A novel integrated system for analysis of thermal depth profiles

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ABSTRACT

In this work a novel system for the study of thermal profiles and time dependent heat diffusion is presented. In this system the modulation of light is made directly using an electronic driver that turns on and off the laser diode. The data acquisition is made with a higher accuracy than in the conventional systems because the electronics that detects the signal is the one that generates the modulating signal. The system is very compact and as a consequence, shows a higher stability, and can be integrated in systems in which other measurements are performed or inside of chambers where the conditions of the surroundings are controlled. In order to show the potential of our system, applications using photoacoustic and photopyroelectric techniques are presented. In the case of photoacoustics, the specific case of the open photoacoustic cell for thermal diffusion characterization is shown. Using a conventional photoacoustic cell, it is shown that the dynamics of evaporation and crosslinking can be followed in polymers. In the case of photopyroelectric technique, thermal depth profiles are also performed and the study of dynamics a as function of time is discussed. The advantages of our system and the different modes of detection are discussed.

1. INTRODUCTION

During the last few years photoacoustic and related photopyroelectric techniques have been used in a wide variety of fields including material science, agriculture, medical and environmental sciences. In addition, there has been a substantial development of new, versatile and competitive instrumentation and experimental methodologies suitable for use in daily practice. This encouraging progress is mainly due to continued improvements made in the development of light sources, transducers and equipment for data collection and processing. For a comprehensive review of the photothermal wave phenomena and their applications, the reader is referred to the books of Rosencwaig[1], Almond[2] and Mandelis[3] and to some of the many reviews published on the subject[4,5].

Photothermal techniques involve the incidence of a modulated beam of light onto a material and the generation of a train of thermal waves in the material. These waves present a strong decay directly proportional to the square root of the quotient of the thermal diffusivity divided by the modulation frequency. This feature is the one that makes these techniques specially suited for the development of depth profiles, because the modulation frequency can be controlled experimentally[5]. On the other hand, it has been shown that the dynamics of complex process can also be studied maintaining a constant modulation frequency, but the thermal diffusion length of the sample changes due to changes induced by phase transitions, evaporation or crosslinking[6].

Photoacoustic (PA) spectroscopy looks directly at the heat and pressure waves generated in a sample, followed by the absorption of light. In the conventional PA experimental arrangement a sample enclosed in an air-tight cell is exposed to modulated light. As a result of the periodic heating of the sample, the pressure in the chamber oscillates at the modulation frequency and can be detected by a sensitive microphone coupled to the cell. The resulting PA signal depends not only on the amount of heat generated in the sample (i.e. on the optical absorption coefficient and the sample light-into-heat conversion efficiency), but also on how this heat diffuses through the sample. This configuration has been modified, in such a way that the sample is positioned out of the photoacoustic chamber. This methodology is

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specially suited to study the thermal contact or thermal diffusivity of liquid materials, and it has been shown that it is very useful in the study of dynamic process induced by the surrounding conditions on the sample[6,7].

In the open photoacoustic cell an electret microphone is used, in this case the sample is attached directly to the top of the microphone with vacuum grease. The sample is illuminated with modulated light and the membrane of the microphone detects the heat diffused through the sample. This is known as a heat transmission configuration and it is specially suited for the study of thermal diffusion[8].

Photopyroelectric technique consists on the detection of the thermal wave phenomena using a pyroelectric material. This technique is classified as a photothermal contact technique and has been also used successfully in the study of thermal and optical properties of a great variety of materials. These techniques can also be used in the configuration in which the sample or the substrate is illuminated. In particular one the most interesting options is to use a PVDF material (Polyvinyldifluoride)[9].

In this work we present a compact and stable system that can work with conventional photoacoustic, open photoacoustic as well as photopyroelctric cells. In this system incident modulated light of a diode laser is turned on and off, using an electronic driver. Our system shows higher stability than the conventional ones, because it does not depend on external modulation and can be integrated in larger systems and can be used in chambers where controlled conditions are needed. Other important characteristic of this system is that can work from very low frequencies (mHz), necessary in the photopyroelectric measurements up to KHz, needed when monitoring high velocity process using photoacoustics.

