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Thermal analysis applied to irradiated propolis

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Abstract

Propolis is a resinous hive product, collected by bees. Raw propolis requires a decontamination procedure and irradiation appears as a promising technique for this purpose. The valuable properties of propolis for food and pharmaceutical industries have led to increasing interest in its technological behavior. Thermal analysis is a chemical analysis that gives information about changes on heating of great importance for technological applications. Ground propolis samples were ^{60}Co gamma irradiated with 0 and 10 kGy. Thermogravimetry curves shown a similar multi-stage decomposition pattern for both irradiated and unirradiated samples up to 600°C. Similarly, through differential scanning calorimetry , a coincidence of melting point of irradiated and unirradiated samples was found. The results suggest that the irradiation process do not interfere on the thermal properties of propolis when irradiated up to 10 kGy.

Keywords: Propolis; Ionizing radiation; Thermal analysis

1. Introduction

Propolis is a resinous hive product, collected by bees, known to possess valuable antibacterial, antiviral, fungicidal, local anaesthetic, antiulcer, immunostimulating, hypotensive and cytostatic properties. Propolis contains fatty and phenolic acids, their esters, aromatic aldehydes and alcohols, sesquiterpenes, naphthalene and stilbene derivatives and a considerable number of flavonoid aglycones. Propolis flavonoids seem to be responsible for some of the important physiological properties (Ghisalberti, 1979; Popravko et al., 1982; Debuyser, 1983; Marcucci, 1996).

The food industry has used a variety of methods over the years to preserve or extend the shelf life of food (Thorne, 1991; WHO, 1994). Raw propolis requires a decontamination procedure and irradiation seems to us a promising technique for this purpose.

The valuable properties of propolis for food and pharmaceutical industries have led to increasing interest in its technological behavior. Thermal analysis is a group of techniques in which a physical property of a substance and or its reaction products is measured as a function of temperature whilst the substance is subjected to a controlled temperature program. It is actually a chemical analysis that gives information about changes on heating of great importance for technological applications, provided that: (1) a physical property is measured; (2) the measurement is expressed (directly or indirectly) as a function of temperature; (3) the measurement is made under a controlled temperature program. Survey of the types of thermal analysis techniques used and their applications to numerous areas of research have been published and quoted by Wendlandt (1986).

The most widely used techniques are thermogravimetry (TG) and differential thermal analysis (DTA), followed by differential scanning calorimetry (DSC) and thermomechanical analysis (TMA). Inorganic materials and high polymers are the most widely studied by thermal analysis techniques, followed by metal and metallic alloys and organic substances. In many cases, the use of only a single thermal analysis technique may not provide sufficient information about a given system. As with many other analytical methods, complementary

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or supplementary information, as can be furnished by other thermal analysis techniques, may be required.

This paper presents the results of thermal analysis applied to the study of the effects of irradiation treatment on propolis. TG was the technique applied for measuring mass and differential scanning calorimetry (DSC) for enthalpy.

2. Material and methods

Materials: Ground propolis samples coming from the Southeast region of Brazil were employed.

Irradiation: The samples were ^{60}Co gamma irradiated with doses of 0, 5.0 and 10 kGy in an AECL Gammacell 220, dose rate of about 7 kg/h.

DSC measurements: Portions of about 5 mg of ground samples of propolis were placed in aluminum sample pans of a Shimadzu-50-DSC calorimeter interfaced with a computer for data acquisition and data processing, led from room temperature (about 24°C) to -60°C and heated up to 200°C at 10°C min^{-1} scanning rate with an empty aluminum sample pan as the reference sample. The sample head was purged with a flow of dry nitrogen (50 ml min^{-1}) to avoid condensation of moisture.

TG measurements: Propolis samples of about 5 mg were employed for the TG assay using a Shimadzu-50-TG thermobalance under artificial air at 50 ml min^{-1} and heating rate of 10°C min^{-1}.

