. 3. SEM images of agar–CIP films prepared at 10% without application of external magnetic field.

(Fig. 4A–F). In general, it can be noted that when the magnetic field was applied to the CIP–agar pre-gel solution, the interaction among the carbonyl particles makes them to form chain-like structure and align along the magnetic field. As the gelling process goes on, the chain-like structure of the CIP is fixed in the matrix. It can be also observed that this organization depends directly on the concentration of CIP. When the magnetic field was applied, it can be noted that in films with 5% CIP some particles formed a weak chain-like structure, and others were randomly dispersed (Fig. 4A). For films with 10 and 15% CIP (Fig. 4B and C, respectively), particles form a simple chain structures, with a regular spacing and a successful alignment in a well defined direction, parallel to the field direction. At concentration of 20% and higher (Fig. 4D–F) a loss of the alignment and the formation of particle complexes is observed, resulting from aggregation due to the interaction among CIP. Moreover, some particles were dispersed on the surface of the film as were observed at 25 and 30% CIP (Fig. 4E and F, respectively). Thus, when the concentration of CIP increased, at the highest concentrations, the pattern of aligned particles decreases compared to low CIP concentrations.

Thermal diffusivity values for CIP–agar composites (with and without magnetic field) measured at the different CIP concentration values are shown in Fig. 5. In general, we observed that thermal diffusivity (α) increased at increasing CIP concentrations both in absence and under magnetic field. This was expected, given that the thermal conductivity of iron particles is larger than the thermal conductivity of the polymeric matrix (Almond & Patel, 1996).

The results also showed that thermal diffusivity increased slightly at low concentration (5% CIP) showing the same value ($\sim$0.14 mm^2 s^{-1}) for samples prepared with and without magnetic field, indicating a slight influence of the particles on thermal transport. Under the magnetic field, thermal diffusivity increased substantially when CIP concentration increases from 5 to 10% (from 0.14 to 20 mm^2 s^{-1}). However, this increase is reduced at higher CIP concentration (from 10 to 15%) where α was about the same at both concentrations. For the CIP concentrations at 10, 15 and 20%, the thermal diffusivities were always higher than their corresponding values at each concentration in absence of the magnetic field. In contrast, thermal diffusivity values at 25 and 30% were not significantly different.

Thermal conductivity was determined using Eq. (1), based on the extensive properties of the heat capacity per unit volume of the compound material as follows:

$$k = \alpha(\rho_A C_A + \rho_{CIP} C_{CI})$$

where $\rho_A = 1.325\,g\,cm^{-3}$ ($C_A = 3.49\,J\,g^{-1}K^{-1}$) and $\rho_{CI} = 7.86\,g\,cm^{-3}$ ($C_{CI} = 0.46\,J\,g^{-1}K^{-1}$) are the density (heat capacity) of agar and carbonyl iron respectively (Freile-Pelegrıin et al., 2007; Medina-Esquivel et al., 2012).

Similar to thermal diffusivity behavior, the thermal conductivity increases when the concentration of CIP grows for samples with random and aligned particles (Fig. 6). At low concentration (5% CIP) the thermal conductivity takes the same value ($\sim$0.65 W m^{-1} K^{-1}) for sample prepared with and without magnetic field. This indicates a very small influence of the particles on thermal transport. In samples prepared using the magnetic field, thermal conductivity increased substantially for higher concentrations, from 10 to 20% as compared with samples with random particles. At concentration 25% and higher, thermal conductivity values of samples prepared with and without magnetic field were almost the same. This is the result that at high concentration of CIP, the heat does not follow a defined path along the aligned particles but can follow any other direction, and therefore, samples with aligned and random CIP exhibit the same rate of heat transfer and thermal conductivity.

4. Discussion

In Fig. 1a we show the distribution in size of CIP, provided by the manufacturer. Additionally, the analysis of the particle size inside the film, measured directly from the SEM images (See Fig. 3), are in agreement with those provided by the manufacturer. The response of the CIP to a magnetic fields has been studied previously by Bombard, Joekes, Alcantara, and Knobel (2003). These authors showed that the magnetic susceptibility of the particles, which is the quotient of the magnetization divided by the applied magnetic field, varies with the applied magnetic field, and that for the magnetic field used in this paper, the magnetic susceptibility is approximately 0.16 emu/(g Oe).

