Thermal properties of composite two-layer systems with a fractal inclusion structure

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Abstract
In this work, we study the thermal transport properties of platelike composite two-layer samples made of polyester resin and magnetite inclusions. By means of photoacoustic spectroscopy and thermal relaxation, their effective thermal diffusivity and conductivity were experimentally measured. The composite layers were prepared under the action of a static magnetic field, resulting in anisotropic (fractal) inclusion structures with the formation of chain-like magnetite aggregates parallel to the faces of the layers. In one kind of the bilayers, a composite layer was formed on top of a resin layer while their relative thickness was varied. These samples can be described by known models. In contrast, bilayers with the same concentration of inclusions and the same thickness on both sides, where only the angle between their inclusion structures was systematically varied, show a nontrivial behaviour of their thermal conductivity as a function of this angle. Through a multifractal and lacunarity analysis, we explain the observed thermal response in terms of the complexity of the interface between the layers.

Keywords: composite two-layer systems, fractal structure, thermal properties

(Some figures may appear in colour only in the online journal)
different kinds of materials [23–26]. About the first, there has been an ongoing effort to extend the PA technique for the characterization of multilayered systems, with the purpose to determine their effective thermal diffusivity from the knowledge of the thermal properties of the layers themselves [27–31]. In particular, for two-layer systems, there are some aspects to be taken into account such as the thermal thickness of the layers and their effusivity, that become important at the interface in relation to its thermal resistance [32–34]. On the other hand, the TRM has been complimentarily used for the measurement of the heat capacity of small samples [35–37]. Jointly applied, these techniques allow the determination of the thermal conductivity of different samples.

In this work, by means of the PA technique in combination with the TRM, we study the thermal properties of composite two-layer systems. The layers consist of a polyester resin matrix with powdered magnetite inclusions that present an anisotropic fractal structure, resulting from the application of a magnetic field in the direction parallel to the faces of the layers during their preparation. Two kinds of two-layer samples were studied. For the first, resin–composite bilayers (RCBs) were prepared, where the volume fraction of inclusions of the composite layer was varied as well as the relative thickness of the layers. For the other kind, composite–composite bilayers (CCBs) were prepared, with layers of the same thickness and inclusion concentration on each side. For these, only the angle between the inclusion structures of the layers was systematically varied. The effective thermal properties of the RCBs can be described by well established models, however, the CCBs exhibit a nontrivial behaviour in their effective thermal conductivity as a function of the angle between their anisotropic inclusion structures. Results from this work confirm our previous findings [23], where the increase of thermal resistance was associated with the formation of overlapping domains of resin and magnetite aggregates, in this case purposefully induced at the interface of the two-layer systems by varying the angle between the inclusion structures on its sides. On the other hand, the same results show a clear way for the development of bilayer systems with a controllable thermal response, by controlling the thermal resistance at the interface of the layers in relation with the complexity of the interface inclusion structure formed by the inclusion structures of the layers that compose the system.

2. Experimental details

2.1. Samples preparation

First of all, we obtained the magnetite particles by grinding mineral magnetite crystals, as those shown in figure 1(a), with the use of an agate mortar and pestle until the size of the particles obtained was less than 44 µm. For this, we sifted the powder through a mesh sieve. Figure 1(b) shows a scanning electron microscope (SEM) micrograph from the resulting powder that is very polydisperse, as can be appreciated. This material was selected as the inclusion material due to its magnetic response, as the composite layers were subjected to a magnetic field in order to control their inclusion structure.

Additionally, the magnetite powder was analyzed with a Panalytical Empyrean (Cu-β, λ = 1.5406 Å) x-ray diffractometer to prove its purity. The diffractogram was compared with the Powder Diffraction File (PDF) with reference code 01-089-0691, showing a good correspondence for magnetite in its crystalline form (see figure 2 in reference [23]).

