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Thermal diffusivity, thermal conductivity and resistivity of candelilla wax

V Dossetti-Romero, J A Méndez-Bermúdez[1] and E López-Cruz

Instituto de Física, Universidad Autónoma de Puebla, Apartado Postal J-48,
Puebla 72570, Mexico

E-mail: jmendezb@sirio.ifuap.buap.mx

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Abstract

We report the values of some thermal and electrical properties of candelilla wax (from Euphorbia cerifera). The open-cell photoacoustic technique and another photothermic technique—based on the measurement of the temperature decay of a heated sample—were employed to obtain the thermal diffusivity ($\alpha_s = 0.026 \pm 0.000\,95$ cm^2 s^{-1}) as well as the thermal conductivity ($k = 2.132 \pm 0.16$ W mK^{-1}) of this wax. The Kelvin null method was used to measure the dark decay of the surface potential of the sample after a corona discharge, giving a resistivity of $\rho_e = 5.98 \pm 0.19 \times 10^{17}$ Ω cm.

1. Introduction

In recent years there has been growing interest in the electronic and optical properties of organic materials [1]. Some works have focused on particular aspects of the material under study [2] or on certain applications [3]. At the very beginning of insulator and electret research, one of the phenomena extensively studied was the Costa-Ribeiro effect [4]; among the materials exhibiting this effect are certain waxes (natural as well as synthetic ones) and organic semiconductors [5].

In this work we are interested in studying some electrical and thermal properties of candelilla wax, a natural wax derived from a bush growing wild in northern Mexico. We measured the thermal diffusivity, thermal conductivity and heat capacity of this material using the standard method of photoacoustic (PA) spectroscopy [6] combined with measurements of the thermal decay in a cooling process in vacuum [7] to obtain the value of the product of the mass density and heat capacity. The electric conductivity was studied using corona discharge and the Kelvin null method [8].

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[1] Author to whom any correspondence should be addressed.

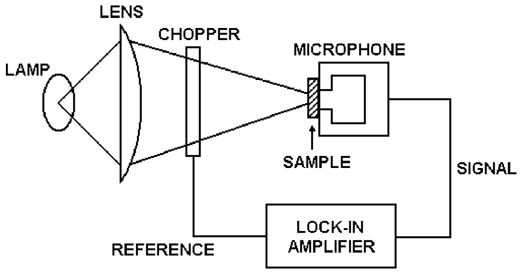

Figure 1. The experimental arrangement used to measure the thermal diffusivity α_s.

2. Experimental details

The samples were small pieces of candelilla wax fused and cooled in order to produce platelets $\sim$500 μm in thickness and $\sim$1 cm^2 in area. The measured fusion temperature of this wax is $T_c \simeq 69\,^\circ$C, which is in good agreement with the values in the range 67–69 °C reported in the literature [9].

2.1. The open-cell photoacoustic technique

The PA technique used in this work was the open-cell method widely reported in the literature [10]. The thermal diffusivity, α_s, was measured using the experimental arrangement shown in figure 1. The sample was directly mounted onto a commercial electret microphone. The beam of a 170 W tungsten lamp was focused onto the sample and mechanically chopped. As a result of the periodic heating of the sample by absorption of the modulated light, the microphone produced a signal that was monitored using a lock-in amplifier as a function of modulation frequency. The temperature reached by the periodically illuminated sample was 44 °C, which is far below the fusion temperature T_c.

2.2. Description of the method used for measuring ρc

Figure 2 shows the experimental set-up used for measuring the product of the mass density and the specific heat [7]. Prior to the measurements, both faces of the sample are sprayed with black paint in order to make its emissivity approximately equal to one. The sample is positioned inside the vacuum chamber with one of its faces (which we will call the front face) illuminated by the light beam of a 60 W tungsten lamp, properly focused. The temperature of the back face (the non-illuminated face) of the sample is traced with a Cu–constantan-type thermocouple connected to a temperature monitor while the temperature increases up to its equilibrium value, about 26 °C above room temperature. Later, the light is interrupted and the temperature is traced out while the sample cools down, to its equilibrium value of room temperature.