2. METHODOLOGY

The schematic diagram of our system using photoacoustic technique is presented in Figure 1. The modulated laser light of a 658 nm, 60 mW Sanyo laser diode was sent onto detection system-sample. The control of the modulation of the diode laser as well as the detection of the photothermal sensor was performed using a SR830 lock-in amplifier. A pair of batteries operating at 12V was used for polarizing the laser diode controller (Thorlabs, model IP500) through a regulator circuit feeding ± 5V.

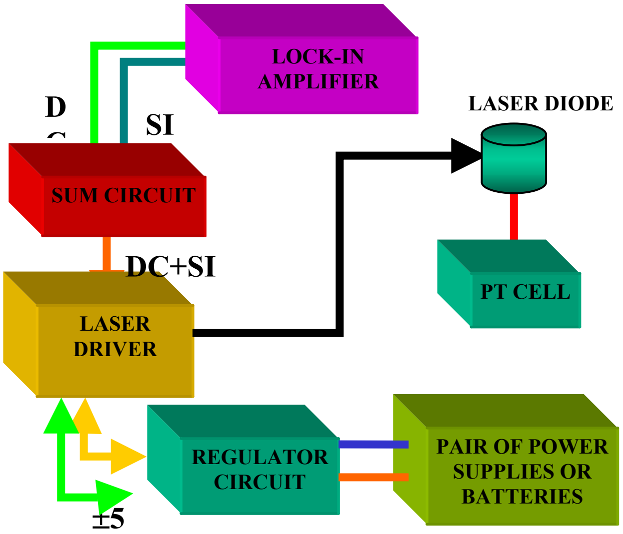


Fig. 1. Schematic diagram of the experimental arrangement for the photothermal measurements.

The IP500 is a universal laser diode controller capable of supporting all pin configurations for laser diodes, in either constant current mode (ACC mode) or constant power mode (APC mode)[10]. Other characteristics of the laser diode controller are that it is optimized for 500mA maximum injection current but current and power limits can be modified using individual 25-turn potentiometers, laser diode inputs are shorted during idle operation to protect the device and supports analog modulation up to 50 kHz.

The IP500 is operated in ACC mode in order to prevent changes in the efficiency due to changes in temperature that could produce the operating current overdrive the laser. Another reason to use the ACC mode is because of the analog modulation that allows varying the amplitude of the laser injection current over time by connecting a signal generator to the IP500. For 100% depth of modulation we apply a sinusoidal input, which must have peak-to-peak amplitude equal to ILIM/0.05, where ILIM is the current limit (in this case 500 mA) and a DC offset equal to ½ of the amplitude must be applied (the signal should always be above zero volts). This special signal is accomplished by adding to the sinusoidal signal output of the lock-in, a DC signal using an Operational amplifier circuit (model TL081) taking care of all the considerations mentioned above.

In this work three modes of detection of thermal waves were used in the same experimental arrangement: the conventional photoacoustic cell, the open photoacoustic cell and the photopyroelectric cell.

In the case of the open photoacoustic cell (OPC) technique the procedure reported in references[8,11] was followed. In this heat-transmission configuration the sample is mounted directly onto the front sound inlet of an electret microphone (Radio Shack, model 270-092) and fixed with vacuum grease. The sound inlet is a circular hole of 3 mm diameter, and the front microphone air chamber adjacent to the metallized face of the diaphragm is a cylinder of 7 mm diameter and roughly 1 mm long.

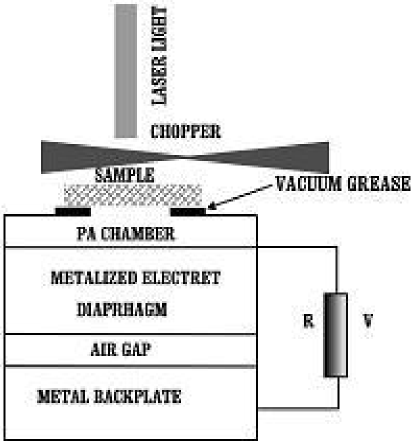


Figure 2. Schematic diagram of the open photoacoustic cell

In order to obtain the PA signal, the sample was illuminated by the modulated diode laser beam. The signal from the microphone is connected to a lock-in amplifier (Stanford Research Systems, model 830) in which the signal amplitude and phase are both recorded as a function of the modulation frequency.