The samples were prepared, layer by layer, on top of a microscope glass slide with cover slips (with thickness of about 200 µm), piled up and glued together around the sample ‘pocket’, in order to control the thickness of each layer (see figure 2(a)). The mixture of resin (acting as the matrix) and magnetite particles (acting as the inclusions) was prepared by agitation in 1 ml syringes that had their tip cut off; at this point, the catalyzer to accelerate the resin’s polymerization process had already been added to the mixture. For the first layer (layer 1) with thickness \( t_1 \), the mixture was spilt on top of the bottom glass slide and in between the cover slip piles. Afterwards, another glass slide was placed on top of the arrangement and the resin was let to cure as illustrated in figure 2(b). In order to control the inclusion structure of the magnetite particles, the composite layers were subjected to a magnetic field with an intensity of 12.17 kA m\(^{-1}\) during the polymerization process, and applied through a pair of
Helmholtz coils—to ensure the uniformity of the field—in the direction parallel to the surface of the layers (see figure 2(e)). The resin used in this work consists of an orthophthalic (clear casting) polyester resin with a gel time of 14 ± 2 min and a curing time of 30 ± 5 min according to the manufacturer. Thus, after the gel time had been reached (about 15 min), the top glass slide was removed from the arrangement and more cover slips added symmetrically on both sides of the sample to control the thickness of the second layer (see figure 2(c)). By then, the first layer was solid enough to keep the inclusion structure frozen, but not completely cured so it would stick to the second layer to be applied. Following the same procedure, the second layer (layer 2) with thickness $l_2$ was formed on top of the first one. Figure 2 shows a step by step schematic diagram of the whole process. Special care was taken to avoid the formation of air bubbles inside the layers. This began with the preparation of the mixture itself, inside the syringe, working the plunger to remove the bubbles. Our aim was to prepare samples with total thickness of around 850 µm, however, their final thickness was measured with a micrometer (see table 1).

The concentration of magnetite particles, $\eta_m$, was measured in volume fraction, considering that the magnetite used has a density of 5.2 g cm$^{-3}$. Two kinds of bilayer samples were prepared: RCBs and CCBs, regarding the composition of the materials used for each layer. The RCBs are, in one side made of pure resin with thickness $l_1$ and the other made of composite material with thickness $l_2$, with a total thickness $l = l_1 + l_2$ (see figure 2(f)). For these, the control parameters are $\eta_m$ and $x = l_2/l$, corresponding to concentration of magnetite on the composite side, and the ratio of the thickness of the composite layer ($l_2$) and the total thickness of the sample ($l$), respectively. On the other hand, the CCBs consist of the same composite material on both sides, with the same concentration of inclusions and the same relative thickness, i.e. $l_1 = l_2$. For these, only the angle $\theta$ between the inclusion structures on each side of the interface was varied between 0° and 90° in steps of 22.5°. After the curing process we still waited around 8 h before removing the samples from the glass arrangement to later cut them in the form of an octagon of about 9 mm in width.

In order to measure the thermal properties of the raw materials used in the preparation of the layered ones, samples consisting of a single layer with a thickness of approximately the same size as our two-layer systems were also prepared. In this way, one sample made of pure resin, one made of solid magnetite and five composite single layers (CSLs) with $\eta_m = 0.005$, 0.0075, 0.01, 0.015, 0.02 were thermally characterized. The

Table 1. Summary of the results for the properties of the samples studied in this work. The second set corresponds to the CSLs. The third and fourth sets correspond to the RCBs and the CCBs, respectively.

