Thermal properties of composite materials with a complex fractal structure

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Abstract

In this work, we report the thermal characterization of platelike composite samples made of polyester resin and magnetite inclusions. By means of photoacoustic spectroscopy and thermal relaxation, the thermal diffusivity, conductivity and volumetric heat capacity of the samples were experimentally measured. The volume fraction of the inclusions was systematically varied in order to study the changes in the effective thermal conductivity of the composites. For some samples, a static magnetic field was applied during the polymerization process, resulting in anisotropic inclusion distributions. Our results show a decrease in the thermal conductivity of some of the anisotropic samples, compared to the isotropic randomly distributed ones. Our analysis indicates that the development of elongated inclusion structures leads to the formation of magnetite and resin domains, causing this effect. We correlate the complexity of the inclusion structure with the observed thermal response through a multifractal and lacunarity analysis. All the experimental data are contrasted with the well-known Maxwell–Garnett effective media approximation for composite materials.

Keywords: composite materials, fractal structure, thermal properties

(Some figures may appear in colour only in the online journal)

1. Introduction

Tuning the effective thermal properties of composite materials, by controlling their internal structure and composition, is a topic of great interest nowadays due to potential applications that span many different kinds of systems: from fusion reactors to electronic devices. Experimentally, this has been achieved by varying the relative volume fraction and size of the constituents [1–3], by controlling the microstructure and interface properties of the inclusions [4], by means of mechanical strains (stretching the material to orient one of the constituents in the stretching direction) [5], by controlling the morphology of the inclusions [6, 7], and even by engineering multilayered composites where the diffusive heat flow is guided in order to obtain a desired thermal conduction [8], among other approaches.

On the other hand, experimental techniques such as the photoacoustic (PA) technique in combination with the thermal relaxation method (TRM) have proven to be reliable and useful tools for measuring the thermal properties such as the thermal diffusivity, conductivity and heat capacities of materials [9]. In particular, the PA technique has been used to characterize the thermal transport properties (thermal diffusivity and effusivity) of materials occurring in many different forms like transparent liquids, polymers, and powdered and solid samples [1, 10–19]. The principle of the PA effect is based on the light-induced heat release and consequent generation of acoustic waves from a material, when it is irradiated with a modulated optical radiation. Complementarily, the TRM allows the measurement of heat capacities of small samples in the temperature range around room temperature [20]. Experimentally, the sample is placed inside a closed cell where a partial vacuum has been established. Then, the sample is subjected to a constant illumination so that its temperature rises, reaching a maximum, and thermal equilibrium is established between its illuminated and non-illuminated faces. Afterwards, the illumination is...
interrupted and the sample is allowed to cool down mainly through radiative processes in a characteristic time known as the relaxation time. By measuring the difference between the maximum and room temperatures and the relaxation time, it is possible to determine the volumetric heat capacity of the sample [9]. From the application of both techniques, the thermal conductivity of different materials can be obtained.

In this work, by means of the PA technique in combination with the TRM, we study the thermal properties of composite platelike samples consisting of a polyester resin matrix with powdered magnetite inclusions. Three kinds of inclusion structures were considered: one isotropic and two anisotropic. For the isotropic samples, the inclusion dispersion was prepared to be as random as possible. For the anisotropic samples, a magnetic field was applied during the polymerization process, resulting in two different kinds of inclusion structures, depending on how the chains formed by the magnetite particles are oriented: perpendicular or parallel to the faces of the platelike samples. The volume fraction of inclusions was systematically varied in all cases in order to observe the effect on the effective thermal conductivity of the samples. Our results show that, as the volume fraction of the inclusions increases, the thermal conductivity of the isotropic samples behaves according to the well known Maxwell–Garnett effective medium approximation for composite materials with a random distribution of spherical inclusions [21]. In contrast, the thermal conductivity of the anisotropic transverse samples (those for which the magnetite chains run parallel to the faces of the samples but transverse to the illumination direction) is always smaller than the isotropic ones with a non-trivial behaviour. For the anisotropic longitudinal samples (in these the magnetite chains run perpendicular to the faces of the samples but along the illumination direction), those with lower volume fraction of inclusions behave in the same way as the isotropic ones; however, with further increases of the concentration of inclusions, the thermal conductivity drops. Our analysis shows that the formation of large chains of magnetite particles in some of the samples leads to the development of (inclusion and matrix) domains, causing the effective thermal conductivity to decrease in accordance with recent theoretical results [22].

2. Experimental details

In this section, we provide details regarding the sample preparation and the experimental setups for the PA technique and thermal relaxation.