2.3. Corona discharge and the Kelvin null method

The experimental set-up for measuring the resistivity is a standard one [8] as seen in figure 3. The sample was provided with an ohmic contact on the back face and mounted with the free surface upward, as shown in the figure. It was placed on an arm that could be moved in the horizontal plane. In one position (figure 3(a)) it was charged by a negative 30 kV corona discharge in air; in the other (figure 3(b)) the surface potential was measured by a Kelvin

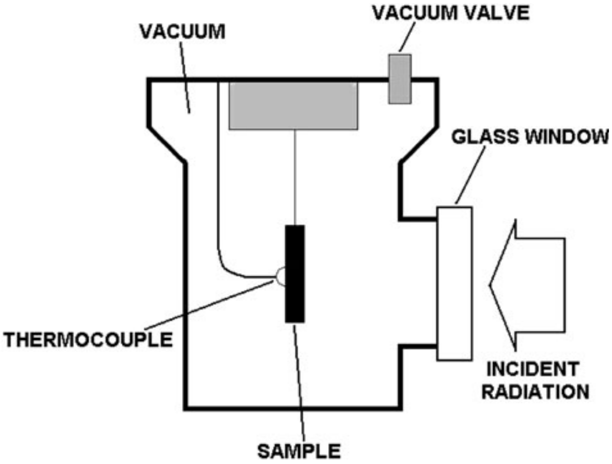

Figure 2. The experimental arrangement used to measure the product ρc.

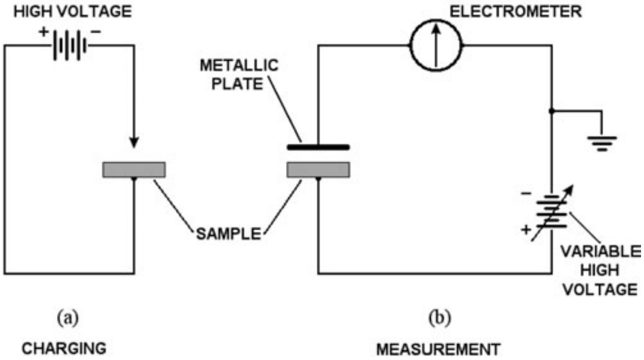

Figure 3. The experimental arrangement used to measure the electrical resistivity ρ_e.

method. The discharge was driven from the tip of a fine wire using a DC voltage amplifier. The tip was positioned about 5 mm above the sample. After charging of the sample, this was moved into the measuring position under the tracing electrode. The electrode consisted of a conducting metal plate of about the same size as the sample and was driven back and forth in a vertical motion by a mechanical set-up at a rate of approximately 1 Hz over a path of 1 mm. The sample was positioned in such a way as to be 1 mm away from the tracing electrode plate at the closest approach. This vibrating capacitor gave an output signal that was detected using an electrometer. Then the signal was balanced to a null voltage when the two plates (electrode and sample) were at the same potential. The balancing voltage was driven by a variable high-DC-voltage power supply. The whole system was shielded by a Faraday box.

3. Results and discussion

3.1. Measurement of the thermal diffusivity

In the open-cell PA technique, it is well known that the acoustic signal has two main contributions, one coming from the thermal diffusion phenomenon and the other one from the thermoelastic bending effect [11–13]. In order to differentiate which one of these two contributions dominates in generating the PA signal, one has to compare the experimental measurement with the expression that describes those contributions. By means of this comparison we have found that the thermoelastic bending effect is predominant in the generation of the PA signal when it comes to samples of candelilla wax. Once one has identified where the main contribution to the PA signal comes from, one can calculate the thermal diffusivity α_s from the modulation frequency dependence of the signal phase. For a thermally thick sample, the expression for the pressure fluctuations inside the PA chamber induced by the thermoelastic bending effect is

$$p_{el} \simeq \frac{3\alpha_T R^4 \gamma P_0 I_0 \alpha_s}{4\pi R_c^2 l_s^2 l_g k_s f} \left[\left(1 - \frac{1}{x}\right)^2 + \frac{1}{x^2} \right]^{1/2} \mathrm{e}^{\mathrm{i}[\omega t + (\pi/2) + \phi]} \tag{1}$$

where α_T is the linear thermal expansion coefficient, R is the microphone inlet hole radius, γ is the specific heat ratio of air, P_0 is the ambient pressure, I_0 is the absorbed light intensity, R_c is the radius of the PA chamber in front of the diaphragm, f is the modulation frequency, $x = l_s(\pi f/\alpha_s)^{1/2}$, l_i, k_i and α_i are the length, thermal conductivity and thermal diffusivity of material i, with subscripts g and s standing for gas media and the sample respectively, and $\tan\phi = 1/(x - 1)$.