This arrangement corresponds to the heat transmission configuration, that is, the heat is deposited at the rear face of the sample and diffuses through the sample before reaching the PA chamber, where it causes the pressure fluctuations that are detected by the microphone. The thermal wave behaviour in the sample is basically determined by its thermal properties. The modulation frequency dependence of the PA signal is the usual way of extracting information about the thermal diffusivity of the sample under study[1,5].

For the rear-side illumination configuration, the thermal diffusion model of Rosencwaig and Gersho[1], for optically opaque and thermally thick samples, predicts that the output voltage of the microphone is given by

$$V = \frac{Ae^{-a\sqrt{f}}}{f} \tag{1}$$

where A is a factor involving the thermal properties of the material and the air, microphone characteristics and response time as well as the incident radiation intensity, f is the modulation frequency of the incident light, $a=l_s(\pi/\alpha)^{1/2}$ with l_s the thickness of the sample and α its thermal diffusivity, and $\alpha=k/\rho C$, where k is thermal diffusivity, ρ is the density and C is the heat capacity. In the case of a thermally thin material, the voltage of the microphone is given by

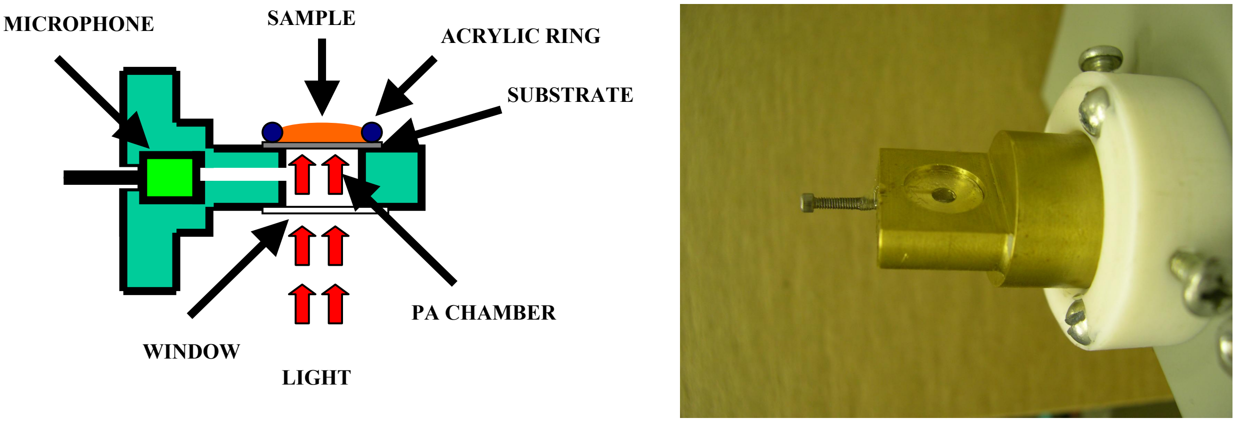
$$V = \frac{B}{f^{3/2}} \tag{2}$$

With B a factor similar to A, having the same dependence in the microphone characteristics.

In the case of the conventional photoacoustic cell, the schematic diagram and a photograph are shown in Figure 3. In this configuration the PA cell is closed, at the bottom end, by a glass window and at the top end, by a removable reference substrate. An electret microphone (Radio Shack, model 270-092) is used, coupled to the cavity wall, to sense the pressure fluctuations in the PA chamber produced by the periodic heating of the substrate, due to the pumping beam. The liquid sample to be studied is deposited inside of a 1mm height acrylic ring on the external surface of the reference material. The pumping beam light was produced by the diode laser modulated at a fixed frequency. The microphone signal is fed into a lock-in amplifier (SR830), from where the output signal amplitude is recorded, as a function of time, in a personal computer.
According to the Rosencwaig and Gersho model[1], the PA signal is determined by the temperature fluctuation (θ) at the air-substrate interface. Solving the thermal diffusion equations for this configuration this temperature can be determined. The PA signal with sample (θ) and without sample (θ_0) is given by [6]:

$$\theta = \theta_0 \left[\frac{b \tanh(\sigma l) + 1}{b \coth\ h(\sigma l) + 1} \right] \tag{3}$$