| $\eta_m$ (v.f.) | $l$(µm) | $x$ (deg) | $\alpha \times 10^{-6}$ (m$^2$ s$^{-1}$) | $k$ (W m$^{-1}$ K$^{-1}$) |
|----------------|----------|-----------|---------------------------------------|----------------------------|
| 0.0050 790     | 0.0050 899 | 20.50 ± 0.60 | 23.10 ± 0.69                        |
| 0.0075 830     | 0.0050 899 | 20.50 ± 0.60 | 23.10 ± 0.69                        |
| 0.0100 870     | 0.0050 899 | 20.50 ± 0.60 | 23.10 ± 0.69                        |
| 0.0150 810     | 0.0050 899 | 20.50 ± 0.60 | 23.10 ± 0.69                        |
| 0.0200 823     | 0.0050 899 | 20.50 ± 0.60 | 23.10 ± 0.69                        |
| 0.0100 850 0.25| 0.0050 899 | 20.50 ± 0.60 | 23.10 ± 0.69                        |
| 0.0100 900 0.50| 0.0050 899 | 20.50 ± 0.60 | 23.10 ± 0.69                        |
| 0.0100 840 0.75| 0.0050 899 | 20.50 ± 0.60 | 23.10 ± 0.69                        |
| 0.0050 896 0.50| 22.5°      | 33.90 ± 0.88 | 32.18 ± 0.94                        |
| 0.0075 870 0.50| 22.5°      | 35.00 ± 2.05 | 35.36 ± 2.14                        |
| 0.0100 842 0.50| 22.5°      | 38.00 ± 1.65 | 38.39 ± 1.76                        |
| 0.0150 920 0.50| 22.5°      | 32.40 ± 1.23 | 40.31 ± 1.60                        |
| 0.0200 844 0.50| 22.5°      | 36.60 ± 1.85 | 45.48 ± 2.37                        |
| 0.0100 793 0.50| 45.0°      | 23.80 ± 1.26 | 27.28 ± 1.49                        |
| 0.0100 840 0.50| 67.5°      | 34.60 ± 0.83 | 42.05 ± 1.14                        |
| 0.0100 906 0.50| 90.0°      | 41.00 ± 1.42 | 48.04 ± 1.76                        |
The left column of figure 3 shows micrographs taken from selected CSLs with a thickness of \( \sim 400 \mu m \). The inclusion structure formed by the arrangement of magnetite particles were characterized through the singularity spectrum, \( f(\alpha) \), and the generalized fractal dimension, \( D(Q) \), shown respectively in the right column of figure 3. These results were obtained by analyzing binarized images (not shown) of the micrographs on the left with the plugin FracLac for ImageJ. This open software calculates both quantities using the box counting method and has been successfully used to analyze other systems [38, 39]. The singularity spectrum 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 \( \alpha \). In combination with the generalized fractal dimension, these quantities are used to characterize the fractal properties of a given structure. For our CSLs, the singularity spectrum shows the typical hump corresponding to a pattern with multifractal properties, a fact that is corroborated with the plots of \( D(Q) \) versus \( Q \) with their decreasing and sigmoidal dependence around \( Q = 0 \), as shown in the figures.

Additionally, with the objective to study the interface structure of the CCBs, equivalent bilayer samples of about 400 \( \mu m \) in total thickness were prepared, where the composite layers on each side had a thickness of about 200 \( \mu m \). The micrographs in the middle column of figure 4 correspond to the best focus of the interface, taken from the side of the second layer (layer 2), while the last column corresponds to the best focus of the interface taken from the side of the first layer (the substrate layer or layer 1). The yellow lines are provided as an aid to identify the angle between the inclusion structures as seen from each side, while the red horizontal bar at the bottom right corner of each micrograph corresponds to a scale of 500 \( \mu m \). All of the micrographs were taken with an optical microscope with a magnification of \( \times 80 \). The binarized images on the
first column, obtained by processing the images in the middle one, were employed to characterize the fractal properties of the interface inclusion structure. The results for the singularity spectrum $f(\alpha)$ and the generalized fractal dimension $D(Q)$ are presented in figure 5 that, as explained before, also show multifractal properties. These binarized images were also used to characterize the interface structure via a lacunarity analysis, as discussed later in section 3. We must mention that it was harder to control the formation of air bubbles in these samples, as each of their layers is very thin: about half the thickness of the layers present in the two-layer systems that were thermally characterized.

2.2. Experimental setups

In this work, we used the well established open-cell method [40–42] in order to obtain the PA spectra of our samples. The experimental setup is schematically represented in the diagram of figure 6. In this arrangement, the sample is directly mounted onto a commercial electret microphone
The beam of a 250 W tungsten lamp (HORIBA LSH-T250) was focused on the sample in such a way that the resulting beam had a diameter of about the same size as the inlet hole of the microphone (\( \sim 3 \) mm). The beam was then mechanically modulated with a Stanford Research Systems (SRS) optical chopper model SR540. As a result of the periodic heating of the sample by absorption of the modulated light, the microphone produces a signal that is fed to a lock-in amplifier (SRS model SR530). From the behaviour of the amplitude and phase of the PA signal, as a function of the modulation frequency, one can determine the thermal diffusivity \( \alpha \) of a given sample.

