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DETERMINATION OF THERMAL CONDUCTIVITY IN AEROGEL, WITH OR WITHOUT THE ADDITION OF GRAPHENE, USING THE HOT WIRE METHOD

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Abstract. This article aims to determine the thermal conductivity of an aerogel sample made from organic products, with and without the addition of graphene oxide GO. In addition to thermal conductivity, the article presents energy absorptivity in the form of thermal radiation, for both samples. The thermal conductivity of the samples was determined by the hot wire method with numerical treatment of least squares. To analyze the radiative absorptivity of the sample in the infrared range, a FTIR 100 IR-NIR spectrometer was used.

Keywords: Thermal conductivity, Aerogel, Hot wire method, Thermal conductivity, Graphene, Absorptivity radiation.

INTRODUCTION

Recent studies have shown interesting alternatives for the use of agricultural residues, mostly sources rich in biomass. In addition, exploring biomass to produce carbon-intelligent materials can be an interesting way to improve the technology and increase the range of applicability. For example, the inclusion of nanostructures or its derivatives in lignocellulose sources, such as a corn cob waste material, it is possible to increase the surface area, capable of obtaining a physical and chemical barrier to gas or liquid.

In this context, additives with dimensions in nanometric scale have been incorporated into these polymeric matrices. Among the different types of nanostructures, we can highlight graphene oxide (GO), such as carbon nanofibers and cellulose nanocrystals, as promising materials, systems considering that the vast majority come from renewable sources [1].

Considering the advances in nanostructured systems, recently more materials were adjusted in the form of aerogel systems with low thermal conductivity, high surface area and high porosity, have been increasing their range of applications, such as in nanocatalysis, storage or energy generators and filter systems [2,3].

Aerogels are obtained by dispersion of reticulation agent or polymeric material (in this case the biomass) in specific solvent. After the dispersion process, the spaces occupied by this solvent being replaced by air through a controlled drying process. Furthermore, the incorporation of GO, obtaining customizable surfaces, makes aerogels suitable as thermal, electrical and gas barrier [4,5,6,7].

When graphene oxide is added to some materials, it is possible to notice an improvement in the mechanical properties. The impact strength of pure epoxy resin, for example, is 28.66 kJ/m², while for a sample containing graphene with a weight concentration of 0.5 % the impact strength is 79.07 kJ/m², the which represents an increase of 117%. The increase in toughness without compromising flexural strength is another advantage of using graphene oxide, for mixing epoxy resin, with a concentration of 0.5% by weight of GO, observing a drop in flexural strength of only 1% , for example.[14] .

Despite the increase in mechanical properties, it is necessary to study how any type of material that contains graphene behaves in terms of thermal conductivity, for example when graphene is added to a mixture based on biomass, which should, in principle, behave as a thermal insulator. Therefore, the purpose of this article is to determine the impact on the thermal conductivity of biomass when GO is added to aerogel.

MATHEMATICAL FORMULATION

The hot wire method was used in this work because it is a versatile and simple method to assemble. This method has the advantage that it can be used for materials that are: porous materials, granulated materials and liquids. According to ISO 8894-2, the hot wire method is a procedure that evaluates the temperature evolution of a sample as a function of time. The thermal source is a thermal wire that dissipates heat through the sample through the joule effect when the wire is subjected to an electric current. The diffusivity of heat through the material can be expressed as [2]:

$$\partial T(r,t)/\partial t = \alpha \nabla^2 T \quad (1)$$

Being:

T- temperature [$^{\circ}\text{C}$]

t- time [s]

α - material heat diffusivity [m^2/s]

r- distance from the heated wire [m]

The Eq. (2), (3) e (4) indicate the boundary and initial conditions applied on the solution of the differential equation represented by Eq. (1).