2.1. Inclusion preparation

The preparation of the composite samples begins with the obtaining of the inclusions from mineral magnetite crystals through a grinding process with the use of an agate mortar and pestle. The mineral magnetite itself is a naturally occurring dark iron oxide (Fe₃O₄) with molecular weight of 231.55 g mol⁻¹ [23], that only presents one crystalline phase [24]. We selected magnetite as the inclusion material due to its magnetic response, given the fact that some of the samples were prepared in the presence of magnetic fields in order to obtain a desired inclusion structure (see below). The magnetite crystals shown in figure 1(a) were crushed in the mortar until the size of the particles obtained was less than 44 µm.
resulting from the process of grinding of the magnetite crystals of the field. The presence of the magnetic field induced through a pair of Helmholtz coils in order to ensure uniformity of the field. The polymerization process of the anisotropic samples, just after adding the catalyst, a resin before adding the catalyst so that they could be dispersed making the curing time rather fast. Additionally, the viscosity of the resin and the size of our inclusions helped to prevent any sedimentation process from taking place. For these reasons, our bulk samples were much smaller than that (about 3 g), 14 min, while the curing time for the same amount is 22 min. The gel time for 100 g of the polyester resin at room temperature is about 3 cm3—one for each kind of inclusion structure and for the resulting powder with different magnification factors are presented. As is evident from the figures, the magnetite inclusions are very polydisperse, with nanometric to micrometric sizes. Additionally, the magnetite powder was analysed with an x-ray diffractometer to characterize the magnetite crystals used in this work. Figure 2 shows the diffractogram obtained with a PANalytical Empyrean (Cu Kα, λ = 1.5406 Å) diffractometer in the 2θ range from 10° to 80°. By comparing the position and relative amplitude of the narrow peaks in the x-ray diffractogram against the Powder Diffraction File (PDF) with reference code 01-089-0691, we were able to determine that our magnetite powder was made of almost pure magnetite in its crystalline form [25].

2.2. Sample preparation

The samples were prepared in bulk in plastic cubic cells of about 3 cm3—one for each kind of inclusion structure and for each concentration of inclusions. The matrix of the samples, consisting of polyester resin, uses a peroxide as catalyst in order to accelerate its solidification process. The gel time for 100 g of the polyester resin at room temperature is about 14 min, while the curing time for the same amount is 22 min. Our bulk samples were much smaller than that (about 3 g), making the curing time rather fast. Additionally, the viscosity of the resin and the size of our inclusions helped to prevent any sedimentation process from taking place. For these reasons, the magnetite inclusions were aggregated and mixed with the resin before adding the catalyst so that they could be dispersed as homogeneously as possible inside the matrix. In the case of the anisotropic samples, just after adding the catalyst, a magnetic field was applied during the polymerization process through a pair of Helmholtz coils in order to ensure uniformity of the field. The presence of the magnetic field induced the formation of chains of magnetite particles inside the matrix. The intensity of the magnetic field applied was always 12.17 kA m⁻¹, regardless of the concentration of inclusions.

We let 8 h pass before taking the bulk samples out of the molds to ensure that they had achieved maximal hardness. Then, a section of about 1 cm³ was obtained from the centre of each bulk sample in order to avoid any possible distortions in the inclusion structure that could come from the surface in contact with the mold itself. Square platelike samples about 1 mm thick and 7 mm in linear size were later obtained from these centre sections. In the case of isotropic samples, a single slice was extracted. In the case of anisotropic samples, two slices were extracted from the centre section: one perpendicular to the direction of the applied field (for the anisotropic longitudinal sample) and one parallel to the direction of the applied field (for the anisotropic transverse one). Each of the platelike samples was then sanded and polished to the desired thickness with a special die, consisting of a cylindrical body with diameter of about 3.5 cm and a plunger with a diameter of 1 cm, to ensure that their faces were parallel. For each kind of composite sample (isotropic, anisotropic longitudinal and anisotropic transverse) the concentration of inclusions \( \eta_m \), measured as a volume fraction, was systematically varied within the interval 0.013 to 0.089.

Additionally, two more platelike samples were prepared: one made of resin without inclusions and one made of solid magnetite. These samples were used to determine the thermal properties of the two constituent materials of the composite ones. The results for them were later introduced in the Maxwell–Garnett effective medium approximation (see below) in order to compare the experimental measurements with the theoretical prediction.