Here $\sigma=(1+i)a$ is the complex thermal diffusion coefficient, defined by $a=(\pi f/\alpha)^{1/2}$, α and l are the thermal diffusivity and thickness of the reference material. $b = \varepsilon_b / \varepsilon$, is the thermal coupling coefficient, with ε and ε_b the thermal effusivities of the substrate and sample, respectively. Thermal effusivity is defined as $e=(k\rho C)^{1/2}$. This property evaluates the heat interchange between the sample and the surrounding medium. K is a factor depending on the sensor, f is the modulation frequency of the lamp. $\theta_0 = (I_0/2k\sigma) \coth(\sigma l)$ is the expression for the temperature fluctuation in the absence of the sample on the substrate. In arriving at equation (3), the fact that the effusivity of air is much smaller than the thermal effusivity of the substrate is used. Due to fact that the substrate is optically opaque, it has been considered that the optical absorption coefficient, β, is much larger than the absolute value of the complex thermal diffusion coefficient, $|\sigma|$, for the frequency used here. Moreover, the sample thickness, l_b, is supposed to be much larger than its thermal diffusion length, which is given by $\mu_b = (\alpha_b/\pi f)^{1/2}$, being α_b the thermal diffusivity of the sample. According to this equation the changes in the thermal properties due to the dehydration, phase transitions or crosslinking will induce a change in the photoacoustic signal.



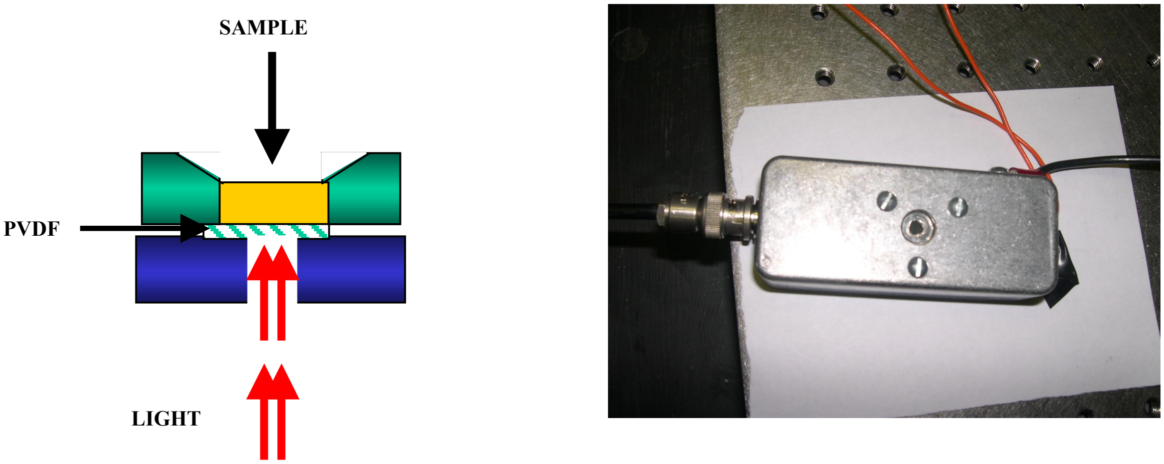
(A) (B)

Figure 3. Conventional two beams PA cell without backing. (A) Schematic diagram, (B) the real cell.

