Thermal properties measurement of chitosan-based films for agricultural applications

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Background – Nowadays, the use of pesticides for preservation of horticultural products represents a big issue concerning environmental contamination. Therefore, new sources based on natural polymers should be sought. Among these polymers, chitosan is of special interest due to its non-toxicity, biodegradability, barrier properties, antimicrobial activity and film forming capacity. Moreover, antimicrobial effectiveness can be improved with bioactive agents such as essential oils and propolis. An additional way to enhance the effect of the coating films is nanotechnology due to the surface area to volume ratio which increases this activity. Although some physiological and quality variables have been evaluated for the coated-fruit or vegetables, there is few information about its thermal properties, which are related to the variables above mentioned before through the fruit ripening process and storage. In the present study the thermal diffusivity and thermal effusivity were measured by using open photoacoustic cell (OPC) and photopyroelectric techniques, respectively. From the results, highest diffusivity and lowest effusivity values were found for chitosan-based NPs film.

Methods – For nanoparticles elaboration, the nanoprecipitation method [1] was followed. Briefly, a chitosan solution (0.05%) was prepared using glacial acetic acid and distilled water. On the other hand, a solution containing methanol (40 mL) and the bioactive agent (thyme essential oil or propolis, 5%) and Tween 20 (1%) was prepared. Then, 2.5 mL of the chitosan solution was dropped into the methanol and active agent solution with a peristaltic pump and finally concentrated to 2 mL by using a rotary evaporator. A formulation, based on the synthesized nanoparticles (33%), glycerol (0.3%), and a chitosan solution at 1% (66.7%), was placed into a homogenizer and cast-films elaborated in a convection oven at 40±1 °C for 3 h. For films thermal characterization, thermal diffusivity was measured by OPC technique, based on the periodic heating of the sample by absorption of laser light pulses, on the sample front surface, which results in a temperature variation of a thin air layer, in contact with the sample back surface, inside of the photoacoustic cell causing a pressure fluctuation that can be registered by the microphone. The thermal effusivity was measured through the front-photopyroelectric technique using the thermal wave resonance cavity (TWRC), in which a small cut piece of the film was placed in a chamber composed of a metal foil and a piezoelectric temperature sensor. Then, the light of a laser beam modulated by an oscillator was absorbed by the metal foil acting as thermal wave generator. Then, the temperature variation was measured by a pyroelectric sensor as function of sample thickness. The signal was detected by a lock-in amplifier [2].

Results – Thermal diffusivity (D), effusivity (e) and conductivity (k) results are shown in Table 1. Representative graphs of thermal diffusivity of chitosan NPs film and thermal effusivity for propolis-chitosan NPs film are shown in figures 1a) and 1b), respectively.

$$k = e\sqrt{D} \qquad \text{Eqn. 1}$$

Table 1. Thermal properties values for the chitosan-based films

Film	$\boldsymbol{D}$ [x 10^{-3} m^2/s]	$\boldsymbol{e}$ [$Ws^{1/2}/m^2K$]	$\boldsymbol{k}$ [x 10^{-3} $Wm^{-1}K^{-1}$]
Chitosan NPs	0.00010±0.00002	45.618±0.001	0.456±0.046
Thyme essential oil-chitosan NPs	0.00009±0.00031	56.039±0.002	0.532±0.030
Propolis-chitosan NPs	0.00008±0.00001	67.592±0.007	0.605±0.022

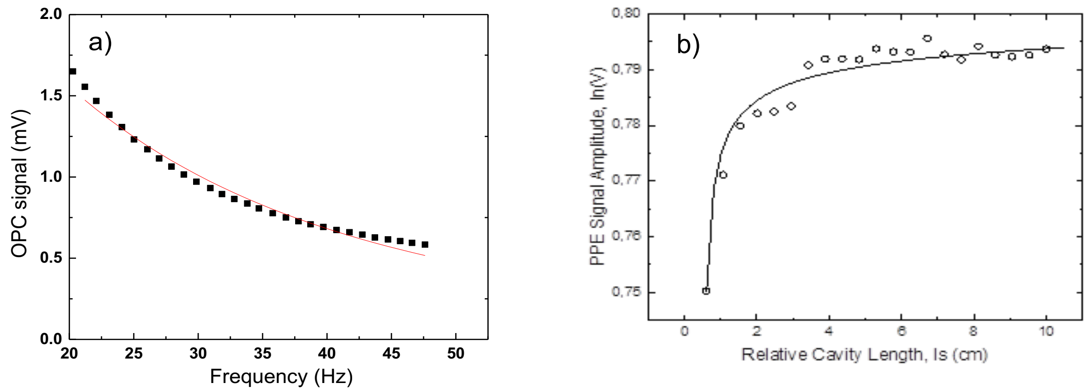

Fig. 1. a) Thermal diffusivity and **b)** thermal effusivity graphs for chitosan NPs film. The line is the best fit for the experimental values (dots).

From the results, the highest value of thermal diffusivity was for the chitosan NPs film and the lowest for the propolis-chitosan NPs. The effusivity behaviour was the opposite as expected. From calculations, the highest thermal conductivity value was for propolis-chitosan NPs. The results found in this work are of special interest because the senescence process of the fruit is usually associated to water loss from the agricultural produce and the barrier property of the coatings for gas and liquid exchange.

Conclusions – For the studied chitosan-based NPs films, lower diffusivity and higher effusivity was obtained for the propolis-chitosan NPs, followed by the thyme essential oil-chitosan NPs, and finally the chitosan NPs. More studies related to water vapor permeability and moisture content are in progress.

References

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