From equation (1) one finds that the thermoelastic contribution to the PA signal amplitude, at high modulation frequencies ($x \gg 1$), varies as f^{-1} and its phase ϕ_{el} approaches 90° as

$$\phi_{el} \simeq \pi/2 + \arctan[1/(\sqrt{b_s f} - 1)]. \tag{2}$$

Here, b_s is a fitting parameter. The other condition that must be fulfilled for an optically opaque sample to be thermally thick is $f \gg f_c$, where the cut-off frequency f_c is given by $f_c = \alpha_s/(\pi l_s^2)$.

In a process where the main contribution to the PA signal comes from the thermal diffusion phenomenon, the amplitude and phase of the signal have dependences on the frequency of the forms $(1/f)\exp -a_s\sqrt{f}$ and $\phi_{th} = -(\pi/2) - a_s\sqrt{f}$, respectively; see [13]. Here, a_s is a fitting parameter which is related to the diffusivity α_s by $a_s = l_s\sqrt{\pi/\alpha_s}$.

Figure 4 shows the amplitude and the phase of the PA signal for the candelilla wax sample. We can notice a good correspondence with the models presented before, corresponding to the thermoelastic bending effect. In the case of the amplitude of the PA signal (figure 4(a)), the f^{-1} dependence with an exponent equal to -1.0866 is reproduced very well. Equation (2) was used to fit the results shown in figure 4(b) (continuous curve) together with our measured values (open circles) for the phase of the PA signal. It is possible to estimate the thermal diffusivity α_s from the fitting parameter b_s by considering the relationship

$$\alpha_s = \frac{\pi l_s^2}{b_s} \tag{3}$$

and using $l_s = 643$ μm. In this case, $f_c \simeq 2$ Hz; thus from figure 4 we can see that we are in the thermally thick-sample regime.

Finally we obtained the value $\alpha_s = 0.026 \pm 0.00095$ cm^2 s^{-1} for the thermal diffusivity of candelilla wax.

3.2. Measurement of ρc and computation of the thermal conductivity

When one of the faces of the sample is illuminated as shown in figure 2, with a constant flux of light, a lack of equilibrium between the front (illuminated) and back (traced) faces of the sample is established. For the case where the width of the sample (including the two coats of black paint), l, is smaller than its transverse dimension, which is the case that we consider,

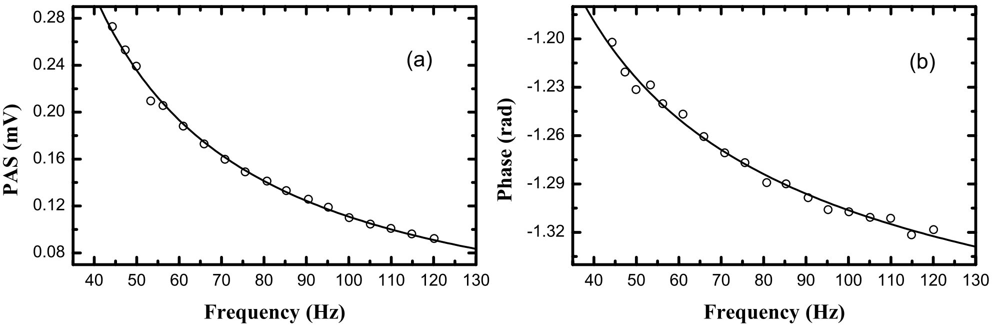

Figure 4. The fitting of (a) the amplitude and (b) the phase of the PA signal as a function of the modulation frequency for a sample of candelilla wax.

this phenomenon can be described by a 1D equation. Thus, the conservation condition for the energy is

$$J_0 - \sigma T_1^4 - \sigma T_2^4 = \frac{\mathrm{d}}{\mathrm{d}t}\int_0^1 \rho c T(x,t)\,\mathrm{d}x, \tag{4}$$

where J_0 is the flux of incident light over the front face, σ is the Stefan–Boltzmann constant, T_1 is the temperature of the front face, T_2 is the temperature of the back face, ρ is the mass density of the sample and c is its specific heat at a 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 one [14].