The odd rows in figure 3 show micrographs of selected samples, taken with an optical microscope with a magnification of \( \times 80 \), for the three types considered in this work: isotropic in (a) to (d), anisotropic longitudinal in (e) and (f), and anisotropic transverse in (g) and (h). In order to produce these micrographs, it was necessary to obtain an additional slice from the centre section for each composite sample, this time sanded and polished to a thickness of about 100 μm. This allowed us to observe a few layers of the inclusion structure, as can be appreciated in the corresponding binarized images, shown in the even rows of the figure. Afterwards, the inclusion structure was characterized via a multifractal analysis and lacunarity measurements, as discussed later in detail in section 3.

We must mention that the polydispersity of the magnetite particles used in this work induced the aggregation of particles, i.e., large particles tend to get covered by smaller ones; see, for example, figures 1(b) and (c). This feature prevented a better dissolution of the inclusions in the resin, resulting in less homogeneous samples than desired. Because of this and in order to have a more accurate value of the concentration of inclusions, the density of the composite samples was measured, and their concentration \( \eta_m \) was calculated from \( \eta_m = 1 - (\rho - \rho_m)/(\rho_l - \rho_m) \), where \( \rho, \rho_l \), and \( \rho_m \) correspond to the densities of the composite sample, resin and magnetite, respectively. For this, the density of the platelike samples was determined with the following procedure:
Figure 3. Micrographs of composite samples (odd rows) and their corresponding binarized images (even rows), taken with an optical microscope with a magnification ×80. The white bar at the bottom right corner of the micrographs corresponds to a scale of 500 µm. From (a) to (d), selected isotropic samples with volume fraction concentration of inclusions \( \eta_m = 0.034, 0.066, 0.077, 0.089 \), respectively, are shown. In (e) and (f), selected anisotropic longitudinal samples with \( \eta_m = 0.042, 0.064 \), respectively, are shown. In (g) and (h), selected anisotropic transverse samples with \( \eta_m = 0.033, 0.041 \), respectively, are shown. Notice the formation of large elongated structures of magnetite particles and the development of magnetite and resin domains in (f), (g) and (h). These samples have lower values of the thermal conductivity and cannot be described using the Maxwell–Garnett EMA for composite materials with a random distribution of inclusions (see the text for more details).

(i) A photograph of one of the sample’s faces was taken along with a reference scale and its area determined by processing the photograph with ImageJ.
(ii) The thickness \( l_s \) of the sample was measured with a digital micrometer and its volume calculated.
(iii) Finally, the sample was weighed using an analytical balance and its mass density \( \rho \) calculated.

As an example, the density measured from our solid magnetite sample is 5.2 g cm\(^{-3}\), which agrees very well with the reported one, 5.17 g cm\(^{-3}\) [23]. The results obtained for \( \eta_m \), \( l_s \) and \( \rho \) are presented in table 1 for each of the samples studied in this work. Given the methods used to measure these quantities, only systematic errors are produced in their determination, and these are thus neglected.

2.3. Experimental setups

The PA technique used in this work is the well established open-cell method widely reported in the literature [9, 11]. The thermal diffusivity, \( \alpha_s \), was measured using the experimental setup represented in the schematic diagram of figure 4. In this arrangement, the sample is directly mounted onto a commercial electret microphone (in this case a RadioShack 270-0090). The beam of a 150 W tungsten lamp (Thorlabs
3. Results and discussion

3.1. Measurement of the thermal diffusivity

It is well known that a PA signal, especially one produced from plate-like samples, has two main contributions: one coming from the thermal diffusion phenomenon and the other one from the thermoelastic bending effect \[10, 11\]. For this, there are well established models that allow one to distinguish which one of these contributions dominates. The thermal diffusivity, \( \alpha_s \), is then obtained from the dependence of the detected PA signal on the modulation frequency \( f \), as discussed in detail in \[9, 11\].

In first place, one must determine whether the sample is thermally thin or thick. These two regimes are separated by a cutoff frequency given by \( f_c = \frac{\alpha_s}{(\pi l_s^2)} \), where \( l_s \) is the thickness of the sample. A thermally thin sample fulfills the condition \( f \ll f_c \) and the amplitude of the PA signal behaves as \( f^{-1.5} \), independently of the properties of the sample. On the other hand, thermally thick samples fulfill the condition \( f \gg f_c \). In this regime, if the thermoelastic bending contribution dominates, the amplitude of the PA signal varies as \( p_{\text{el}} \propto f^{-1} \), while its phase \( \phi_{\text{el}} \) approaches 90° as

\[
\phi_{\text{el}} \approx \frac{\pi}{2} + \arctan \left[ \frac{1}{\sqrt{b_s f}} \right],
\]