$$\Delta T(r,t)=0 \quad (t \leq 0, \quad 0 \leq r \leq R) \quad (2)$$

$$\lim_{r \rightarrow 0} \left(r \frac{\partial T}{\partial r} \right) = - \frac{q}{2\pi k} \quad (r = 0, t \geq 0) \quad (3)$$

$$\lim_{r \rightarrow \infty} \Delta T(r \rightarrow R, t) = 0 \quad (r \rightarrow R, t \geq 0) \quad (4)$$

Being:

ΔT – Difference of increase in temperature in the conductor wire [$^{\circ}\text{C}$] with respect to ambient temperature.

k – thermal conductivity [$\text{W}/(\text{m}\cdot\text{K})$]

q – constant heat flow released by the hot wire [W]

The conditions imposed by the equations 2 to 4 respectively states that:

- The wire and the sample at the beginning of the experiment are in thermal equilibrium with the external environment.
- The heat flow generated by the wire is fully absorbed by the sample.
- The external surface of the sample is in thermal equilibrium with the external environment, besides that the temperature does not vary throughout the experiment.[8]

The Eq. (5) is the analytical solution of Eq.(1), which represents the hot wire method, considering the boundary conditions represented by Eqs(2-4). The Eq.(5) will be used to determine the thermal conductivity of the material.[3] It is important to mention that the solution was obtained taking into account the Fourier number, $Fo \gg 1$ [13]. The wire resistivity was considered constant throughout the experiment.

$$T(t) - T(0)|_{(r=0,t)} = T(t) - T(0) = - \frac{q}{4\pi k} \ln(t) \quad (5)$$

For the process of transmissivity of energy in the radiative form, whose beam falls normally on the surface of the sample, the following equation is considered to describe the total partition of the energy involved during the process, respecting the law of conservation of energy:

$$\rho(\text{reflectivity}) + \tau(\text{transmissivity}) + \alpha(\text{absorptivity}) = 1 \quad (6)$$

DESCRIPTION OF THE EXPERIMENT

The hot wire method basically consists of a conductive wire carried by an electric current, which, due to the joule effect, dissipates heat to the structure that surrounds the wire, without any type of energy loss to the external environment. For this experiment, a cylinder with a length of 93.4 mm and an opening of 29.4 mm, filled with aerogel, was considered. The ambient temperature throughout the experiment was controlled, corresponding to a value in Celsius of 20.2668 ± 0.0285 .

The Fig. (1.a) shows the cylinder filled with the biomass without and with GO (1.b).

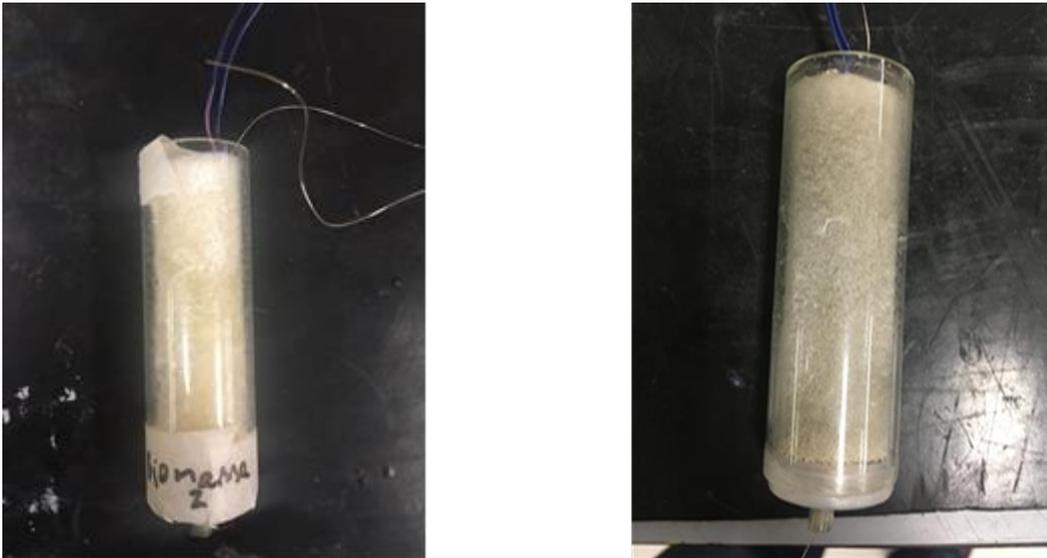


Figure 1 Samples used for the determination of thermal conductivity, without (1.a) and with the addition of graphene (1.b)