We also measured the volumetric heat capacity, \( \rho c \), corresponding to the product of the mass density and the constant pressure specific heat, respectively. For this, we employed the thermal relaxation method that is also well established in the literature [35–37]. Before the measurement, both faces of the sample were sprayed as before with the same matte black paint, in order to make its emissivity approximately equal to one. The sample was positioned inside a sealed chamber where a partial vacuum had been established. Then, the light beam from the 250 W lamp was focused with an arrangement of two lenses and a first surface mirror through a glass lid at the top of the chamber and onto one face of the sample. The temperature of the opposite non-illuminated face of the sample rises to an equilibrium value above room temperature. Afterwards, the illumination is interrupted and its temperature traced as a function of time. The volumetric heat capacity (\( \rho c \)) can be calculated from the thermal decay that happens mainly.

**Figure 5.** Singularity spectrum \( f(\alpha) \) and generalized fractal dimension \( D(Q) \) for the interface inclusion structures of the CCBs shown in figure 4; from top to bottom \( \theta = 22.5^\circ, 45^\circ, 67.5^\circ, 90^\circ \). The multifractal analysis was performed inside the white square of the binarized images in the first column of figure 4. According to these results, the interface inclusion structures of the CCBs also present multifractal properties.

**Figure 6.** Schematic diagram of the experimental setup used to measure the thermal diffusivity \( \alpha \), using the open-cell PA technique (see text for details). (RadioShack 270-0090). The beam of a 250 W tungsten lamp (HORIBA LSH-T250) was focused on the sample in such a way that the resulting beam had a diameter of about the same size as the inlet hole of the microphone (\( \sim 3 \) mm). The beam was then mechanically modulated with a Stanford Research Systems (SRS) optical chopper model SR540. As a result of the periodic heating of the sample by absorption of the modulated light, the microphone produces a signal that is fed to a lock-in amplifier (SRS model SR530). The illuminated face of the samples was painted with a matte black alkyd enamel in order to ensure that all of the light was absorbed in the surface of the sample. The paint coating amounts to about 20 \( \mu \)m of the thickness of the samples and was sprayed, coat by coat, until the desired thickness (measured with a micrometer) was obtained. From the behaviour of the amplitude and phase of the PA signal, as a function of the modulation frequency, one can determine the thermal diffusivity \( \alpha \) of a given sample.

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through radiative processes. Figure 7 shows a schematic diagram of the experimental setup used for these measurements.

3. Results and discussion

3.1. Determination of the thermal properties

The PA signal produced from platelike samples, when all of the light is absorbed at their surface, is known to have two main contributions: one coming from the thermal diffusion phenomenon and the other from the thermoelastic bending effect [40]. In this work we used the model from Rosencwaig and Gersho [43], that allows one to distinguish which one of these contributions dominates. The thermal diffusivity \( \alpha \), can be obtained from the dependence of the PA signal’s amplitude and phase on the modulation frequency \( f \), as discussed in detail in [25, 40].

First, one must consider that a sample can be thermally thin or thick, regarding the ratio of its thermal diffusion length \( \sqrt{\frac{\pi c}{\rho f \phi}} \) and the thickness \( l \) of the sample. These two regimes are separated by a cut-off frequency given by \( f_c = \frac{\pi}{2l^2} \sqrt{\frac{\rho c}{\phi}} \). Thermally thin samples fulfill the condition \( f \ll f_c \). In this regime, the amplitude \( \rho \) and phase \( \phi \) of the PA signal behaves as \( f^{-1} \), independent of the properties of the sample; this regime allows for the microphone’s frequency response to be determined, which is later used to compensate the PA signal amplitude. Conversely, thermally thick samples fulfill the condition \( f \gg f_c \). In this regime, if the thermal diffusion phenomenon dominates in the generation of the PA signal, its amplitude \( \rho d \) and phase \( \phi d \) depend on the modulation frequency as

\[
\rho_d = \frac{1}{f} \exp \left[-\sqrt{bf}\right], \tag{1}
\]

\[
\phi_d = -\frac{\pi}{2} - \sqrt{bf}. \tag{2}
\]