In the case of the photopyroelectric measurements, the experimental arrangement is shown in Figure 4. The cell was constructed in such a way that the sample was inside the cell, and the bottom of it was closed by a 110 polyvinyldifluoride (PVDF). The laser light is sent directly on the PVDF and then sample is periodically heated through the sensor. Considering the fact that the sample and sensor are thermally thick and thermally thin respectively, the photopyroelectric signal is inversely proportional to the effusivity of the sample[9]:

$$V = K\frac{\sqrt{f}}{e_m} \tag{4}$$

Thermal effusivity (e_m) is related to the heat capacity per unit volume (ρC) and to thermal conductivity (k) by $e_m = \sqrt{k\rho C}$.



(A) (B)

Figure 4. Photopyroelctric cell. On the left schematic diagram, on the right a photograph.

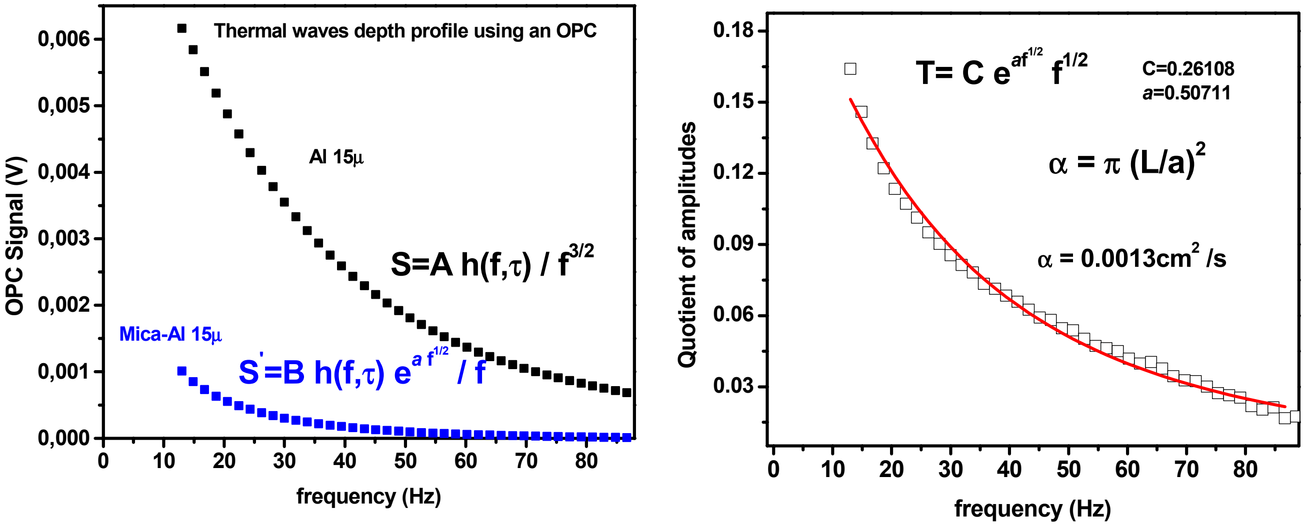
3. RESULTS AND DISCUSSIONS

3.1 Open photoacoustic cell measurements

In Figure 5, typical result results for depth profiles using OPC detection for of aluminum and mica are presented. As can be observed, the behavior of the mica sample is typical of the thermally thick sample (See equation 1) and aluminum presents the corresponding to a thermally thin one. Making the quotient between the amplitude of the signal of the mica divided by the one of the aluminum, an equation independent of the microphone characteristics can be obtained. This is done with the finality of suppress the microphone response dependence that is always an important contribution in this range of frequency[8,11] Fitting the equation obtained with the normalized experimental data, the value of thermal diffusivity can be obtained.