By the Fig. (2.a-b) it is possible to observe that wire is in direct contact with the samples, in this experimental, the wire is in thermal equilibrium with the Biomassa. The evolution of the wire temperature over time is obtained through a data acquisition board, where a thermocouple is connected in contact with the resistance wire. The Fig. (2) presents in a simplified way the test bench used to obtain the data regarding the thermal conductivity of the fibers, which is the aim of analysis if the present research.[16]



Figure 2–(2.a) Simplified test bench layout. (2.b) 1- Apparatus with Biomassa; 2- Power supply; 3- Data acquisition card; 4- Central process unit; 5 e 6- Nickel-chrome resistance wire; 7- Termocouple.[15]

As already mentioned, the heat dissipation for the material occurs through the Joule effect, the electrical energy being converted into heat due to the current that runs through the wire. The values of voltages and current throughout the experiment are shown in Table 1.

Table 1 – Technical data regarding voltage and current for wet and dry samples.

	Supply voltage (V)	Electric current (A)
Biomassa	1.3881 ± 0.000120	0.8737 ± 0.000025

Biomassa with GO	1.3445 ± 0.007705	0.5852 ± 0.002134
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The power dissipated by the wire was 1.2129 ± 0.00029 W and 0.787 ± 0.007 W for sample without and with GO, respectively.

RESULTS

The Fig.(3.a) shows the evolution of the temperature of the hot wire fully immersed in the aerogel sample, with respect to time. It is interesting to note that the temperature grows exponentially in the first moments of the experiment, and then enters thermal equilibrium. It is through the abrupt rise that it is possible to determine the thermal conductivity according to Eq.(5). The linear region of the graph on a logarithmic scale, Fig.(3.b) corresponds to this region of almost instantaneous rise.

The Figs.(4.a-b) follows the same logic as Figs(3.a-b)