On the other hand, if the thermoelastic bending contribution dominates, the amplitude \( \rho b \) and the phase \( \phi b \) of the PA signal depend on the modulation frequency as

\[
\rho_b \propto f^{-1}. \tag{3}
\]

\[
\phi_b \approx \frac{\pi}{2} + \arctan \left[ \frac{1}{\sqrt{bf} - 1} \right]. \tag{4}
\]

In all of the cases, \( b \) is the fitting parameter from which the thermal diffusivity can be estimated through the relation

\[
\alpha = \frac{\pi^2}{4b}. \tag{5}
\]

Figure 8 shows the typical dependence of the amplitude and phase of the PA signal on the modulation frequency for the two-layer samples we studied in this work. The results shown in the figure correspond the CCB with \( \theta = 90^\circ \) and \( \eta_n = 0.01 \). A slope of \(-1.01\) shown by \( \rho_d \) as a function of \( f \) in the log–log plot of figure 8(a), means that the thermoelastic bending effect dominates in the generation of the PA signal. The value of the thermal diffusivity \( \alpha \) was then obtained by fitting the experimental data for the phase of the PA signal with equation (4), shown in figure 8(b). All of our two-layer samples, including the pure resin one, exhibited this behaviour. Only the pure solid magnetite sample showed thermal diffusion as the dominating PA effect. The experimental data for this sample were fitted instead with equations (1) and (2).

In order to determine the volumetric heat capacity \( \rho c \), we used the TRM. For this technique, one face of the sample is illuminated with a constant flux of light as illustrated in the schematic diagram shown in figure 7. As a consequence, 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 \( l \) of the sample is much smaller than its width. The energy conservation condition is given by

\[
I_0 - \sigma T_1^4 - \sigma T_0^4 = \frac{d}{dx} \int_0^l \rho c T(x, t) \, dx, \tag{6}
\]

where \( I_0 \) is the flux of incident light, \( \sigma \) is the Stefan–Boltzmann constant, \( T_i \) is the temperature of the illuminated face, \( T_n \) is the temperature of the non-illuminated face, \( \rho \) is the mass density of the sample and \( c \) is its specific heat at constant pressure. Here, we have explicitly used the fact that both faces of the sample are coated with a thin layer of black paint that has an emissivity coefficient approximately equal to one [35].

For long times, when thermal equilibrium is established, and for the values of \( I_0 \) and \( \rho c \) used, the condition \( dT(x, t)/dx \ll T_i(t) \approx T_n(t) \) is fulfilled. Moreover, using the fact that \( e \) does not depend on the position and that it is practically constant in the interval of a few degrees above room temperature, equation (6) can be solved for the thermal decay of the non-illuminated face after the illumination on the sample is interrupted. Considering this process is mainly due to radiative processes, the solution can be written as

\[
T_n(t) = T_{n,0} + \left( T_{n,\text{max}} - T_{n,0} \right) \exp \left( -t / \tau_d \right), \tag{7}
\]