(1)

where \( b_s \) is the fitting parameter. On the other hand, if the thermal diffusion phenomenon dominates in the generation of the PA signal, the amplitude, \( p_{\text{td}} \), and phase, \( \phi_{\text{td}} \), of the signal have dependences on the modulation frequency of the forms

\[
p_{\text{td}} = \frac{1}{f} \exp \left[ -\sqrt{b_s f} \right]
\]

(2)

and

\[
\phi_{\text{td}} = -\frac{\pi}{2} - \sqrt{b_s f}.
\]

(3)

Depending the model used, the thermal diffusivity can be estimated through the relation

\[
\alpha_s = \frac{\pi l_s^2}{b_s}.
\]

(4)

Figure 6 shows the typical dependence of the amplitude and phase of the PA signal on the modulation frequency \( f \) for the composite samples that we studied. In particular, the results shown in the figure correspond to an isotropic sample with volume fraction concentration of inclusions \( \eta_m = 0.076 \). Notice the slope \(-1.1\) of the amplitude \( p_{\text{el}} \) as a function of the modulation frequency \( f \) in the log–log plot of figure 6(a). This means that the thermoelastic bending effect dominates in the generation of the PA signal. This was the case for all
of our samples, including the pure resin and pure magnetite ones. According to our discussion above, the value of the thermal diffusivity \( \alpha_s \) is obtained by fitting the experimental data for the phase of the PA signal with equation (1) as shown in figure 6(b).

On an additional note, in order to verify that our experimental setup was operating properly, calibration measurements of the thermal diffusivity of an iron sample with thickness \( l_s = 745 \, \mu m \) were systematically performed. For this particular sample, the thermal diffusion phenomenon dominates in the generation of the PA signal (not shown) and the thermal diffusivity value is obtained by fitting the experimental data with equations (2) and (3). We measured a value of \( 2.39 \pm 0.12 \times 10^{-5} \, m^2 \, s^{-1} \) that agrees with the reported one, \( 2.3 \times 10^{-5} \, m^2 \, s^{-1} \) [23].

### 3.2. Measurement of \( \rho c \) and the thermal conductivity

As shown in the schematic diagram of figure 5, one of the faces of the sample is illuminated with a constant flux of light; therefore, a lack of equilibrium between the illuminated and non-illuminated faces of the sample is established. This phenomenon can be approximately described by a 1D equation when the thickness \( l_s \) of the sample (including the two coats of black paint) is much smaller than its transverse dimension. The conservation condition for the energy is

\[
I_0 - \sigma T_i^4 - \sigma T_n^4 = \frac{d}{dt} \int_0^{l_s} \rho c T(x, t) \, dx,
\]

where \( I_0 \) is the flux of incident light over the front face, \( \sigma \) is the Stefan–Boltzmann constant, \( T_i \) is the temperature of the illuminated face, \( T_n \) is the temperature of the non-illuminated (opposite) face, \( \rho \) is the mass density of the sample and \( c \) is its specific heat at constant pressure. In this equation we use explicitly the fact that the sample is painted with a thin coat of black paint that has an emissivity coefficient approximately equal to 1 [20].

For long times, when the equilibrium is reached and the fluxes of incident and emitted radiation cancel each other out, the illuminated and non-illuminated faces of the sample reach the saturation temperatures \( T_{i, \text{max}} \) and \( T_{n, \text{max}} \), respectively. Moreover, for the values of \( l_s \) and \( I_0 \) that we used in the laboratory, the condition \( l_s \, dT(x, t)/dx \ll T_i(t) \approx T_n(t) \) is fulfilled; thus \( T_{i, \text{max}} \approx T_{n, \text{max}} \).

Using the fact that \( c \) does not depend on the position and that it is practically constant in the interval of a few degrees above room temperature, equation (5) can be approximately solved for the decrease of temperature of the non-illuminated face of the sample, from \( T_{n, \text{max}} \) to \( T_{n,0} \), after the illumination is interrupted, with the resulting expression

\[
T_n(t) = T_{n,0} + (T_{n, \text{max}} - T_{n,0}) \exp(-t/\tau_d).
\]

Here, \( T_{n,0} \) is the initial temperature of the sample before the illumination process starts. It is also the temperature that the sample reaches, for long times, after the illumination is interrupted. In this case, the mean relaxation time \( \tau_d \) is given by

\[
\tau_d = \frac{\rho c l_s}{8\sigma T_{n,0}^4}.
\]

Details of this solution’s derivation can be found in [9].