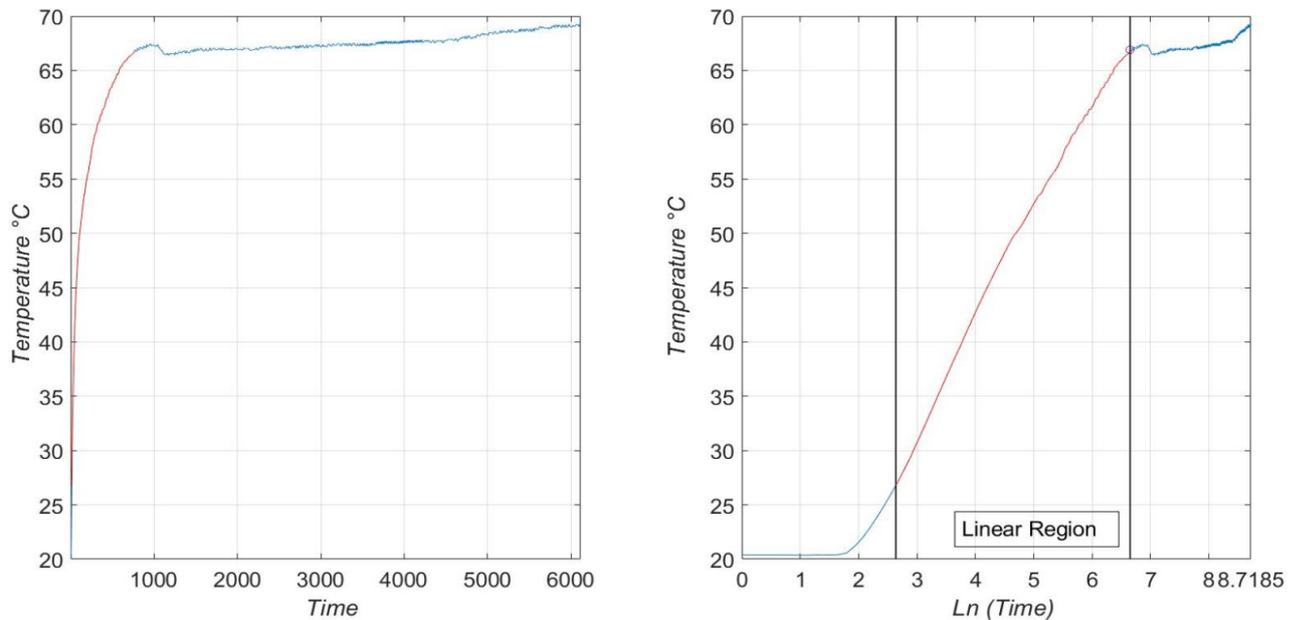


Figure 3- The evolution of wire temperature with time in normal scale (3-a) and in logarithmic time scale (3-b), for a sample without GO

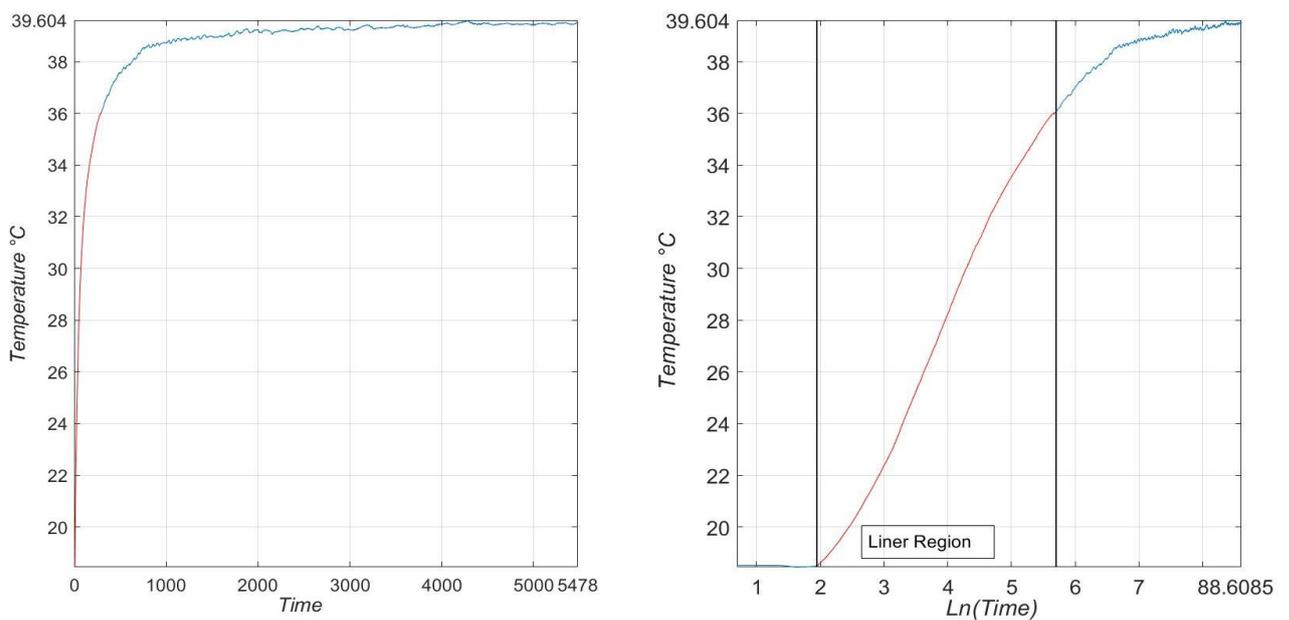


Figure 4- The evolution of wire temperature with time in normal scale (4-a) and in logarithmic time scale (4-b), for a sample with GO.