We define $\Delta T_i(t) = T_{i,max} - T_i(t) (i = 1, 2)$, where $T_{1,max}$ and $T_{2,max}$ are the maximum temperatures reached by the front and back faces of the sample respectively, for long times where the equilibrium is reached. Substituting $\Delta T_i(t)$ into equation (4) and linearizing the resultant equation in terms of $\Delta T_i/T_i$ we obtain

$$J_0 - \sigma T_{1,max}^4 - \sigma T_{2,max}^4 + 4\sigma T_{1,max}^3\,\Delta T_1(t) + 4\sigma T_{2,max}^3\,\Delta T_2(t) = \frac{\mathrm{d}}{\mathrm{d}t}\int_0^1 \rho c T(x,t)\,\mathrm{d}x. \tag{5}$$

The sum of the first three terms of this equation is equal to zero, since for long times the flux of incident radiation and the flux of emitted radiation cancel each other out. The integral on the right-hand side can be written as

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_0^1 \rho c T(x,t)\,\mathrm{d}x \approx \frac{\rho c l}{2}\frac{\mathrm{d}}{\mathrm{d}t}[T_1(t) + T_2(t)] = -\frac{\rho c l}{2}\frac{\mathrm{d}}{\mathrm{d}}[\Delta T_1(t) + \Delta T_2(t)] \tag{6}$$

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. It is also a fact that for the values of l and J_0 that we used in the laboratory it is the case that $l\frac{\mathrm{d}T(x,t)}{\mathrm{d}t} \ll T_1(t) \cong T_2(t)$. From this condition, we can assume that $\Delta T_1(t) \cong \Delta T_2(t)$; thus for a decrease of the temperature from $T_{2,max}$ to $T_{2,0}$ after the light is interrupted, equation (4) can be written as

$$8\sigma T_{2,0}^3\,\Delta T_2(t) = -\rho c l\frac{\mathrm{d}\,\Delta T_2(t)}{\mathrm{d}t}. \tag{7}$$

Substituting in the definition for $\Delta T_2(t)$ and using the boundary conditions $\Delta T_2(0) = 0$ and $\Delta T_2(\infty) = T_{2,max} - T_{2,0}$, we obtain the solution

$$T_2(t) = T_{2,0} + (T_{2,max} - T_{2,0})\exp(-t/\tau_d) \tag{8}$$

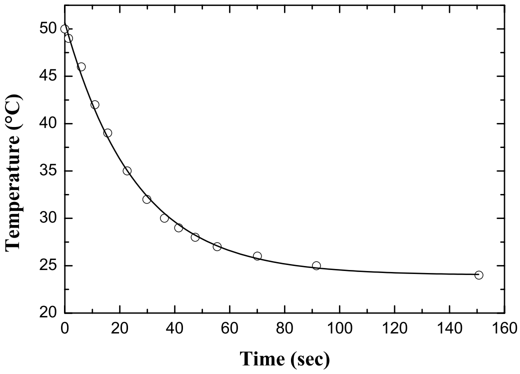

Figure 5. Typical behaviour of the thermal decay of a candelilla wax sample as a function of time.

for the decay of the temperature immediately after the illumination of the sample is interrupted. In this case the relaxation mean time τ_d is given by

$$\tau_d = \frac{\rho c l}{8\sigma T_{2,0}^3}. \tag{9}$$

Figure 5 presents the evolution of the temperature of the sample as a function of time in a typical thermal decay experiment. From the time constant $\tau_d = 26 \pm 1$ s, which fits very well with the relationship given by equation (8), one obtains the value of the product ρc from equation (9). In our case, $\rho c = 820\,030.44$ J m^{-3} K^{-1} with an error of $\pm 3.89\%$, where $T_{2,0} = 23.88$ °C and $l = 377$ μm.

In order to obtain the thermal conductivity k, we can use the very well known relationship

$$\alpha_s = \frac{k}{\rho c}, \tag{10}$$

which yields $k = 2.132 \pm 0.16$ W mK^{-1}.