Figure 7 shows a typical experiment on thermal relaxation for the composite samples studied here. The results shown in the figure correspond to the measured temperature \( T_n \) (clear circles)—as a function of time—of the non-illuminated face of the isotropic sample with \( \eta_n = 0.076 \), while the solid line corresponds to a fit with equation (6). Then, the value of the product \( \rho c \) is obtained from equation (7), while the thermal conductivity \( k \) is calculated from the very well known relationship

\[
k = \rho c \alpha_s.
\]
3.3. The effective medium approximation

Since its invention, the effective medium approximation (EMA) has been employed in the study of several kinds of macroscopically inhomogeneous media. For example, the EMA can be used to estimate the effective properties of systems where a random distribution of inclusions is embedded in a given continuous matrix [26]. These properties include the dielectric function, the elastic modulus, the electrical conductivity and the thermal conductivity, the latter being the one that we are interested in here, in this work. If the inhomogeneities inside the medium are large enough, such that in each space portion of the material the behaviour of the property is described or controlled by macroscopic constitutive equations, it is only necessary to find a reasonable way of averaging the existing statistical variations in the material. Conversely, the same basic problem arises in different fields such as those of heat flow, diffusion and elastic properties [27–31].

In this work, we use the Maxwell–Garnett approximation, one of the most commonly used approximation methods. By nature of its construction, this approximation is exact only at first order in the volume fraction. At second order, there are big discrepancies with an error up to 50% [21]. In the case of composite materials, one evaluates their effective properties as a function of the properties of their components. Here, the Maxwell–Garnett approximation is applied to systems of two components, where one of them is considered as a continuum (polyester resin) that supports the other one (magnetite inclusions). Additionally, our composite samples were prepared in a regime of low concentration. In order to evaluate their effective thermal conductivity we used the following equation:

$$k = k_e + \frac{3\eta_m\gamma}{1 - \eta_m\gamma} k_m$$  \hspace{1cm} (9)

with

$$\gamma = \frac{k_m - k_e}{k_m + 2k_e},$$  \hspace{1cm} (10)

where \(k_m\) and \(k_e\) are the magnetite and polyester resin thermal conductivities, respectively, while \(\eta_m\) is the volume fraction occupied by the magnetite particles [21]. In particular, these expressions should be able to predict the effective thermal conductivity of the isotropic samples where the inclusions are randomly distributed inside the matrix.

The broken curves with symbols in figure 8(a) show the measured thermal conductivity \(k\) for the isotropic (black dashed line with clear circles) samples and for the anisotropic longitudinal (red dotted line with solid squares) and transverse (blue dash–dotted line with solid triangles) samples as a function of the volume fraction concentration of magnetite particles, \(\eta_m\). The black solid line corresponds to the Maxwell–Garnett EMA given in equations (9) and (10).

As expected, our results show a good agreement between the experimental measurements for the isotropic samples with this approximation. Given the fact that magnetite has a larger (more than double according to table 1) thermal conductivity than the polyester resin matrix, the effective thermal conductivity of these samples should increase with the concentration of inclusions. Recent results on the development of numerical tools for mesoscopic systems have even extended the range of prediction for effective medium theories to include composite materials where the concentration of inclusions is not necessarily low, as long as the inclusions remain randomly distributed. Under these conditions, the effective thermal conductivity of composite samples still increases with the concentration of inclusions [32].

Contrastingly, the anisotropic longitudinal samples show a drop in the thermal conductivity for \(\eta_m\) above 0.061, while the anisotropic transverse samples show a non-trivial behaviour with \(\eta_m\), as shown in figure 8(a), with lower thermal conductivities than the isotropic ones. It has been observed that disorder on crystallographic sites largely controls the thermal conductivity of mixed crystals and that mass disorder increases the anharmonic scattering of phonons through a modification of their vibration eigenmodes, resulting in an increase of the thermal resistivity [33–35]. Moreover, a model for anisotropic periodic composites with wire and cylindrical inclusions (nanowires and cylindrical nanowires), where the heat flow is applied in the longitudinal direction of the inclusions, predicts a decrease in the effective thermal conductivity due to the introduction of additional surface scattering in relation to the ballistic phonon transport [36].