To determine the coefficient of the straight line that relates the most probable theoretical value with the values obtained by the measurements performed, the method of least squares was used. The Fig. (5) shows the dispersion of theoretical data in relation to experimental data, in the linear region of the curve represented in Fig. (3.b) for the sample without graphene, and Fig.(6) obtained in a similar way from the Fig.(5) for the sample with GO.

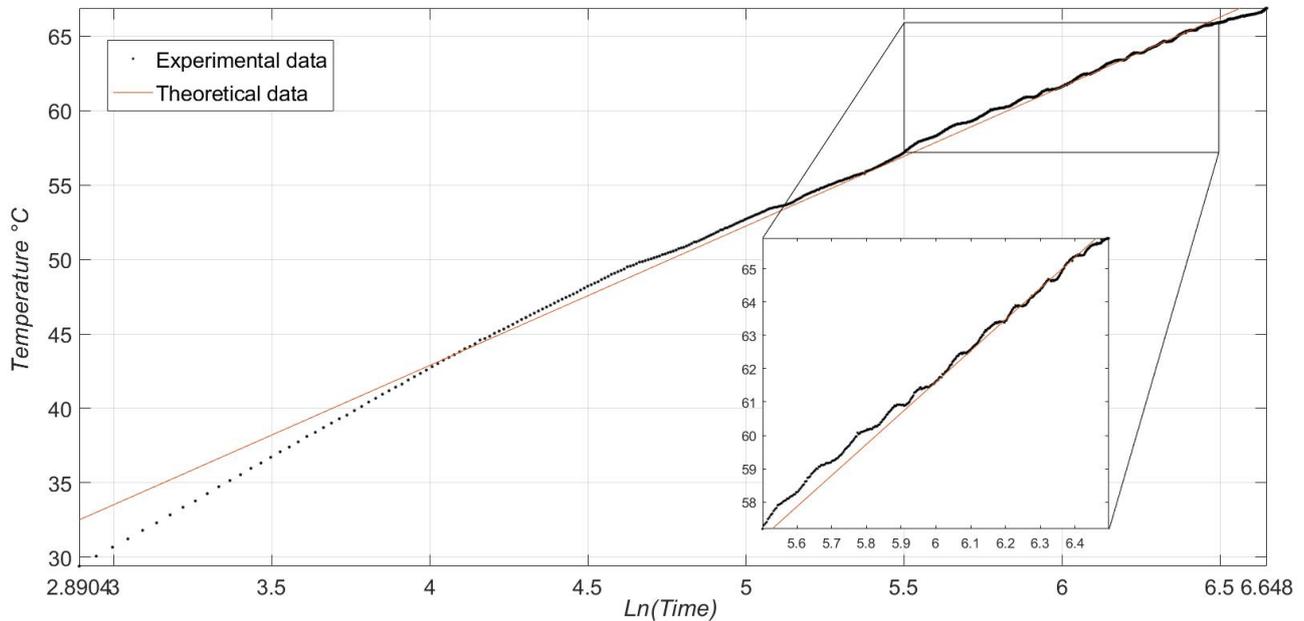


Figure 5. Delimitation of the linear region of temperature evolution on a logarithmic scale, with sample without GO.

