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Photopyroelectric Calorimeter for Phase Transitions Monitoring: Application to Chocolate

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ABSTRACT

In this work we report about the design and construction of a simple and cheap calorimeter for phase transitions monitoring using Peltier elements and based in the well known inverse (front) photopyroelectric method for thermophysical characterization of materials. We describe its application for the detection of phase transitions in chocolate samples, as an alternative, for example, to the most widely used and more expensive Differential Scanning Calorimetry technique. The manufacture of chocolate requires an understanding of the chemistry and the physical properties of the product. Thus the involved problems during the confection process are those of the so-called materials science. Among them, those related with tempering are of particular importance. Because the fats in cocoa butter experience the so-called polymorphous crystallization, the primary purpose of tempering is to assure that only the best form is present in the final product. One way to characterize this is by measurement of the temperature dependence of the thermal properties of the chocolate and the monitoring of the temperature at which phase transitions take place. We show that the photopyroelectric method, aided with Peltier cells temperature control, can be a useful choice for this purpose.

INTRODUCTION

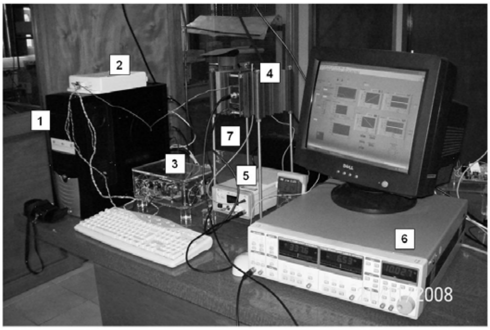
In the last years the photopyroelectric (PPE) technique [1] in its several experimental configurations has become great attention due its possibilities to perform the thermal characterization of materials. In the most used configurations, the analyzed sample is placed in intimate thermal contact with one of the metal coated surfaces of the sensor, while a periodical intensity modulated light beam impinges on its opposite metalized side or on the sample's surface, which act as a light absorber. Following the absorption of light energy, the pyroelectric (PE) temperature fluctuates periodically at the modulation frequency of the incident beam (these temperature oscillations are the so-called thermal waves) thereby generating a voltage, whose amplitude at a given frequency can be measured using a Lock-in amplifier. Due to the good thermal contact that can be achieved between liquids and detector, the majority of the published works concern the characterization of these kind of materials. When the light beam impinges on the metal contact of the sensor, the experimental variant is called the front or inverse PPE technique, which has been found mainly suitable for thermal effusivity measurements [2]. In the other useful configuration light is absorbed by a sample, and the thermal diffusivity can be determined [3]. Applications in the fields of foods characterization [4], study of liquid mixtures [5], thermal characterization of colloidal suspensions of nanometric sized particles (the so-called nanofluids) [6], among others, demonstrate the usefulness of these photothermal (PT) techniques. Because thermal properties are very sensitive to temperature changes the PPE technique has found also applications related to phase transitions monitoring [4,7], which is very important in the manufacturing of several foods, for example chocolate. Among the several processes involved in its fabrication, the tempering is common to all production methods. It involves four principal steps: 1) complete melting of the chocolate to remove most or all the crystalline material; 2) cooling to the crystallization point; 3) maintaining this holding temperature for crystallization for a given time interval; and 4) reheating to melt out unstable crystals. The tempering time varies with recipes, equipment and the purpose of the final product, whose melting temperature depends strongly on it. Therefore, the development of techniques for reliable and precise measurement of this temperature in the industry is of great importance [8]. In this work we report on a development of a calorimeter suitable for PPE measurements and its application for the detection of phase transitions in this confectionary material.

EXPERIMENT

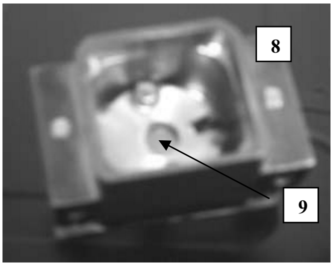
In the figure 1 we show a photograph of a photopyroelectric based calorimeter, suitable for phase transitions monitoring in a temperature interval ranging from -20 to 60 ^{0}C. This was achieved using Peltier thermoelectric Cells and a home made interface aided with a data acquisition card from National Instruments and Software developed using LabVIEW [9]. The pyroelectric (PE) sensor (0.6 cm diameter) was a polyvinyledene difluoride (PVDF) polymer film with metalized surfaces serving as electrodes providing an output voltage [10]. The excitation source was a semiconductor diode laser, whose light beam is intensity modulated using the TTL voltage output of a Lock-In amplifier, which is also used for measurement of the PE signal in both amplitude and phase angle channels. The modulated laser light beam is focused onto the sensor using an optical fiber. The system was calibrated by measuring the sensor absolute temperature with a thermocouple. After calibration, a small piece of chocolate sample (Bremen S.A. de C.V.) (0.2 cm thick and 0.5 cm diameter) was placed in intimate contact with the PE sensor. The inverse detection scheme was used for phase transition detection, in which illumination takes place onto the PE metalized face opposite to the sample. A more detailed discussion about our experimental set-up is given elsewhere [11].