Even though our composite samples are not crystalline, the formation of large quasi-continuous structures of inclusions and the development of domains in some of the anisotropic samples may explain the observed decrease in their effective thermal conductivity. In particular, the transverse section of the magnetite chains in anisotropic longitudinal samples increases with \(\eta_m\), as can be appreciated in figures 3(e) and (f). Nonetheless, in samples with \(\eta_m \leq 0.061\), these structures are isolated and commensurate with those present in isotropic samples with similar concentrations. Moreover, the magnetite chains are more evenly distributed inside the matrix than in the isotropic samples themselves. For these samples, a good correspondence with the EMA is observed—for some samples it is even better than that of similar isotropic samples!
contrast, it is only for the anisotropic longitudinal samples with concentration $\eta_m > 0.061$ that the inclusion structure has a counterintuitive effect, with a sharp drop in their thermal conductivity. As is apparent in figure 3(f), above this ‘critical’ concentration, the transverse section of the magnetite chains becomes so large that the chains are able to aggregate laterally, with the consequent formation of elongated structures and the development of domains of magnetite and resin. Obviously, such samples cannot be described with the Maxwell–Garnett EMA, as the inclusions are no longer randomly distributed. For these, an analysis of the inclusion structure is provided below.

### 3.4. The inclusion structure and thermal conduction

In order to explain the decrease in thermal conductivity for some of the anisotropic samples, we analysed the multifractality and lacunarity of some of them.

The typical singularity spectrum, $f(\alpha)$, and generalized fractal dimension, $D(\alpha)$, are presented for isotropic samples in figures 9(a) and (d), for anisotropic longitudinal samples in figures 9(b) and (e), and for anisotropic transverse samples in figures 9(c) and (f), respectively. These results were obtained using the plug-in FracLac for ImageJ from binarized images such as those presented in the even rows of figure 3. In these images, the black patterns correspond to the inclusion structure, while the white areas correspond to the resin matrix. This open software calculates both quantities using the box counting method, which has been successfully applied for this kind of analysis for other systems [37, 38]. When the image analysed has a pattern with multifractal properties, the function $D(\alpha)$ versus $\alpha$ is decreasing and sigmoidal around $\alpha = 0$. In our samples, this occurs for the isotropic and anisotropic longitudinal ones, exemplified in figures 9(d) and (e). In the case of anisotropic transverse samples, they show a monofractal pattern, as the plot for $D(\alpha)$ tends to be horizontal for $\alpha > 0$, as shown in figure 9(f).

The generalized fractal dimension is usually used in combination with other multifractal measures such as the singularity spectrum $f(\alpha)$. The latter is used to characterize the variety within a pattern regarding the scale at which the pattern is observed. Monofractals show less variation than multifractals in their dependence of $f(\alpha)$ on $\alpha$. The singularity spectrum for a monofractal (see figure 9(c)) converges to a value, while the spectrum for a multifractal is typically humped (see figures 9(a) and (b)). From the behaviour of the singularity spectra obtained for our samples, the results obtained from the generalized fractal dimension are confirmed, in that the inclusion structures of isotropic and anisotropic longitudinal samples have multifractal characteristics, while the structure in anisotropic transverse samples is monofractal.

Additionally, the mean lacunarity of the inclusion structure, $\Lambda_\alpha$, and that of the matrix, $\Lambda_m$, were obtained with FracLac from the binarized images. The results are shown in figure 8(b). In short, a lacunarity analysis is a multiscaled method for describing patterns of spatial dispersion [39]. In contrast with measures such as the fractal dimension, which describes how much space is filled, lacunarity indicates how the space is filled. In this sense, lacunarity is a parameter that describes the distribution of the sizes of gaps or lacunae in a given structure. Greater lacunarity reflects a greater size distribution of the lacunae or, put another way, a higher degree of ‘gappiness’, although it has been also defined as visual texture, inhomogeneity, translational and rotational invariance, etc. Nonetheless, lacunarity pertains to both gaps