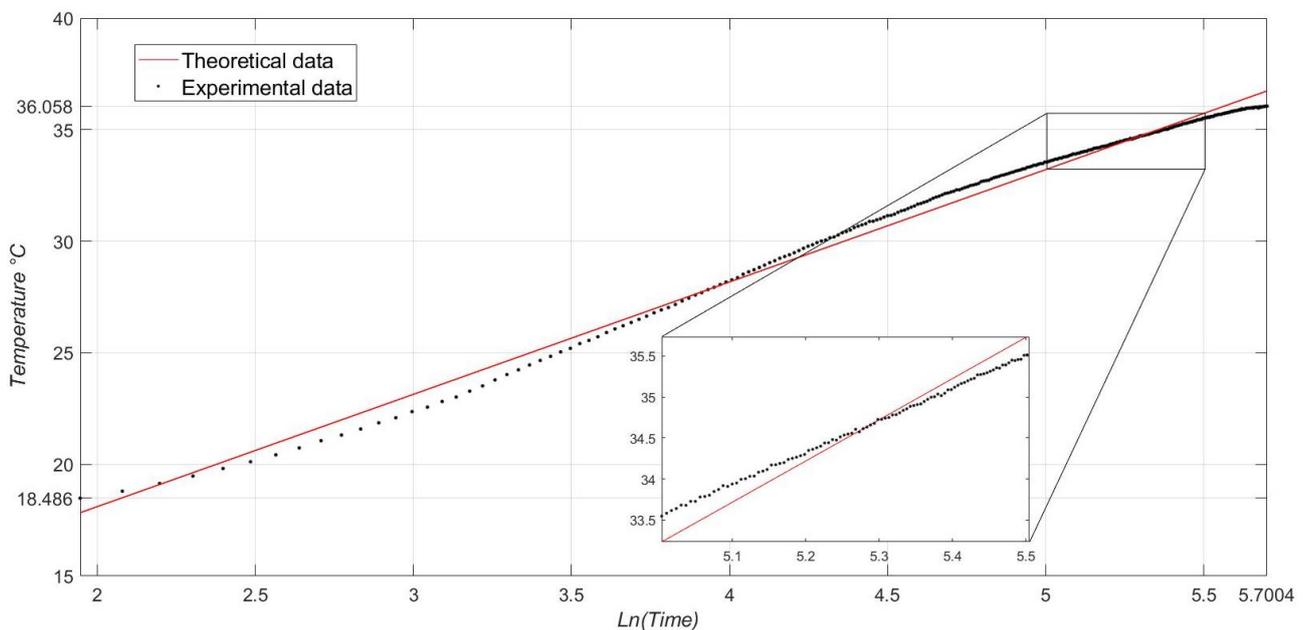


Figure 6. Delimitation of the linear region of temperature evolution on a logarithmic scale, with sample with GO.

For the material to also be considered a thermal insulator, it is not enough to present a numerical value of low magnitude for conductivity, it is necessary that the material is not transparent to thermal radiation in the infrared range. The result of the energy transmissivity test in the form of radiation, obtained by the spectrometer for the sample without the use of graphene is presented in Fig.(7). For the sample with graphene, no signal was obtained, which shows that graphene fully absorbs the radiative energy in the infrared band.