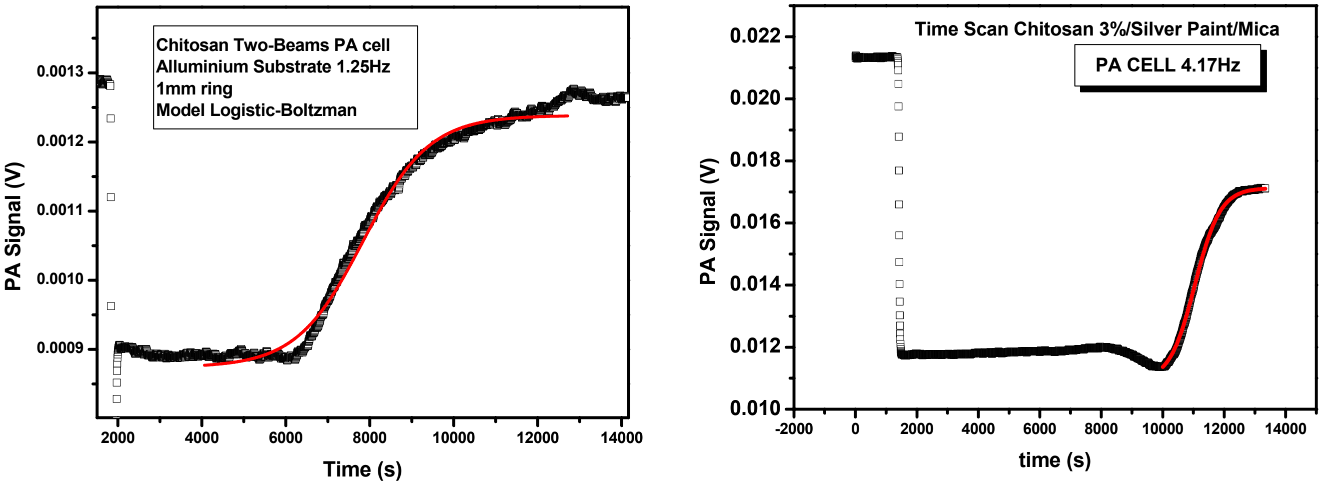
3.1 Conventional photoacoustic cell measurement of dynamical processes.

In Figure 6, the results of typical measurements of the time evolution of the photoacoustic signal amplitude for the process of evaporation-crosslinking in a sample of chitosan is shown. In this case the samples correspond to a 3% of chitosan diluted in a water-acetic acid solution. In Figure 6.A, the results for an aluminium substrate is shown, on the other hand a quite different result is obtained using mica covered by silver pain substrate (Figure 6.B). This technique could be helpful in the study of the dynamics of the process and in the interaction with the substrate during the process[4,6].



(A) (B)

Figure 5. A) OPC signal of aluminum and B) Mica and PPE signal of water versus frequency.

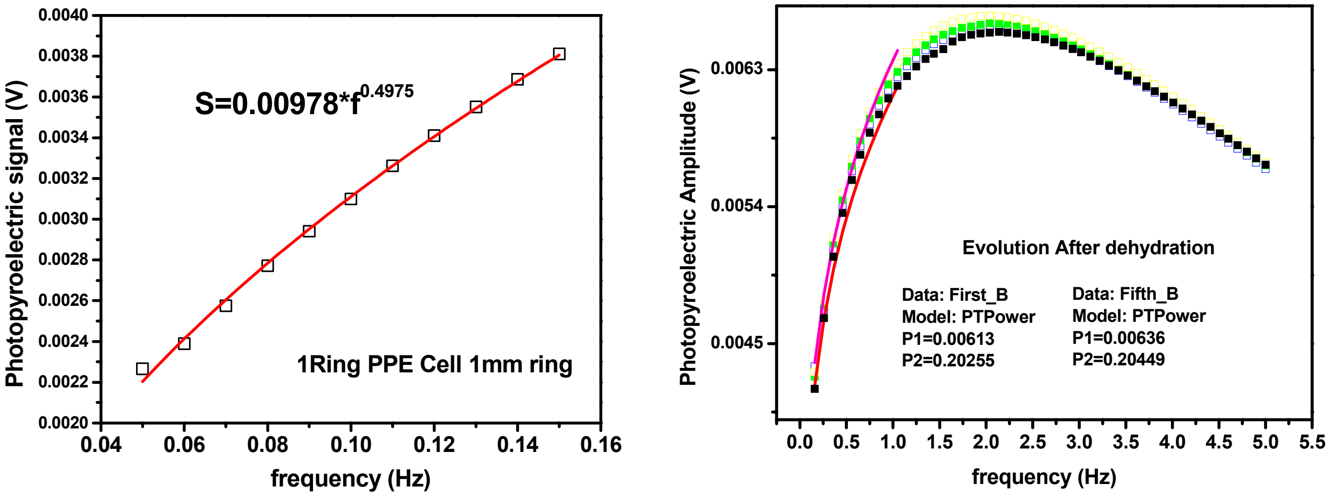


(A) (B)

Figure 6. Photoacoustic signal of the conventional PA Cell as a function of time for chitosan samples on an aluminum substrate (A) and a silver paint-mica substrate (B).