| $\eta_m$ (v.f.) | $l_i$ (\(\mu m\)) | $\rho$ (kg m\(^{-3}\)) | $\alpha_i \times 10^{-6}$ (m\(^2\)s\(^{-1}\)) | $\rho c \times 10^3$ (J m\(^{-3}\)K\(^{-1}\)) | $k$ (W m\(^{-1}\)K\(^{-1}\)) |
|----------------|-------------------|------------------------|-----------------------------------|-----------------------------------|-------------------|
| Resin          | 1032              | 1100                   | 24.65 ± 0.18                      | 8.36 ± 0.48                       | 20.60 ± 1.48      |
| Magnetite      | 908               | 5200                   | 48.49 ± 3.60                      | 13.30 ± 0.35                      | 64.59 ± 5.12      |
| 0.013          | 1047              | 1150                   | 28.96 ± 0.66                      | 6.96 ± 0.19                       | 20.14 ± 0.70      |
| 0.032          | 1020              | 1230                   | 29.45 ± 0.81                      | 7.30 ± 0.26                       | 21.49 ± 0.96      |
| 0.034          | 1066              | 1240                   | 31.78 ± 0.69                      | 6.68 ± 0.17                       | 21.21 ± 0.71      |
| 0.062          | 973               | 1360                   | 29.25 ± 0.75                      | 7.07 ± 0.27                       | 20.67 ± 0.94      |
| 0.066          | 1024              | 1370                   | 29.60 ± 1.23                      | 6.94 ± 0.16                       | 20.55 ± 0.97      |
| 0.076          | 980               | 1410                   | 29.66 ± 0.75                      | 7.00 ± 0.18                       | 20.76 ± 0.74      |
| 0.077          | 980               | 1420                   | 30.97 ± 0.83                      | 7.13 ± 0.20                       | 22.06 ± 0.85      |
| 0.089          | 985               | 1470                   | 24.85 ± 0.49                      | 9.10 ± 0.26                       | 22.63 ± 0.78      |
| 0.016          | 962               | 1168                   | 30.90 ± 0.62                      | 6.84 ± 0.22                       | 21.13 ± 0.81      |
| 0.042          | 1014              | 1273                   | 31.66 ± 1.52                      | 6.73 ± 0.22                       | 21.31 ± 0.81      |
| 0.049          | 996               | 1304                   | 31.86 ± 0.44                      | 6.73 ± 0.19                       | 21.44 ± 0.66      |
| 0.061          | 953               | 1352                   | 28.25 ± 0.99                      | 8.14 ± 0.14                       | 22.98 ± 0.89      |
| 0.064          | 956               | 1364                   | 22.43 ± 0.29                      | 6.99 ± 0.15                       | 15.67 ± 0.40      |
| 0.069          | 998               | 1383                   | 22.91 ± 0.51                      | 6.33 ± 0.18                       | 14.49 ± 0.51      |
| 0.014          | 805               | 1158                   | 22.62 ± 0.31                      | 7.20 ± 0.20                       | 16.28 ± 0.50      |
| 0.023          | 960               | 1194                   | 31.60 ± 1.52                      | 5.47 ± 0.19                       | 17.27 ± 1.02      |
| 0.033          | 982               | 1238                   | 33.51 ± 0.42                      | 5.77 ± 0.18                       | 19.34 ± 0.66      |
| 0.039          | 900               | 1261                   | 30.29 ± 0.28                      | 6.79 ± 0.23                       | 20.57 ± 0.73      |
| 0.041          | 981               | 1271                   | 28.41 ± 0.69                      | 6.58 ± 0.16                       | 18.69 ± 0.64      |
| 0.044          | 1002              | 1281                   | 23.73 ± 0.56                      | 7.38 ± 0.19                       | 17.50 ± 0.60      |
| 0.051          | 995               | 1310                   | 19.08 ± 0.98                      | 6.56 ± 0.18                       | 12.51 ± 0.72      |
| 0.052          | 995               | 1316                   | 15.95 ± 0.69                      | 6.94 ± 0.23                       | 11.06 ± 0.60      |
domains (see the text for details).

commensurate due to the development of inclusion and matrix structure,
symbols correspond to the mean lacunarity of the inclusion or matrix,
\( / \Lambda_1 \) measured thermal conductivity

dependence of the Maxwell–Garnett EMA,

samples with large enough concentrations (those inside the grey square), that cannot be described by the standard Maxwell–Garnett effective medium approximation. In this paper, we have studied the thermal conductivity of isotropic and anisotropic samples consisting of a polyester resin matrix with embedded inclusions of magnetite particles in a fractal structure. Our results show that all of the isotropic samples and some of the anisotropic longitudinal ones, where the distribution of inclusions or inclusion structures (with these structures isolated from each other) remains random, present an effective thermal conductivity that can be described using the standard Maxwell–Garnett effective medium approximation. In contrast, some of the anisotropic samples and heterogeneity, and has been applied to the study of many different systems including microvascular ones [40].