In the present study, measurements of heat transfer using photothermal radiometry of composites containing aligned and random CIP embedded in an agar matrix are reported. Thermal diffusivity of agar without CIP was comparable to those reported by Tomas et al. (2004) for other algal polysaccharides (kappa-carageenan and sodium-alginate). The imposed magnetic field oriented the magnetic dipoles and when the particles were closely spaced (at 10 and 15% of CIP concentration), mutual particle interactions occurred. Due to these attractive forces, a pearl chain structure was developed. This phenomenon is called magneto-rheological effect (Nakano & Koyama, 1997). This has been described in magnetorheological materials under a uniform magnetic field, where the magnetic particles interacts with others but do not interact with the polymer network. Under these conditions, the polymer network immobilizes the ordered structure, and the direction of the magnetization within the particle is fixed, although the rotation of particles in the gel is allowed (Filipcsei, Csetneki, Sziágyi, & Zrínyi, 2007). Thus, in terms of orientation, the particles can form separate chains, three-dimensional simple lattice structures (consisting in separate chains), or even more complex structures, in which particles have multiple interaction points. This effect was observed in CIP–agar composites at concentration of 20% and higher (Fig. 4D–F), where particle complexes, resulting from the aggregation, were connected to each other by magnetic forces, forming several thicker parallel chains close to each other along the axis, decreasing the alignment pattern.