3.3. Measurement of the electrical resistivity

We consider a laminar sample with parallel surfaces (of thickness l and surface area A) which after corona charging behaves as an RC circuit with time decay constant $\tau_e = RC$.

The resistance R and the capacitance C of the sample are given by $R = \rho_e(d/A)$ and $C = \xi(A/4\pi d) \times (1.1 \times 10^{12})$, where ρ_e is the electrical resistivity and ξ is the dielectric constant (R and C are given in ohms and farads, respectively; A and d are in centimetres). Then we have that $\tau_e = (\rho_e \xi / a\pi) \times (1.1 \times 10^{12})$ s. We can make the approximation $\xi \approx \pi$, valid for many materials [15], and obtain

$$\rho_e = \tau_e \times 10^{12}\ \Omega\ \text{cm}. \tag{11}$$

It is known that the process for the discharge of a RC circuit as a function of time is an exponential decay for the charge: $q(t) = q_0 \exp(-t/\tau_e)$.

A typical experiment on the dark decay of the surface potential in a negatively charged candelilla wax sample is illustrated in figure 6, which is a plot of the surface potential as a function of time. Since the surface potential is proportional to the charge ($V = qC$), the experimental results in figure 6 can be fitted to the relationship

$$V(t) = V_0 \exp(-t/\tau_e). \tag{12}$$

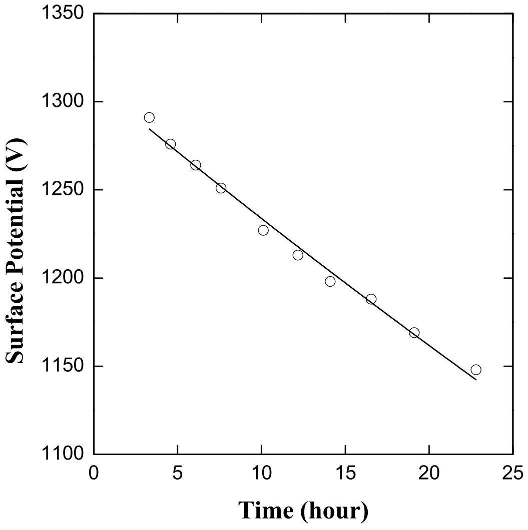

Figure 6. The dark decay of the surface potential as a function of time for a candelilla wax sample.

The time constant obtained from these results was $\tau_e = 166.17 \pm 5.48$ h and using equation (11) one obtains a resistivity of $\rho_e = 5.98 \pm 0.19 \times 10^{17}\ \Omega$ cm.

4. Conclusions

Although candelilla wax has a huge number of industrial applications, some of its electrical and thermal properties are not well understood. In some handbooks one can find the value of its dielectric constant but not its thermal diffusivity, its thermal conductivity or its resistivity [9]. From the standard open-cell PA and thermal decay techniques, one very easily finds some of the above-mentioned physical properties. Using equations (3) and (9) we obtained the thermal diffusivity α_s and the product ρc respectively, starting with the values obtained from the fittings of the data to equations (2) and (8). One can calculate the heat capacity once one has measured the mass density ρ of the sample. In our case the heat capacity was measured to be $c = 754.71 \pm 29.35$ J kg^{-1} K^{-1} and the thermal diffusivity $\alpha_s = 0.026 \pm 0.000\,95$ cm^2 s^{-1}. The density measured in this work is $\rho = 1086.54$ kg m^{-3}. The thermal conductivity was obtained from relation (10) as $k = 2.132 \pm 0.16$ W m^{-1} K^{-1}.

Concerning the electric properties of candelilla wax, the time constant for the dark decay of the surface potential found in this work provides evidence that we are dealing with a very high-resistivity material. As we can see from figure 6, the dark decay of the surface potential follows quite well the behaviour of an insulator, considered from the point of view of a parallel-plate capacitor as presented in section 3.3. In this work we found from the fitting of the data to equation (12) that a time constant $\tau_e = 166.17 \pm 5.48$ h means a resistivity of $\rho_e = 5.98 \pm 0.19 \times 10^{17}\ \Omega$ cm, given by equation (11).

We can say also that for high-resistivity materials, the combination of PA spectroscopy, the thermal decay method and the dark decay of the surface potential is a well recommended approach, since one can obtain some physical properties for materials of this kind in a very simple way.

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