where \( T_{n,0} \) is the final temperature reached by the non-illuminated face after cooling down, while \( T_{n,\text{max}} \) is its maximum saturation temperature reached before the illumination is interrupted. The relaxation mean time \( \tau_d \) is related to \( \rho c \) by
As we showed in section 2.1, the inclusion structure formed by the phase that agrees with the reported values $87 \times 10^{-6} \text{m}^2 \text{s}^{-1}$ for the thermal diffusivity [40] and $149 \text{W} \text{m}^{-1} \text{K}^{-1}$ for the thermal conductivity. The thermal properties of a $\mu$-type silicon sample with thickness $l = 829 \mu\text{m}$, the thermal diffusion phenomenon dominates in the generation of the PA signal. The clear circles in (b) correspond to the measured phase of the curve. In this case, a slope of $-1.01$ indicates that thermoelectric bending dominates in the generation of the PA signal. The clear circles in (a) correspond to the measured amplitude in mV, while the solid line was obtained by fitting equation (4) to the experimental data with $\tau_d$ as the fitting parameter. We must mention that we tested our experimental setups by measuring the thermal properties of a $p$-type silicon sample with thickness $l = 535 \mu\text{m}$. For this sample, the thermal diffusion phenomenon dominates in the generation of the PA signal. The thermal diffusivity and conductivity obtained from our experimental results are $87.7 \pm 3.3 \times 10^{-6} \text{m}^2 \text{s}^{-1}$ and $143.4 \pm 5.7 \text{W} \text{m}^{-1} \text{K}^{-1}$, respectively, that agree with the reported values $87.7 \pm 3.3 \times 10^{-6} \text{m}^2 \text{s}^{-1}$ and $143.4 \pm 5.7 \text{W} \text{m}^{-1} \text{K}^{-1}$, respectively. The thermal diffusivity of samples with similar inclusion structure as our CSLs, i.e. with the magnetite chains parallel to the faces of the samples, was smaller than that of the resin and the magnetite themselves. We associated this result with the overlap of resin and magnetite domains—by domains meaning areas occupied by either resin or magnetite aggregates—from different substrates of the samples, increasing the thermal resistance in the direction of transmission of the heat, as the layers of inclusion structure were not aligned in this direction. Here, our CSLs were prepared in platelike form between glass slides, with the inclusion structure in close reach of the slides’ surfaces. The measured thermal conductivity for these samples is higher that of the resin but smaller than the value obtained for the magnetite. This is due to a strong surface effect that allows the magnetite chains to also develop vertically, i.e. perpendicular to the faces of the samples, thus forming vertical ‘walls’ of magnetite aggregates in the direction of heat transport. This is shown in figure 10, where micrographs of the top and side views of the RCB with $\eta_m = 0.01$ and $x = 0.75$ are presented. Notice the absence of a stratified structure on the side view of the composite layer of this sample, as opposed to what can be appreciated from the top view. These kind of structures are not present when the samples are prepared in bulk.

Additionally, figure 3 shows micrographs from our CSLs with a thickness of about $400 \mu\text{m}$, that is very close to the thickness of the layers found in the CCBs, for example. As can be appreciated, not much overlap between domains of resin and magnetite is noticeable from different substrates of the samples due to the wall-like formation of magnetite aggregates in the vertical direction (perpendicular to the faces of the samples). These wall-like aggregates create pathways for the heat to flow, consequently enhancing the thermal properties of our CLSs with respect to their resin matrix. Figure 11(a) shows the results for the measured thermal conductivity of these samples as a function of the time $t$ for the pure resin sample with thickness $l = 829 \mu\text{m}$. The solid line corresponds to a fit with equation (7).

A summary of the results for the samples studied in this work is presented in table 1.

Figure 8. Typical dependence of the PA signal’s amplitude $p_a(a)$ and phase $\phi_a(b)$ on the modulation frequency $f$ for the samples studied in this work. The clear circles in the log–log plot in (a) correspond to the measured amplitude in mV, while the solid line corresponds to the fitted slope of the curve. In this case, a slope of $-1.01$ indicates that thermoelectric bending dominates in the generation of the PA signal. The clear circles in (b) correspond to the measured phase of the signal while the solid line corresponds to a fit with equation (4). The results shown correspond to the CCB with $\theta = 90^\circ$ and $\eta_m = 0.01$.

\[
\tau_d = \frac{\rho c l}{8\sigma T_{n,0}}. \tag{8}
\]

Details for the solution of equation (6) can be found in [25]. Afterwards, the thermal conductivity $k$ can be calculated from the equation

\[
k = \rho c a. \tag{9}
\]

A summary of the results for the samples studied in this work is presented in table 1.

Figure 9. Typical experiment of thermal relaxation. The clear circles correspond to the measured temperature $T_n$ of the non-illuminated face as a function of the time $t$ for the pure resin sample with thickness $l = 829 \mu\text{m}$. The solid line corresponds to a fit with equation (7).
in this work, the thermal conductivity increases with \( \eta_m \) as shown by the solid curve with solid squares. This provided us with a good starting point, as our composite layers had a larger thermal conductivity than that of the resin. It is worth mentioning that this kind of enhancement in the thermal properties, due to the anisotropic formation of chain-like aggregates (wall-like in this case) of particles with higher conductivity than the supporting material, has also been observed in magnetic fluids under the action of applied fields [7–9].