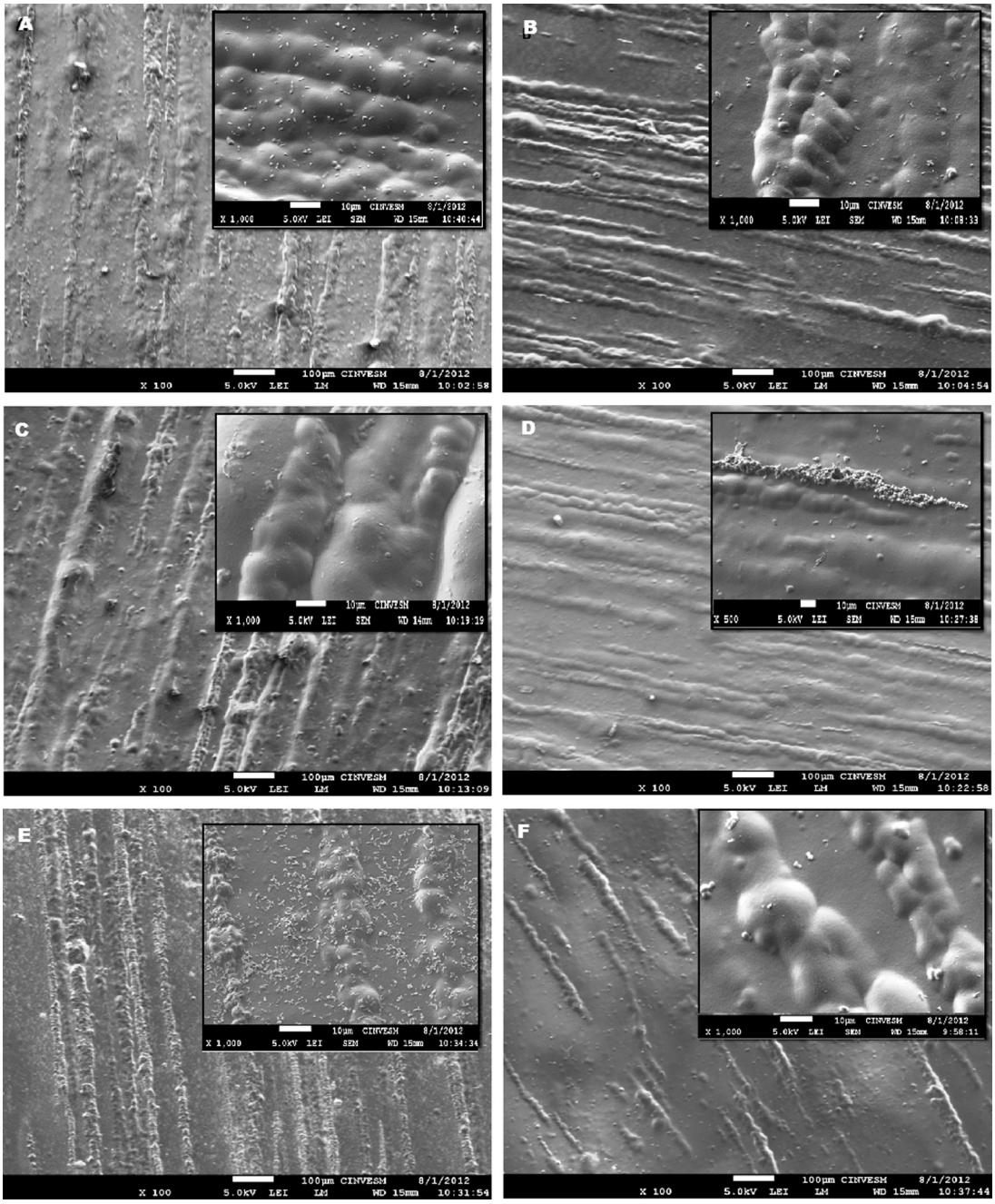

Fig. 4. SEM images of agar–CIP films prepared at (A) 5%, (B) 10%, (C) 15%, (D) 20%, (E) 25%, (F) 30% with application of external magnetic field.

The particle network structure of aligned CIP–agar composites had a significant influence on the thermal diffusivity and thermal conductivity at concentrations ≤20%. This is due to the fact that the magnetic field arranges the particles in chain structures, which facilitate the heat conduction through them and therefore, enhance the overall thermal diffusivity and thermal conductivity with respect to their corresponding values when the particles are distributed randomly. The above is confirmed by the SEM images (Fig. 4B–D). Thermal diffusivity and thermal conductivity values were similar than those obtained with other matrix (*i.e.* silicone oil and polyester resin) containing aligned CIP at 20% concentration (Medina-Esquivel, Yáñez-Limón, & Alvarado-Gil, 2008; Medina-Esquivel et al., 2012).

When the CIP concentration achieves 25 and 30%, the arrangement of the particles did not influence the thermal behavior, therefore, thermal diffusivities and conductivities were similar in both randomly arranged and aligned particles composites. This behavior indicates that for low CIP concentrations (5–15%) the increase of the number of particles favors the arrangement of larger chain-like structures and, therefore, higher thermal diffusivity and thermal conductivity; whereas for higher CIP concentrations (>20%), the particles have reduced space to follow the alignment induced by the magnetic field, leading to multiple interaction points and more complex structures, with a decrease in the orderly arrangement. Under high CIP concentrations (≥ 25%), the pattern of aligned particles is reduced and its behavior is similar to the samples with random particles. Therefore, spatial distribution of CIP, with and without magnetic field, is equivalent. This pattern has also been previously described for magnetically aligned CIP-polyester resin composites (Medina-Esquivel et al., 2012). A similar effect

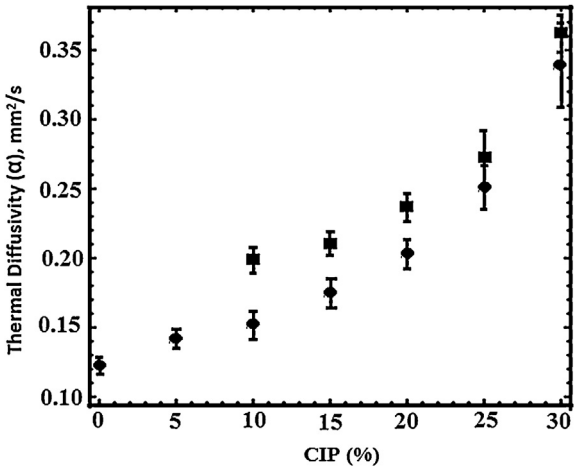

Fig. 5. Thermal diffusivity (α) of agar–CIP films as a function of the concentration of CIP; (●) with unaligned particles, (■) with particles oriented by an external magnetic field.