3.1 Photopyroelectric measurements.

In Figure 7.A, the depth profile, signal amplitude at very low modulation frequency for water using photopyroelectric detection is shown[1,9]. It can be seen that the dependence of the amplitude with the modulation frequency follows Equation 4 very closely. When this technique is applied to the study of chitosan, the results in Figure 7B are obtained. In this case a sample with 1% of chitosan sample is deposited, measured immediately; two more measurements were made one hour later and the last one twelve hours later. An increase in the amplitude is observed with a change in the slope of the process. The changes observed are due to the combined effect of crosslinking and evaporation occurring in the sample.



(A) (B)

Figure 7. Frequency scan at low frequency of (A) water, (B) A chitosan sample measured at different periods of time.

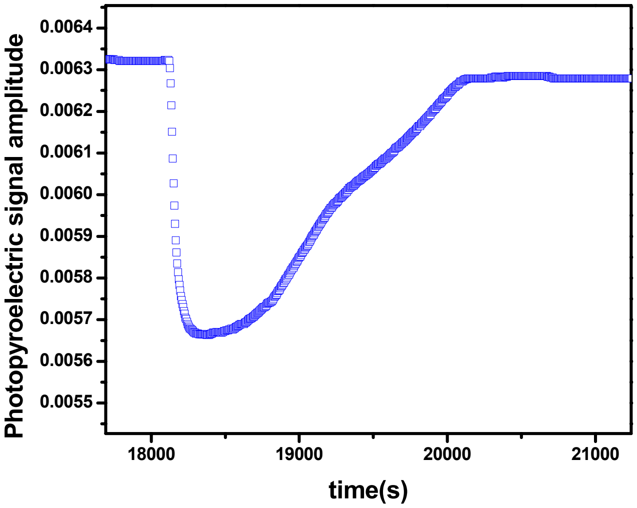


Figure 8. Photopyroectric signal amplitude as a function of time for a 1% chitosan sample.

In Figure 8, the amplitude of the signal is shown as a function of time for a 1% of chitosan sample at a modulation frequency of 1.25Hz. In this case the results are different as compared the ones obtained with the conventional photoacoustic cell, because the substrates are different, in the photoacoustic technique, aluminium and silver paint-mica were used, and in the photopyroelectric case, it is shown that PVDF plays an important role as substrate and detector. The process of evaporation-crosslinking studied by the conventional photoacoustic cell can also be studied using photopyroelectric technique.

4. CONCLUSIONS

In this work it has been shown a system for making photothermal measurements, in which the thermal waves are induced using a modulated laser diode. It has been shown that this system is very stable, versatile and compact. It works with a minimal noise due to the fact that the electronics that induce the modulation is the one that detects the signal of the sensors. Examples of applications using open photoacoustic cell, conventional photoacoustics and photopyroelctric measurements have shown the capabilities of the system. It has also been used in a wide range of modulation frequencies, from mHz to hundreds of Hz, giving stable and reliable results. The monitoring of the chitosan samples in time shows the high potential of the system in the analysis of complex dynamical process and in the interaction with the surroundings, in particular with the substrate. The system also has the capability of accepting laser of different wavelength and performing modulation frequencies of thousands of MHz, with an important potential in the study of high frequency phenomena as the study of carrier recombination in semiconductors, roughness analysis and vibration. The application in other photothermal techniques, such as photothermal radiometry, thermoreflectance and mirage technique is in progress.

ACKNOWLEDGMENTS

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