3. Results and discussion

The thermal analysis technique of (TGA) is one in which the change in sample mass (mass loss or gain) is determined as a function of temperature and/or time in which the sample is heated in an environment whose temperature is changing in a predetermined manner at a linear rate. The resulting mass-change versus temperature curve provides information concerning the thermal

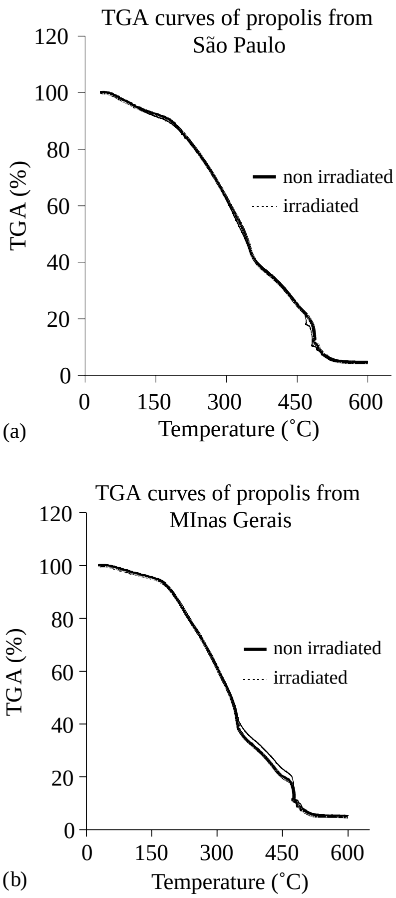

Fig. 1. (a) TGA curves of propolis from São Paulo. (b) TGA curves of propolis from Minas Gerais.

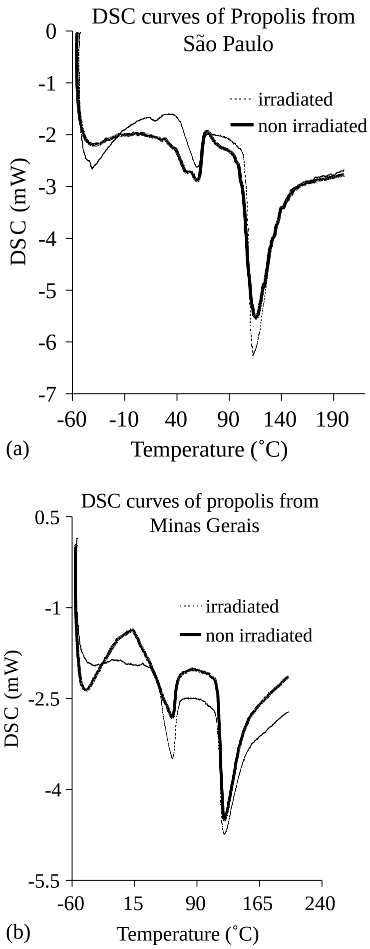

Fig. 2. (a) DSC curves of propolis from São Paulo. (b) DSC curves of propolis from Minas Gerais.

stability and composition of the initial sample, the thermal stability and composition of any intermediate compounds that may be formed, and the composition of the residue, if any. TGA curves corresponding to propolis samples from São Paulo and Minas Gerais (Figs. 1a and 2b) show similar multi-stage decomposition patterns for both non-irradiated and irradiated samples up to 600°C.

DSC is a thermal technique in which the temperature of a sample, compared with the temperature of a thermally inert material, is recorded as a function of the sample, inert material or furnace temperature as the sample is heated or cooled at a uniform rate. Temperature changes in the sample are due to endothermic or exothermic enthalpic transitions or reactions such as those caused by phase changes, fusion, crystalline structure inversions, boiling, sublimation, and vaporization, dehydration reactions, dissociation or decomposition reactions, oxidation and reduction reactions, destruction of crystalline lattice structure, and other chemical reactions. The main sources of endothermic and exothermic enthalpy changes in organic compounds are fusion, vaporizations, solid–solid transitions, sublimation, dehydration, decomposition and combustion. Figs. 2a and b show the dynamic DSC curves for non-irradiated and irradiated with 10 kGy propolis samples from São Paulo and Minas Gerais. In this case, DSC was used to determine whether the melting process could be affected by radiation. A coincidence of melting point of irradiated and non-irradiated samples was found for all the samples.

The results suggest that the irradiation process do not interfere on the thermal properties of propolis when irradiated up to 10 kGy.

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