Regarding our two-layer systems, we will first discuss the RCBs. For these, we only considered samples where the composite layer has a concentration \( \eta_m = 0.01 \). These samples consist of a resin layer and a composite one, with thicknesses around 200, 400 or 600 \( \mu m \) depending on the value of \( x = l_2/l_1 \). We must point out that, for the modulation frequencies used in this work, the layers with thicknesses around 200 \( \mu m \) (either resin or composite) are thermally thin with a cut-off frequency \( f_c \geq 163 \) Hz. Layers with thicknesses larger than 400 \( \mu m \) are already thermally thick for the modulation frequencies used. Measuring the thermal diffusivity of bilayers consisting of layers with different thermal thicknesses requires special care, as it is known that their thermal properties tend to the values of the thermally thick layer [33]. In this way, the PA spectrum of RCBs with layers of different thermal thicknesses were measured with their thermally thin layer facing the modulated light beam.

On the other hand, the effective thermal diffusivity of two-layer systems can be described by the equation

\[
\alpha = \left[ \frac{x^2}{\alpha_2} + \frac{(1-x)^2}{\alpha_1} + \frac{2x(1-x)}{\sqrt{\alpha_1\alpha_2}} \right]^{-1},
\]

when both layers are thermally thick or, as a particular case, when their thermal effusivities are equal regardless of their thermal thicknesses [32, 33]. For the case of our RCBs, \( \alpha_1 \) corresponds to the thermal diffusivity of the pure resin layer with thickness \( l_1 \), \( \alpha_2 \) to the composite layer with thickness \( l_2 \), and \( x = l_2/l_1 \) with \( l = l_1 + l_2 \) as defined before. The dotted curve with clear circles in figure 11(b) corresponds to the measured thermal diffusivity of these samples, as a function of \( x \), while the thick solid line to equation (10), calculated using the values obtained for the pure resin sample (the value at \( x = 0 \)) and the CSL with \( \eta_m = 0.01 \) (the value at \( x = 1 \)). Considering that some of our RCBs have layers with different thermal thicknesses, the good correspondence between our experimental data with this approximation suggests that the resin and composite layers have almost identical values for their effusivities.

We will now focus our attention on the CCBs. In these symmetric bilayers, only the angle between the inclusion structures on each side of the interface changes. Results for the measured thermal diffusivity \( \alpha \) of CCBs with \( \eta_m = 0.01 \) are presented in figure 12(a), with the left axis and the dashed curve with clear circles. Notice how \( \alpha \) first decreases with the increasing \( \theta \), reaching a minimum at \( \theta = 45^\circ \), to later increase again. Equation (10) predicts a constant value for the effective thermal diffusivity of our CCBs, given the fact that both of their composite layers are thermally thick. The nontrivial dependence of \( \alpha \) on \( \theta \) means that there is a thermal resistance with origin at the interface. This is an emergent effect resulting from the overlap of inclusion structures in this region, not exhibited by the RCBs. Moreover, the volumetric heat capacity \( \rho c \) is practically the same for all our CCBs, so the V-shaped dependence of \( \alpha \) on \( \theta \) is also reflected on their
thermal conductivity $k$, corresponding to the right axis and the solid curve with solid circles in figure 12(a). In order to explain these results, let us analyze the inclusion structures of CCBs on both sides of the interface for the different orientations.

The last column of figure 4 shows the best focus on the interface taken from the side of layer 1, as explained before. Notice how the magnetite aggregates in these layers form long and thick chains. These kind of structures, pointed out with the white rectangles for $\theta = 67.5^\circ$, $90^\circ$, expose a large effective area to the transmission of heat due to their fractal properties. These kind of structures can also be seen in layer 2 for $\theta \leq 45^\circ$ in the middle column. Nonetheless, for $\theta > 45^\circ$, the magnetite aggregates seen in layer 2 are thinner and shorter as pointed out with the white rectangles for $\theta = 67.5^\circ$, $90^\circ$ in the same column. These kind of aggregates expose less effective areas to the transmission of heat but tend to be denser, developing vertically from face to face inside the layer. Their shape comes about in the presence of the magnetized aggregates of layer 1, forming a close to right angle with the direction of the applied field during their formation. In summary, the inclusion structure of magnetite particles in layer 2 for $\theta > 45^\circ$ is very different from the inclusion structures of the other layers in our CCBs, either layer 1 or layer 2.