In figure 8(b) one can appreciate that, for isotropic samples, \( \Lambda_1 \) (the black solid curve with solid circles) or \( \Lambda_m \) (the black dashed curve with clear circles) remains very low while the other is high. This is also the case for the anisotropic longitudinal samples with thermal conductivities in agreement with the EMA—for these, \( \eta_m \leq 0.061 \)—where \( \Lambda_1 \) (the red solid curve with solid squares) is large while \( \Lambda_m \) (the red dashed curve with clear squares) is very low. We associate this behaviour with the fact that the inclusions or inclusion structures formed inside the matrix are randomly distributed, thus fulfilling the conditions of the EMA used in this work. In consequence, either the inclusion structure or the matrix retains a high degree of homogeneity and translational and rotational invariance. On the other hand, even when some of the anisotropic transverse samples with the smaller \( \eta_m \) show this behaviour, where \( \Lambda_1 \) (the blue solid curve with solid triangles) is large and \( \Lambda_m \) (the blue dashed curve with clear triangles) very small, these samples, along with the rest of the anisotropic transverse ones, cannot be described using the EMA, as they do not fulfil the condition of having randomly distributed inclusions. This is obviously due to the formation of large chains of magnetite particles across the matrix, all aligned in the same direction.

It is interesting to note that anisotropic longitudinal samples with \( \eta_m > 0.061 \) have moderate values for \( \Lambda_1 \) and \( \Lambda_m \) that are commensurate. This is also the case for anisotropic transverse samples as \( \eta_m \) increases, behaviour that is pointed out in figure 8(b) for the data inside the grey square, that can be associated with the development of domains of inclusions and matrix. See, for example, figures 3(f), (g) and (h) where one can identify large and elongated structures of magnetite particles intertwined with portions of matrix with zero or very low concentration of inclusions. From the point of view of the lacunarity analysis, this structure retains a moderate degree of homogeneity and translational and rotational invariance, both in the inclusion structure and in the matrix itself. At this point, it is necessary to remind ourselves that the samples from which these images were obtained are very thin (\( \sim 100 \mu \text{m} \)) and only depict a few layers of inclusion structure. One must extrapolate this to the thicker (\( \sim 1 \text{mm} \)) samples that were thermally characterized, where domains of inclusion structures and matrix overlap in a disorderly fashion, each one presenting a high thermal impedance or resistivity to the one below, thus quenching the thermal transport in the direction of illumination. Our observation is consistent with the prediction of the model developed for fractal-like tree networks proposed by Yu and Li [22]. They found that the effective thermal conductivity of composites with such inclusion networks decreases with increase of the length of the branches or density of the network. Moreover, they conclude that the thermal conductivity of the network itself may be less than that of the original material by several orders of magnitude. For our composite samples which present long chains of inclusions in a fractal or multifractal structure this seems to be the case, with a drop in their effective thermal conductivity, as it is apparent that the inclusion structure has a lower thermal conductivity than the magnetite and resin themselves.

4. Conclusions

Figure 8. In (a), the curves with broken lines correspond to the measured thermal conductivity \( k \) of the samples studied here as a function of \( \eta_m \). The transverse bars correspond to the propagated experimental error, while the black solid curve corresponds to the Maxwell–Garnett EMA given in equations (9) and (10). Notice the good correspondence with the isotropic samples and the non-trivial dependence of \( k \) on \( \eta_m \) for the anisotropic samples. (b) Mean lacunarity \( \Lambda \) for selected samples. The solid curves with solid symbols correspond to the mean lacunarity of the inclusion structure, \( \Lambda_1 \), while the dashed curves with clear symbols correspond to the mean lacunarity of the matrix, \( \Lambda_m \). Notice how \( \Lambda_1 \) or \( \Lambda_m \) remains very low while the other is high for isotropic samples. In contrast, for anisotropic (longitudinal and transverse) samples with large enough concentrations (those inside the grey square in the figure), that cannot be described by the standard Maxwell–Garnett EMA, \( \Lambda_1 \) and \( \Lambda_m \) are both moderate and commensurate due to the development of inclusion and matrix domains (see the text for details).
longitudinal samples and all of the anisotropic transverse ones, where the development of long chains of magnetite particles leads to the formation of magnetite and resin domains in a multilayered fashion, show a drop in their measured thermal conductivity with values lower than those of the isotropic ones. These samples cannot be described using the Maxwell–Garnett approximation; however, our results are consistent with the work of Yu and Li [22] on the effective thermal conductivity of composite samples with a fractal inclusion structure. Our study indicates that the thermal conductivity of the magnetite inclusion structure has a lower thermal conductivity than the magnetite and resin themselves, making the effective thermal conductivity of these samples highly dependent on the structural properties of the inclusion arrangement. The results of this study could be used to direct the development of composite materials with tuned effective thermal conductivities, by controlling the aggregation processes in the inclusion structure.

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