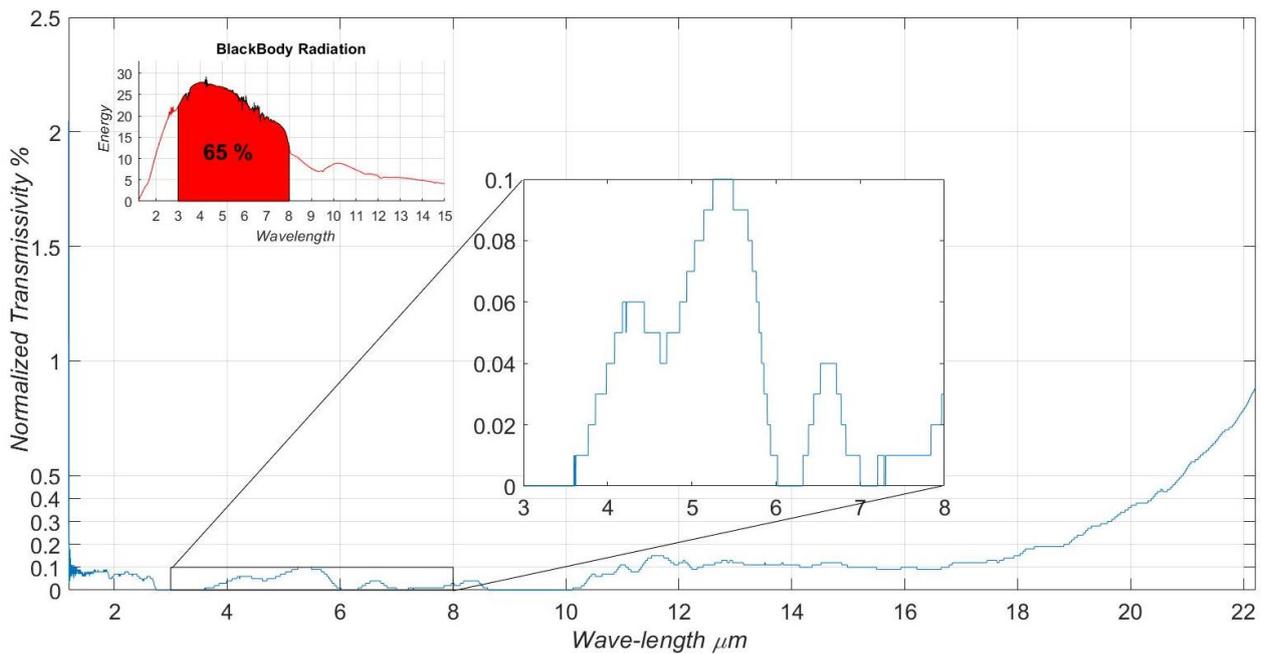


Figure 7. Representation of the transmissivity of the sample, for the expectral band belonging to thermal radiation.

According to Eq.(6), the material's ability to absorb energy in the form of radiation, for the considered band, can be calculated from the complement of the transmitted energy, since no signal was observed for the reflectivity experimental.

TREATMENT OF PROCESS UNCERTAINTY AND EFFICIENCY

Once the conductivity value is determined, it is necessary to analyze the efficiency of the linear model, through the error function. The error is nothing more than the Euclidean distance between experimental values and theoretical values.

In order to determine the uncertainty of the conductivity measurements, it is first necessary to analyze the error propagation, corresponding to the measurements of the variables to which is linked with the conductivity determination.

According to the Equation below directly derived from Eq. (5), it is important to realize that the measurement of conductivity uncertainty falls both on the power measurement uncertainty and on the temperature measurement uncertainty, performed by the data acquisition board.

$$k = \frac{q}{4\pi\Delta T} \ln(t)$$

Being:

$$\Delta T = T(t) - T(0)$$

The Eq. (6) are used to determine the uncertainty of measuring the conductivity of the samples, as a function of the uncertainties, present both in the reading of the voltage source and in the temperature measurement, and from the uncertainty determination theory [1]:

$$\frac{\Delta k}{\bar{k}} = \pm \sqrt{\left(p_q \frac{\Delta q}{q}\right)^2 + \left(p_{\Delta T} \frac{\Delta \Delta T}{\Delta T}\right)^2} \quad (6)$$

Being:

Δk - Uncertainty in the measurement of thermal conductivity

\bar{k} - Medium thermal conductivity

p_q - Weight function of uncertainty due to the contribution of energy flow

Δq - Uncertainty in the measurement of energy flow due to electrical power

$p_{\Delta T}$ - Weight function of uncertainty due to the contribution of the temperature differential

$I_{\Delta T}$ - Temperature differential measurement uncertainty

$\overline{\Delta T}$ - Temperature differential

The weight functions are defined as:

$$p_q = \frac{\partial k}{\partial q}$$

$$p_{\Delta T} = \frac{\partial k}{\partial \Delta T}$$

Table 2 presents the results obtained for the calculation of the uncertainty, and the thermal conductivities of biomass samples with and without GO.

Table 2 – Conductivity values corrected according to the uncertainties of the experiment

	Pure biomassa [W/(m·K)]	Biomassa with GO [W/(m·K)]
Thermal Conductivity	0.1096 ±0.002	0.1327±0.05

CONCLUSION

The article presented the impact that graphene oxide causes on the thermal conductivity of an aerogel sample, based on biomass. There was an increase of 21% in the thermal conductivity, but from the studies carried out, an increase in the mechanical properties of the material is expected, providing greater resistance. What will define whether the use of graphene oxide is viable or not, will be the specifics of the use of Biomassa.

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