In this way, the thermal response shown in figure 12(a) can be explained from the point of view of two competing pathways for heat transport at the interface of our CCBs: (i) the chain-to-chain one and (ii) the one between magnetite and resin domains. For $\theta$ between 0° and 45°, the purposefully induced overlap of resin and magnetite domains between the inclusion structures of each layer at the interface confirms our previous findings [23], as the thermal resistance of the interface increases with $\theta$. Indeed, it was this result that inspired us to study two-layer systems in order to investigate this effect, in a more controlled manner, by varying the angle between anisotropic inclusion structures in order to expose a larger effective area between domains. This overlap becomes maximal for $\theta = 45^\circ$.

For $\theta > 45^\circ$, an interesting effect from the magnetized substrate of layer 1 renders the magnetite chains of layer 2 thinner and shorter as $\theta$ increases, decreasing the overlap of resin and magnetite domains at the interface and favouring the chain-to-chain heat transport again. Here, by chain-to-chain heat transport, we refer the overlap of chains from both of the layers that are able to reach from side to side of the bilayer.

In order to quantitatively characterize the interface structure of our CCBs, the mean lacunarity of the inclusion ($\Lambda_i$) and of the matrix ($\Lambda_m$) patterns were obtained by analyzing...
the mean lacunarity of the matrix, \( \Lambda \), solid triangles corresponds to the mean lacunarity of the inclusions, \( \theta \), samples in (a). The dashed curve with solid circles as a function of the angle \( \alpha \) for the inclusion and the resin structures, at the interface, domains. As expected, the dependence of the mean lacunarity \( \Lambda \) on \( \theta \) as a function of \( \theta \), if the concentration of inclusions in the \( \eta_m \) also reach a minimum at \( \theta = 45^\circ \). Moreover, one can expect a similar thermal response, as a function of \( \theta \), if the concentration of inclusions in the CCBs changes, at least for the concentrations corresponding to the shaded area in figure 11(a). Additionally, as shown by the dashed curve with clear squares in the same figure, the thermal conductivity of CCBs with \( \theta = 22.5^\circ \) is proportional to \( \eta_m \), so the thermal response presented in figure 12(a) could, in principle, be shifted up or down by varying \( \eta_m \). We must point out the change in tendency for the lacunarity of the sample with \( \theta = 90^\circ \). In this sample, the inclusion structures of the layers that compose the bilayer are most different than in the rest of the CCBs, due to stronger effects from the substrate layer 1 in the formation of the magnetite aggregates of layer 2, because of the steeper angle. More studies are required in order to explain the thermal properties of bilayer systems when the inclusion structures of the layers are significantly different. So far, our results are qualitative regarding the correlation of the lacunarity of the inclusion structures with the effective thermal properties of the bilayer systems under study.

4. Conclusions

In this paper, we have studied the thermal properties of two-layer systems consisting of polyester resin layers and composite layers with an anisotropic inclusion structure of magnetite particles. The thermal properties of bilayers consisting of a resin layer and a composite layer can be described by well established models. On the other hand, bilayers consisting of two composite layers, where only the angle between the anisotropic inclusion structures on the sides of the interface is varied, show a nontrivial dependence of their thermal properties on this angle. We were able to explain this from the point of view of two competing pathways for heat transport: one coming from the close contact of magnetite chains and the other from the overlap of resin and magnetite domains at the interface of these bilayers. The study presented here confirms our previous findings regarding the latter and exhibits new ways to develop composite layered materials with a controllable thermal response. Additionally, a new way for controlling the formation of complex inclusion structures in composite layers is suggested, with the use of magnetized substrates that can later be removed. Our results can be used in the development of materials with a real-time controllable thermal response. We are pursuing this line of research, along with theoretical investigations that correlate the complexity of the inclusion structures with the nontrivial thermal response observed in these kind of composite systems.

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