RESULTS AND DISCUSSION

In order to show the usefulness of our experimental system for phase transitions monitoring in chocolate we show in the figure 2 a typical obtained result. Measurements of the PE voltage were performed at the modulation frequency of 1 Hz in a temperature range between 15 and 40 ^{0}C. A total of 50 signal values were recorder at each temperature value in an automatic way, and their mean value was plotted. The sizes of the error bars showed in the figure were calculated from the standard deviations and taken into account the Lock-in measurement uncertainty.



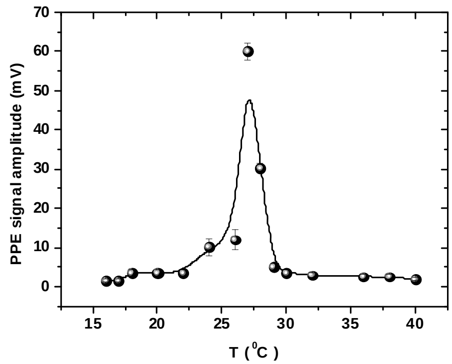
a)



b)

Figure 1. a) The experimental set-up. 1) CPU, 2) Interface NI SCC-68 allowing the connection with the data acquisition card PCI 6221 (already build inside the PC), 3) Power interface for peltier cell control, 4) Measurement cell, with peltier elements (Marlow industries, series DT), PVDF pyroelectric sensor (Kynar films), support for optical fiber and sample's support, 5) Laser diode (BW TEIC) and 6) Lock.in amplifier, SR830 DSP, 7) Optical fiber. b) The measurement cell (8) with the pyrolectric sensor (9) inside it.

We can see a phase transition, which is similar to that reported by other authors [12] as measured using the well established differential scanning calorimetry (DSC) technique. One can easy see the characteristic sharp peak at 27 ^{0}C (at this value the first derivative of the PPE signal vanishes, as showed in part (b) of the same figure), at which the chocolate melts, as well as neighboring broader peaks at lower temperatures that show the existence of different polymorphs in the chocolate [13]. Because the complexity of chocolate arises from the polymorphic nature of its constituent fats, which can come in different crystalline forms and thus with different melting points, this kind of measurement can aid well established methods such as x-ray diffraction for the study of the underlying physical behavior.



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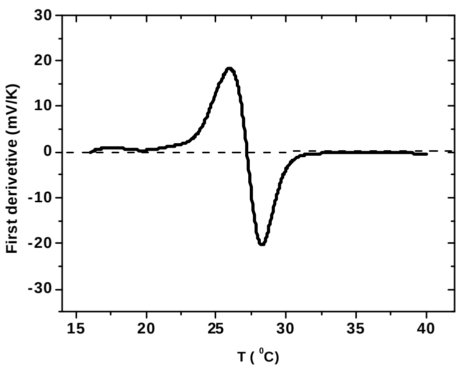

b)

Figure 2. a) PPE signal as a function of the temperature for a chocolate sample. The solid curve is shown only for visualization purposes. b) The first derivative showing the transition (melting) temperature.

Similar results obtained for other commercial samples demonstrate the usefulness of our experimental approach to perform phase transitions monitoring in chocolate. The method proposed here has several advantages when compared with more established techniques such as DSC. Among then we can mention the low cost of the implementation, the ease of use and of the interpretation of the results, the short measurements times, the ease sample's manipulation and the small samples amounts required, among others.

CONCLUSIONS

Due to the polymorphism existing in chocolate the tempering plays an important role during the fabrication process. Thus the development of methods for better understanding of the physical and chemical processes involved in the chocolate production is an impetus. In the present paper we show preliminary results that demonstrated the way in which the photopyroelectric technique, aided with peltier cells based temperature control, can allows the determination of phase transitions in this food product. We have presented an experimental approach that should be easily implemented in both research laboratories and industries involved with the material science of chocolate.

ACKNOWLEDGMENTS

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