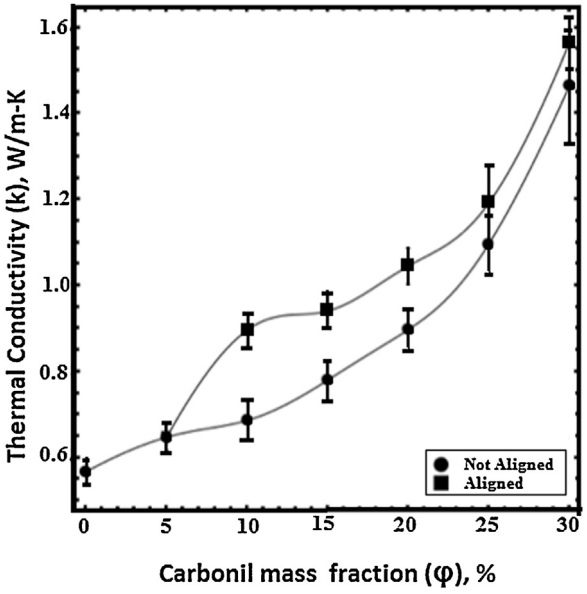

Fig. 6. Thermal conductivity (κ) of agar–CIP films as a function of the concentration of CIP; (●) with unaligned particles, (■) with particles oriented by an external magnetic field.

was also observed by Mitsumata et al. (2009) for κ-carrageenan gel loaded with iron oxide particles (γ-Fe_2O_3) where the magnetically aligned composite showed a reduction in dynamic modulus, contrary to that observed for the gels with random particles.

Composites are a physical combination of two or more materials to create a new material whose properties are superior to those of the original substances in a specific application. Their constituents (a continuous phase or matrix and reinforcing elements), although act in concert, retain their identities and can be physically separated. Using various combinations of proportions of different components, it is possible to produce 'smart' materials with the necessary magnetic, thermal, and other special properties (Chung, 2003). Very few studies have been focused to the use of algal polymers for this purpose. Many attempts to fabricate magneto rheological gels using synthetic polymer, silicone elastomers and rubbers have been performed. In these cases, particles must be coated with a reactive surfactant to avoid sedimentation (Li & Zhang, 2008). On the contrary, agar produces "physical gels" following a 'cross-linked network' model, which means that polymer molecules form gels solely by hydrogen bonds. Since the gelation temperature is relatively high (38–40 °C) agar aqueous solution rapidly forms a strong gel because of its unique property to form very hard gels at very low concentrations (0.1%) compared with other biopolymer (*i.e.* starch and chitosan; Madera-Santana et al., 2010). Moreover, based in Boral and Bohidar (2012) and Craig (2007) the incorporation of a little amount of glycerol and NaOH into the agar improves its original gelling properties, allowing a better film formation, higher elasticity and elongation at the rupture and to avoid sedimentation of magnetic particles.

This study revealed a dominant effect of CIP concentration into an agar matrix over the alignment patterns induced by a magnetic field, which agrees with the behavior of the heat transfer. It is important to emphasize on the effect of the concentration and alignment of the CIP, in which our results indicate that at low concentration (under 5%) and very high (above 25%) heat transfer is not affected when comparing aligned and non-aligned samples at the same concentration. Therefore, it is unnecessary to align the CIP in such concentrations. This could be highly relevant in applications in which magnetic particles need to be inserted in an agar, tissue or a similar matrix. In such case if the heat dissipation, diffusion or conduction needs to be enhanced in a preferential direction, it can be done aligning magnetic particles in a concentration between 5 and 25%. Outside this range no preferential direction for heat transfer would be obtained when employing carbonyl iron aligned particles. Investigation, using larger aspect ratio and higher thermal conductivity particles as well as the improvement of the thermal contact between the particles and the matrix, need to be performed.

"The alignment of the particles induces two effects on the heat diffusion: it can enhance the heat conduction along the direction of the alignment, and particle agglomeration could also favor the heat transfer along the thickness of the film. These two contributions could be the responsible for the observed effects in our experimental data, in which the heat transfer along thickness is favored. On the other hand, working with thin films, in which the size of the microparticles and agglomerates is not very small compared with the thickness of the film, theoretical models should be developed".

Although these and further studies must be done on this subject, CIP–agar composites can be considered as promising materials for hyperthermia treatments in the biomedical field. Because of its combination of renewability, low cost, biodegradability, biocompatibility and high gelling power, agar is a promising candidate to use as a matrix to be used with CIP.

Acknowledgments

This research was partially supported by Project Multidisciplinary Cinvestav 2008. Dianela Diaz-Bleis thanks CONACYT for the scholarship support to carry out this research work. The authors want to express their acknowledgment to C. Chávez Quintal and J. Bante Guerra for their technical support, and to A.R. Cristobal Ramos for her valuable help to obtain the SEM images.

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